(19)日本国特許庁(JP)

(12)**公表特許公報(A)**

(11)特許出願公表番号
特表2004-509182
(P2004-509182A)
(43)公表日 **平成16年3月25日(2004.3.25)**

(51)Int.Cl.^{7}	ＦＩ	テーマコード（参考）
C08F 290/04	C08F 290/04	4J027

審査請求 有　予備審査請求 有　（全 110 頁）

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(87)国際公開日	平成14年3月21日(2002.3.21)		
(31)優先権主張番号	60/232,414		
(32)優先日	平成12年9月14日(2000.9.14)		
(33)優先権主張国	米国(US)		

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(54)【発明の名称】グラフトコポリマーを調製する方法および該グラフトコポリマーから製造された組成物

(57)【要約】

本発明は、グラフトコポリマーを調製するための水性重合法および該グラフトコポリマーから製造されたコポリマー組成物を提供する。本発明の方法は、（ａ）水不溶性マクロモノマー粒子を含有するマクロモノマー水性エマルジョンを形成する工程と、（ｂ）少なくとも一種のエチレン性不飽和モノマーを含有するモノマー組成物を形成する工程と、（ｃ）マクロモノマー水性エマルジョンの少なくとも一部とモノマー組成物の少なくとも一部を組み合わせ、コポリマー組成物を生成させるために開始剤の存在下で、得られた重合反応混合物を重合させる工程とを含む。製造されたコポリマー組成物はグラフトコポリマーの水不溶性粒子を含有する。

【特許請求の範囲】

【請求項１】

（ａ）第１のエチレン性不飽和モノマーの重合単位を含み、

（ｉ）１０から１０００の重合度、

（ｉｉ）少なくとも一個の末端エチレン性不飽和基、

（ｉｉｉ）５重量％未満の重合された酸含有モノマーおよび

（ｉｖ）１モル％未満の重合されたメルカプタン－オレフィン化合物をさらに有するマクロモノマーの一個以上の水不溶性粒子を含むマクロモノマー水性エマルジョンを形成する工程と、

（ｂ）少なくとも一種の第２のエチレン性不飽和モノマーを含むモノマー組成物を形成する工程と、

（ｃ）重合反応混合物を形成させるために前記マクロモノマー水性エマルジョンの少なくとも一部と前記モノマー組成物の少なくとも一部を組み合わせ、グラフトコポリマー粒子を含むコポリマー組成物を生成させるために開始剤の存在下で前記マクロモノマーを前記第２のエチレン性不飽和モノマーと重合させる工程と

を含むグラフトコポリマーを製造する方法。

【請求項２】

前記マクロモノマー水性エマルジョンを形成する工程は、前記マクロモノマー粒子を形成させるために遷移金属キレート連鎖移動剤およびフリーラジカル開始剤の存在下で少なくとも前記第１のエチレン性不飽和モノマーを水性エマルジョン中で重合させることを含む請求項１に記載の方法。

【請求項３】

前記第１のエチレン性不飽和モノマーは、疎水性キャビティを有するマクロモレキュール有機化合物の存在下で重合される請求項２に記載の方法。

【請求項４】

前記モノマー組成物は、前記少なくとも一種の第２のエチレン性不飽和モノマーを含む水性エマルジョンを含む請求項１に記載の方法。

【請求項５】

前記第２のエチレン性不飽和モノマーは前記マクロモノマー粒子中に拡散し、前記マクロモノマー粒子を膨潤させる請求項１に記載の方法。

【請求項６】

前記マクロモノマーは１重量％未満の酸含有モノマーを重合単位として含む請求項１に記載の方法。

【請求項７】

前記第１のエチレン性不飽和モノマーは、α－メチルビニルモノマー、α－メチルビニルモノマー末端非α－メチルビニルモノマーまたはそれらの組み合わせである請求項１に記載の方法。

【請求項８】

前記第１のエチレン性不飽和モノマーは、メチルメタクリレート、エチルメタクリレート、２－エチルヘキシルメタクリレート、イソボルニルメタクリレート、ブチルメタクリレート、ラウリルメタクリレート、ステアリルメタクリレート、α－メチルスチレン末端スチレンまたはそれらの組み合わせである請求項７に記載の方法。

【請求項９】

前記第２のエチレン性不飽和モノマーは、アクリレートエステル、メタクリレートエステル、スチレン、置換スチレン、オレフィン性不飽和ニトリル、オレフィン性不飽和ハロゲン化物、有機酸のビニルエステル、Ｎ－ビニル化合物、アクリルアミド、メタクリルアミド、置換アクリルアミド、置換メタクリルアミド、ヒドロキシアルキルメタクリレート、ヒドロキシアルキルアクリレート、ビニルエーテル、ジエンおよびそれらの組み合わせから成る群から選択される請求項１に記載の方法。

【請求項１０】

前記第２のエチレン性不飽和モノマーは、C_1からC_{18}アルキルアクリレート、スチレン、ブタジエンおよびそれらの組み合わせから成る群から選択される請求項９に記載の方法。

【請求項１１】

前記マクロモノマーおよび前記第２のエチレン性不飽和モノマーは、酸含有モノマー、酸含有マクロモノマーまたはそれらの組み合わせの存在下で重合される請求項１に記載の方法。

【請求項１２】

前記マクロモノマーおよび前記第２のエチレン性不飽和モノマーは、酸含有マクロモノマーの全重量を基準にして５０重量％から１００重量％の酸含有モノマーを重合単位として含む前記酸含有マクロモノマーの存在下で重合される請求項１１に記載の方法。

【請求項１３】

前記マクロモノマーおよび前記エチレン性不飽和モノマーは、疎水性キャビティを有するマクロモレキュール有機化合物の存在下で重合される請求項１に記載の方法。

【請求項１４】

前記すべてのマクロモノマー水性エマルジョンおよびすべてのモノマー組成物を、重合を始める前に組み合わせる請求項１に記載の方法。

【請求項１５】

前記マクロモノマーおよび前記第２のエチレン性不飽和モノマーは、前記開始剤の存在下で前記モノマー組成物の少なくとも一部を前記マクロモノマー水性エマルジョンに徐々にフィードすることにより組み合わせる請求項１に記載の方法。

【請求項１６】

請求項１に記載の方法によって製造されたグラフトコポリマー。

【請求項１７】

水不溶性グラフトコポリマー粒子を含むコポリマー組成物であって、前記グラフトコポリマー粒子が、

（ａ）少なくとも一種の第１のエチレン性不飽和モノマーの１０個から１０００個の重合単位、１モル％未満の重合されたメルカプトーオレフィン化合物および５重量％未満の重合された酸含有モノマーを含む、前記コポリマーの全重量を基準にして２重量％から９０重量％の水不溶性マクロモノマーと、

（ｂ）前記コポリマーの全重量を基準にして少なくとも一種の第２のエチレン性不飽和モノマーの１０重量％から９８重量％の重合単位と

を含むコポリマー組成物。

【請求項１８】

前記マクロモノマーは、前記マクロモノマーの全重量を基準にして１重量％未満の酸含有モノマーを重合単位として含む請求項１７に記載のコポリマー組成物。

【請求項１９】

前記コポリマー組成物は、前記コポリマーの全重量を基準にして０．２重量％から１０重量％の酸含有マクロモノマーまたは酸含有モノマーをさらに含む請求項１８に記載のコポリマー組成物。

【請求項２０】

前記グラフトコポリマーは主鎖および一個以上の側鎖を含み、前記側鎖は前記主鎖から垂れ下がっているとともに前記水不溶性マクロモノマーを含み、前記主鎖は前記第２のエチレン性不飽和モノマーの重合単位を含む請求項１９に記載のコポリマー組成物。

【請求項２１】

前記酸含有マクロモノマーは前記コポリマー粒子の表面に結合される請求項２０に記載のコポリマー組成物。

【発明の詳細な説明】

【０００１】

（発明の分野）

本発明は、水性乳化重合プロセスを用いるグラフトコポリマーを製造する方法、および該グラフトコポリマーから製造されたコポリマー組成物に関する。より詳しくは、本発明は、グラフトコポリマーを含有するコポリマー組成物を生成させるために少なくとも一種のマクロモノマーおよび少なくとも一種のエチレン性不飽和モノマーを重合するための水性乳化重合プロセスに関する。

【０００２】

（発明の背景）

本明細書で用いられる「グラフトコポリマー」は、ポリマー鎖またはコポリマー鎖が側鎖として化学的にポリマー主鎖に結合される時に形成されるマクロモレキュールである。一般に、側鎖は、主鎖とは異なるポリマー組成の鎖である。グラフトコポリマーが多くの場合一分子中で異なるポリマーセグメントを化学的に組み合わせるので、これらのコポリマーは、対応するランダムコポリマーと比べて独特の特性を有する。これらの特性には、例えば、熱力学的に誘導されたポリマーミクロ相分離から生じる機械的フィルム特性、およびグラフトコポリマーの分岐構造からある程度生じる低い溶融粘度が挙げられる。後者に関して、低い溶融粘度は、ポリマーの加工性を有利に改善することが可能である。例えば、Ｈｏｎｇ－Ｑｕａｎ Ｘｉｅ ａｎｄ Ｓｈｉ－Ｂｉａｏ Ｚｈｏｕ、Ｊ．Ｍａｃｒｏｍｏｌ．Ｓｃｉ．－Ｃｈｅｍ．，Ａ２７（４）、４９１～５０７（１９９０）、Ｓｅｂａｓｔｉａｎ Ｒｏｏｓ、Ａｘｅｌ Ｈ．Ｅ．Ｍｕｌｌｅｒ，Ｍａｒｉｔａ Ｋａｕｆｍａｎｎ、Ｗｅｒｎｅｒ Ｓｉｏｌ ａｎｄ Ｃｌｅｎｅｎｓ Ａｕｓｃｈｒａ、「アニオン重合の研究の応用（Ａｐｐｌｉｃａｔｉｏｎｓ ｏｆ Ａｎｉｏｎｉｃ Ｐｏｌｙｍｅｒｉｚａｔｉｏｎ Ｒｅｓｅａｒｃｈ）」、Ｒ．Ｐ．Ｑｕｉｒｋ編、ＡＣＳ Ｓｙｍｐ．Ｓｅｒ．６９６、２０８（１９９８）を参照すること。

【０００３】

本明細書で用いられる「櫛形ポリマー」という用語は、グラフトコポリマーの高分子主鎖が直鎖であり、グラフトコポリマーの各側鎖がポリマー主鎖にグラフトされる「マクロモノマー」によって形成されるグラフトコポリマーの一形式である。「マクロモノマー」は、ポリマー鎖の末端に少なくとも一個の官能基を有する低分子量ポリマーであって、他のモノマーとさらに重合して櫛形コポリマーを生成させることが可能な低分子量ポリマーである。例えば、Ｋａｗａｋａｍｉ ｉｎ ｔｈｅ「Ｅｎｃｙｃｌｏｐｅｄｉａ ｏｆ Ｐｏｌｙｍｅｒ Ｓｃｉｅｎｃｅ ａｎｄ Ｅｎｇｉｎｅｅｒｉｎｇ」、第９巻、１９５～２０４頁、Ｊｏｈｎ Ｗｉｌｅｙ ＆ Ｓｏｎｓ、ニューヨーク（Ｎｅｗ Ｙｏｒｋ）、１９８７を参照すること。本明細書で用いられる「直鎖」という用語は、フリーラジカル重合で通常観察される水素引抜を通して少量の分岐が起きたポリマーを包含することを意図するものである。櫛形コポリマーは、マクロモノマーと従来のモノマー（例えば、エチレン性不飽和モノマー）とのフリーラジカル重合によって一般に調製される。

【０００４】

水不溶性マクロモノマーによって調製される櫛形コポリマーは、塊状重合技術および溶液重合技術を用いて主として調製されてきた。しかし、こうしたプロセスは、好ましくないことには、重合を行う媒体として溶媒またはモノマーを用いる。従って、最近、水性乳化プロセスを介して櫛形コポリマーを調製する方法の開発に努力が向けられてきた。

【０００５】

一例であるＡｍｉｃｋらによる米国特許第５，２４７，０４０号（「Ａｍｉｃｋ」）には、グラフトコポリマーを製造するための二段乳化重合プロセスが開示されている。第一段では、メルカプトーオレフィン化合物の存在下でエチレン性不飽和モノマーを重合することによりマクロモノマーを製造する。第二段では、得られたマクロモノマーを第２のエチレン性不飽和モノマーと水性エマルジョン中で重合する。Ａｍｉｃｋプロセスは、多くの利点を有するけれども、側鎖と主鎖との間に位置するリンケージを有するグラフトコポリマーを生成させ、そのリンケージは特定の条件下で加水分解を受けやすい。これらのリンケージは、マクロモノマーの調製でエステル官能基を有するメルカプトーオレフィン化合物を用いることから生じる。

【０００６】

Ｄａｒｍｏｎらによる米国特許第５，２６４，５３０号（「Ｄａｒｍｏｎ」）には、連鎖移動剤として用いられるマクロモノマーの存在下で一種以上のモノマー物質を重合する乳化フリーラジカル重合プロセスまたは懸濁フリーラジカル重合プロセスが開示されている。マクロモノマーが連鎖移動剤として用いられているので、マクロモノマーは、主として、末端でポリマー鎖に組み込まれる。

【０００７】

Ｈａｄｄｌｅｔｏｎらによる米国特許第５，８０４，６３２号（「Ｈａｄｄｌｅｔｏｎ」）には、コバルトキレート錯体の存在下で、酸官能基を有する低分子量ポリマーを調製し、その後、その低分子量ポリマーの存在下で少なくとも一種のオレフィン性不飽和モノマーを重合して疎水性ポリマーを生成させることを含む水性ポリマー乳化プロセスが開示されている。Ｈａｄｄｌｅｔｏｎの低分子量ポリマーは、そのままで、または酸基の中和後に、低分子量ポリマーを水性媒体にある程度、あるいは、より好ましくは完全に溶解可能にするのに十分な濃度の酸を含有することが教示されている。ある程度のグラフト化が起きることをＨａｄｄｌｅｔｏｎは開示しているけれども、Ｈａｄｄｌｅｔｏｎは、疎水性ポリマー粒子が「逆コアーシェル」ラテックスの形で低分子量ポリマーによって封入されることが考えられるプロセス、あるいは低分子量ポリマーが疎水性ポリマーを生成させるための重合用シードとして単に機能を果たすプロセスに焦点を当てている。従って、Ｈａｄｄｌｅｔｏｎは、櫛形ポリマーなどの所望構造のグラフトコポリマーを製造するプロセスを開示していない。Ｈａｄｄｌｅｔｏｎプロセスを用いると、好ましくないことには、低分子量ポリマーの実質的な量が水相中で反応しないで残ることも考えられる。

【０００８】

Ｈｕｙｂｒｅｃｈｔｓらによる公報ＷＯ９９／０３９０５号（「Ｈｕｙｂｒｅｃｈｔｓ」）には、酸含有マクロモノマーとアミノ官能性モノマーの乳化重合により調製されるアニオン安定化グラフトコポリマー組成物が開示されている。調製されたコポリマー組成物は、ポリマー主鎖中に０．５から３０重量％のアミノ官能性モノマー、およびアミンで中和されるマクロモノマー中に少なくとも５重量％の酸官能性モノマーを含む。しかし、中和を必要としない代替グラフトコポリマー組成物を調製するための水性乳化重合プロセスを提供することが必要とされるであろう。

【０００９】

本発明は、好ましくは耐加水分解性であるグラフトコポリマーを調製するための乳化重合プロセスを提供しようと追求している。本発明は、重合動力学、ポリマー構造、転化率、マクロモノマーの組み込みおよび粒子サイズのようなパラメータに対する制御を好ましくもたらす乳化重合プロセスも提供しようと追求している。

【００１０】

（発明の概要）

本発明の一態様において、マクロモノマーの水不溶性粒子を含有するマクロモノマー水性エマルジョンを形成する工程と、エチレン性不飽和モノマーを含有するモノマー組成物を形成する工程とを含むグラフトコポリマーを製造する方法が提供される。マクロモノマーは、第１のエチレン性不飽和モノマーの重合単位を含み、１０から１０００の重合度、少なくとも一個の末端エチレン性不飽和基、５重量％未満の重合された酸含有モノマーおよび重合単位として１モル％未満の重合されたメルカプトーオレフィン化合物をさらに有する。マクロモノマー水性エマルジョンの少なくとも一部とモノマー組成物の少なくとも一部を組み合わせて、重合反応混合物を形成させ、重合反応混合物中のマクロモノマーと第２のエチレン性不飽和モノマーを開始剤の存在下で重合させて、グラフトコポリマー粒子を含有するグラフトコポリマー組成物を生成させる。

【００１１】

本発明のもう一つの態様において、水不溶性グラフトコポリマー粒子を含有するグラフトコポリマー組成物が提供される。コポリマー粒子は、コポリマーの全重量を基準にして、２重量％から９０重量％の水不溶性マクロモノマーおよび少なくとも一種の第２のエチレ

ン性不飽和モノマーの１０重量％から９８重量％の重合単位を含む。グラフトコポリマー組成物を形成するために用いられるマクロモノマーは、第１のエチレン性不飽和モノマーの１０から１００個の重合単位、１モル％未満の重合されたメルカプトーオレフィン化合物、および５重量％未満の重合された酸含有モノマーを含む。好ましい実施形態において、コポリマー組成物は、コポリマーの全重量を基準にして、０．２重量％から１０重量％の酸含有マクロモノマーをさらに含む。

【００１２】

（詳細な説明）

本発明はグラフトコポリマー、より好ましくは櫛形コポリマーを調製するための水性重合プロセスを提供する。本発明は水性重合プロセスから製造される新規コポリマー組成物も提供する。

【００１３】

本発明のプロセスは、（ａ）マクロモノマーの一個以上の水不溶性粒子を含有するマクロモノマー水性エマルジョンを形成する工程と、（ｂ）エチレン性不飽和モノマーを含有するモノマー組成物を形成する工程と、（ｃ）マクロモノマー水性エマルジョンの少なくとも一部とモノマー組成物の少なくとも一部を組み合わせて、重合反応混合物を形成させる工程とを含む。マクロモノマーおよびエチレン性不飽和モノマーは、グラフトコポリマー粒子を形成させるために開始剤の存在下で重合される。

【００１４】

水不溶性粒子としてマクロモノマー水性エマルジョン中に存在するマクロモノマーは、フリーラジカル重合プロセスで重合することが可能な少なくとも一個の末端エチレン性不飽和基を有する任意の低分子量水不溶性ポリマーまたはコポリマーである。「水不溶性」とは、２５℃から５０℃で１５０ミリモル／リットル以下の水溶解度を有することを意味する。「低分子量」とは、マクロモノマーが好ましくは約１０から約１０００、より好ましくは約２０から約２００の重合度を有することを意味する。「重合度」とは、マクロモノマー中に存在する重合されたモノマー単位の数をいう。

【００１５】

マクロモノマーは、少なくとも一種のエチレン性不飽和モノマーを重合単位として含む。好ましくは、エチレン性不飽和モノマーは、本明細書で前述したようにマクロモノマーに低い水溶解度しか与えないか、または全く水溶解度を与えないように選択される。

【００１６】

マクロモノマーを調製する際に用いるために適するエチレン性不飽和モノマーには、例えば、メチルメタクリレート、エチルメタクリレート、ｎ－ブチルメタクリレート、ラウリルメタクリレート、ステアリルメタクリレートを含むメタクリル酸のC_1からC_{18}ノルマルまたは分岐アルキルエステルなどのメタクリレートエステル；メチルアクリレート、エチルアクリレート、ｎ－ブチルアクリレートおよび２－エチルヘキシルアクリレートを含むアクリル酸のC_1からC_{18}ノルマルまたは分岐アルキルエステルなどのアクリレートエステル；スチレン；メチルスチレン、α－メチルスチレンまたはｔ－ブチルスチレンなどの置換スチレン；アクリロニトリルまたはメタクリロニトリルなどのオレフィン性不飽和ニトリル；塩化ビニル、塩化ビニリデンまたは弗化ビニルなどのオレフィン性不飽和ハロゲン化物；酢酸ビニルなどの有機酸のビニルエステル；Ｎ－ビニルピロリドンなどのＮ－ビニル化合物；アクリルアミド；メタクリルアミド；置換アクリルアミド；置換メタクリルアミド；ヒドロキシエチルメタクリレートなどのヒドロキシアルキルメタクリレート；ヒドロキシアルキルアクリレート；ジメチルアミノエチルメタクリレート、ｔ－ブチルアミノエチルメタクリレートおよびジメチルアミノプロピルメタクリルアミドなどを含むアミン置換メタクリレートなどの塩基性置換（メタ）アクリレートおよび（メタ）アクリルアミド；１，３－ブタジエンおよびイソプレンなどのジエン；ビニルエーテル；またはそれらの組み合わせが挙げられる。本明細書で用いられる「（メタ）」という用語は、「メタ」が任意に存在することを意味する。例えば、「（メタ）アクリレート」はメタクリレートまたはアクリレートを意味する。

【００１７】

エチレン性不飽和モノマーは、例えば、ヒドロキシ、アミド、アルデヒド、ウレイド、ポリエーテル、グリシジルアルキル、ケト官能基またはそれらの組み合わせを含むモノマーを含む官能性モノマーであることも可能である。これらの官能性モノマーは、グラフトコポリマーの全重量を基準にして一般には約０．５重量％から約１５重量％、より好ましくは約１重量％から約３重量％のレベルでマクロモノマー中に存在する。官能性モノマーの例には、例えば、ヒドロキシアルキルアクリレートおよびヒドロキシアルキルメタクリレートのアセトアセトキシエステル（例えば、アセトアセトキシエチルメタクリレート）、ならびにケト含有アミド（例えば、ジアセトンアクリルアミド）などのケト官能性モノマー；アリルアルキルメタクリレートまたはアクリレート；グリシジルアルキルメタクリレートまたはアクリレート；あるいはそれらの組み合わせが挙げられる。こうした官能性モノマーは必要ならば架橋をもたらすことが可能である。

【００１８】

マクロモノマーは、マクロモノマーの全重量を基準にして約１０重量％未満、好ましくは約５重量％未満、より好ましくは約２重量％未満、最も好ましくは約１重量％未満の酸含有モノマーも重合単位として含む。最も好ましい実施形態において、マクロモノマーは酸含有モノマーを含まない。「酸含有モノマー」とは、一個以上の酸官能基、または酸を形成することが可能である官能基を含む任意のエチレン性不飽和モノマー（例えば、無水メタクリル酸などの酸無水物またはｔ－ブチルメタクリレート）を意味する。酸含有モノマーの例には、例えば、アクリル酸、メタクリル酸、イタコン酸、マレイン酸およびフマル酸などのカルボン酸保有エチレン性不飽和モノマー；アクリルオキシプロピオン酸および（メタ）アクリルオキシプロピオン酸；スチレンスルホン酸、ビニルスルホン酸ナトリウム、スルホエチルアクリレート、スルホエチルメタクリレート、エチルメタクリレート－２－スルホン酸、または２－アクリルアミド－２－メチルプロパンスルホン酸などのスルホン酸保有モノマー；ホスホエチルメタクリレート；酸含有モノマーの対応する塩；またはそれらの組み合わせが挙げられる。

【００１９】

また、マクロモノマーは、重合されたものとして、マクロモノマーの全重量を基準にして約１モル％未満、好ましくは約０．５モル％未満のメルカプト－オレフィン化合物しか、より好ましくは全くメルカプト－オレフィン化合物を含まない。メルカプト－オレフィン化合物は、Ａｍｉｃｋによる米国特許第５，２４７，０００号に記載された化合物である。これは本明細書に全体的に参照して組み込まれる。Ａｍｉｃｋに記載されたメルカプト－オレフィン化合物は、加水分解を受けやすいエステル官能基を有する。

【００２０】

本発明の好ましい実施形態において、マクロモノマーは、少なくとも約２０重量％、より好ましくは約５０重量％から約１００重量％、より好ましくは約８０から約１００重量％の少なくとも一種のα－メチルビニルモノマー、α－メチルビニルモノマー末端非α－メチルビニルモノマーまたはそれらの組み合わせから構成される。本発明の最も好ましい実施形態において、マクロモノマーは、マクロモノマーの全重量を基準にして約９０重量％から約１００重量％のα－メチルビニルモノマー、α－メチルビニルモノマー末端非α－メチルビニルモノマーまたはそれらの組み合わせを重合単位として含む。適するα－メチルビニルモノマーには、例えば、メチルメタクリレート、エチルメタクリレート、ブチルメタクリレート、２－エチルヘキシルメタクリレート、イソボルニルメタクリレート、ラウリルメタクリレートまたはステアリルメタクリレートを含むメタクリル酸のC_1からC_{18}ノルマルまたは分岐アルキルエステルなどのメタクリレートエステル； ヒドロキシエチルメタクリレートなどのヒドロキシアルキルメタクリレート； グリシジルメタクリレート； フェニルメタクリレート； メタクリルアミド； メタクリロニトリル； またはそれらの組み合わせが挙げられる。α－メチルビニルモノマー末端非α－メチルビニルモノマーには、α－メチルスチレン末端スチレンが挙げられる。

【００２１】

当業者は、本発明で有用なマクロモノマーを調製するために多くの方法があることを認めるであろう。例えば、マクロモノマーは、米国特許第５，７１０，２２７号または２０００年６月２１日に発行されたＥＰ－Ａ－１，０１０，７０６号に開示されたように高温（例えば、少なくとも約１５０℃）連続プロセスによって調製してよい。これらの特許の開示は本明細書で全体的に引用して援用する。好ましい連続プロセスにおいて、エチレン性不飽和モノマーの反応混合物は、少なくとも約１５０℃、より好ましくは少なくとも約２７５℃の温度を有する加熱域を通過する。加熱域は、大気圧より高い圧力（例えば、約３０バーより高い圧力）で維持してもよい。モノマーの反応混合物は、水、アセトン、メタノール、イソプロパノール、プロピオン酸、酢酸、ジメチルホルムアミド、ジメチルスルホキシド、メチルエチルケトンまたはそれらの組み合わせなどの溶媒を任意に含んでもよい。

【００２２】

本発明において有用なマクロモノマーは、フリーラジカル開始剤および触媒金属キレート連鎖移動剤（例えば、遷移金属キレート）の存在下でエチレン性不飽和モノマーを重合させることにより調製してもよい。こうした重合は、溶液重合法、塊状重合法、懸濁重合法または乳化重合法によって行ってよい。触媒金属キレート連鎖移動剤を用いてマクロモノマーを調製するために適する方法は、例えば、米国特許第４，５２６，９４５号、第４，６８０，３５４号、第４，８８６，８６１号、第５，０２８，６７７号、第５，３６２，８２６号、第５，７２１，３３０号および第５，７５６，６０５号、欧州公報ＥＰ－Ａ－０１９９，４３６号およびＥＰ－Ａ－０１９６７８３号、ＰＣＴ公報ＷＯ８７／０３６０５号、ＷＯ９６／１５１５８号およびＷＯ９７／３４９３４号において開示されている。これらの特許は、参照してここに組み込まれる。

【００２３】

好ましくは、本発明で有用なマクロモノマーは、遷移金属キレート錯体を用いる水性乳化フリーラジカル重合法プロセスによって調製される。好ましくは、遷移金属キレート錯体は、例えば、コバルトのジオキシム錯体、コバルトＩＩポルフィリン錯体、またはビシナルイミノヒドロキシイミノ化合物、ジヒドロキシイミノ化合物、ジアザジヒドロキシイミノジアルキルデカジエン、ジアザジヒドロキシイミノジアルキルウンデカジエンのコバルトＩＩキレート、またはそれらの組み合わせなどのコバルト（ＩＩ）またはコバルト（ＩＩＩ）キレート錯体である。これらの錯体は、任意に、$\mathrm{BF_2}$などの橋架け基を含んでよく、任意に、水、アルコール、ケトン、およびピリジンなどの窒素塩基などの配位子で配位されてもよい。別の適する遷移金属錯体は、例えば、米国特許第４，６９４，０５４号、第５，７７０，６６５号、第５，９６２，６０９号および第５，６０２，２２０号において開示されている。これらの特許の開示は本明細書で全体的に引用して援用する。本発明で有用な好ましいコバルトキレート錯体は、ＣｏＩＩ（２，３－ジオキシイミノブタン－$\mathrm{BF_2}$）$_2$、前の化合物のＣｏＩＩＩ類似体、またはそれらの組み合わせである。こうした錯体の空間配列は、例えば、ＥＰ－Ａ－１９９４３６号および米国特許第５，７５６，６０５号において開示されている。

【００２４】

遷移金属キレート連鎖移動剤を用いる水性乳化重合法によるマクロモノマーの調製に際して、少なくとも一種のエチレン性不飽和モノマーは、従来の水性乳化重合技術に従ってフリーラジカル開始剤および遷移金属キレートの存在下で重合される。好ましくは、エチレン性不飽和モノマーは、本明細書で前述したようなα－メチルビニルモノマーである。

【００２５】

マクロモノマーを形成するための重合は、好ましくは約２０℃から約１５０℃、より好ましくは約４０℃から約９５℃の温度で行われる。重合の完了時の固形物レベルは、水性エマルジョンの全重量を基準にして典型的には約５重量％から約６５重量％、より好ましくは約３０重量％から約５０重量％である。

【００２６】

重合プロセス中に用いられる開始剤および遷移金属キレート連鎖移動剤の濃度は、好まし

くは、マクロモノマーの所望の重合度を得るように選択される。開始剤の濃度は、モノマーの全重量を基準にして好ましくは約０．２重量％から約３重量％、より好ましくは約０．５重量％から約１．５重量％である。遷移金属キレート連鎖移動剤の濃度は、マクロモノマーを形成させるために用いられるモノマーの全モルを基準にして好ましくは約５ｐｐｍから約２００ｐｐｍ、より好ましくは約１０ｐｐｍから約１００ｐｐｍである。

【００２７】

エチレン性不飽和モノマー、開始剤および遷移金属キレート連鎖移動剤は、重合を行うために当業者に対して知られているいかなる方式でも添加してよい。例えば、モノマー、開始剤および遷移金属キレートは、重合プロセス（すなわち、バッチプロセス）の開始時にすべて水性エマルジョン中に存在してよい。あるいは、成分の一種以上は、水溶液に徐々にフィードしてよい（すなわち、連続プロセスまたはセミバッチプロセス）。例えば、水および界面活性剤を含有する溶液に開始剤、モノマーおよび／または遷移金属キレートの全部または一部を徐々にフィードすることが望ましい場合がある。好ましい実施形態において、モノマーおよび遷移金属キレートの少なくとも一部は重合中に徐々にフィードされ、モノマーおよび遷移金属キレートの残りは重合の開始時に水性エマルジョン中に存在する。この実施形態において、モノマーは、そのままフィードしてよいか、あるいはフィードされる前に水溶液中で懸濁してよいか、または乳化してよい。

【００２８】

マクロモノマーを調製するために、適するいかなるフリーラジカル開始剤も用いてよい。開始剤は、好ましくは、一種以上の他の成分（例えば、モノマー、水）中の溶解度、所望の重合温度での半減期（好ましくは約３０分から約１０時間の範囲内の半減期）および遷移金属キレートの存在下での安定性のようなパラメータに基づいて選択される。適する開始剤には、例えば、２，２’－アゾビス（イソブチロニトリル）、４，４’－アゾビス（４－シアノバレリアン酸）、２，２’－アゾビス［２－メチル－Ｎ－（１，１－ビス（ヒドロキシメチル）－２－（ヒドロキシエチル）］－プロピオンアミドおよび２，２’－アゾビス［２－メチル－Ｎ－２－（ヒドロキシエチル）］－プロピオンアミドなどのアゾ化合物、ｔ－ブチルヒドロペルオキシド、過酸化ベンゾイルなどの過酸化物、過硫酸ナトリウム、過硫酸カリウムまたは過硫酸アンモニウム、あるいはそれらの組み合わせが挙げられる。例えば、メタ亜硫酸水素ナトリウム、亜硫酸ナトリウム、ホルムアルデヒドスルホキシル酸ナトリウム、イソアスコルビン酸またはそれらの組み合わせなどの還元剤と組み合わせた過硫酸塩または過酸化物などのレドックス開始剤系も使用してよい。こうしたレドックス開始剤系において鉄などの金属助触媒も任意に用いてよい。炭酸水素ナトリウムなどの緩衝剤も開始剤系の一部として用いてよい。

【００２９】

マクロモノマーを調製するために、乳化剤も好ましくは水性乳化重合プロセス中に存在する。例えば、アニオン乳化剤、カチオン乳化剤または非イオン乳化剤などのモノマーを乳化する際に有効であるいかなる乳化剤も使用してよい。好ましい実施形態において、乳化剤は、例えば、ジアルキルスルホコハク酸のナトリウム塩、カリウム塩またはアンモニウム塩、硫酸化油のナトリウム、カリウム塩またはアンモニウム塩、ドデシルベンゼンスルホン酸ナトリウムなどのアルキルスルホン酸のナトリウム塩、カリウム塩またはアンモニウム塩、ラウリル硫酸ナトリウムなどのアルキルスルフェートのナトリウム塩、カリウム塩またはアンモニウム塩、エトキシル化アルキルエーテルスルフェート、スルホン酸のアルカリ金属塩、C_{12}からC_{24}脂肪アルコール、エトキシル化脂肪酸または脂肪アミド、ステアリン酸ナトリウムおよびオレイン酸ナトリウムなどの脂肪酸のナトリウム塩、カリウム塩またはアンモニウム塩、またはそれらの組み合わせなどのアニオン乳化剤である。水性エマルジョン中の乳化剤の量は、モノマーの全重量を基準にして好ましくは約０．０５重量％から約１０重量％、より好ましくは約０．３重量％から約３重量％である。

【００３０】

こうして調製されたマクロモノマーは、グラフトコポリマー粒子を含有するコポリマー組成物を生成させるためにエチレン性不飽和モノマーと乳化重合される。重合は、マクロモ

ノマー水性エマルジョン中の水不溶性粒子としてマクロモノマー、およびモノマー組成物中のエチレン性不飽和モノマーを供給することにより行われる。マクロモノマー水性エマルジョンの少なくとも一部は、モノマー組成物の少なくとも一部と組み合わされて、開始剤の存在下で重合される重合反応混合物を生成させる。

【００３１】
決して理論に縛られるつもりではないけれども、水性エマルジョン中の水不溶性マクロモノマー粒子の形でマクロモノマーおよび別個のモノマー組成物中のエチレン性不飽和モノマーを供給することにより、組み合わせた際に、重合が中で起きるマクロモノマー粒子中にエチレン性不飽和モノマーが拡散することが考えられる。好ましくは、マクロモノマー粒子中へのエチレン性不飽和モノマーの拡散は、マクロモノマー粒子の膨潤によって証明される。

【００３２】
本発明において有用なマクロモノマー水性エマルジョンは、当業者に対して知られているいかなる方式でも形成してよい。例えば、既知のいずれかの方法によって製造されたマクロモノマーは（例えば、噴霧乾燥された）固形物として単離してよく、水中で乳化してよい。例えば、マクロモノマーは、乳化系重合法または水性重合法を介して調製される場合、そのままで使用してもよく、または水で希釈してもよく、あるいは所望の固形物レベルに濃縮してもよい。

【００３３】
本発明の好ましい実施形態において、マクロモノマー水性エマルジョンは、本明細書で前述したように遷移金属キレート連鎖移動剤の存在下でのエチレン性不飽和モノマーの乳化重合から形成される。この実施形態は多くの理由で好ましい。例えば、所望の粒子サイズ分布（好ましくは狭い、例えば、２未満の多分散性）をもたらすために、マクロモノマーの重合を容易に制御することが可能である。例えば、マクロモノマーを固形物として単離するなどの余分のプロセス工程も避けることができ、より良好なプロセス経済性につながる。さらに、単一反応器で連続工程によってマクロモノマー、マクロモノマー水性エマルジョンおよびグラフトコポリマーを調製することが可能であり、それは、商用製造設備において望ましい。

【００３４】
本発明において有用なマクロモノマー水性エマルジョンは、マクロモノマー水性エマルジョンの全重量を基準にして約２０重量％から約６０重量％、より好ましくは約３０重量％から約５０重量％の少なくとも一種の水不溶性マクロモノマーを含有する。マクロモノマー水性エマルジョンは、マクロモノマーの混合物をも含有する。マクロモノマー水性エマルジョンは、マクロモノマー水性エマルジョンの全重量を基準にして好ましくは約５重量％未満、より好ましくは約１重量％未満のエチレン性不飽和モノマーを含有する。

【００３５】
水不溶性マクロモノマー粒子は、所望の粒子サイズのグラフトコポリマーを形成する粒子サイズを有する。例えば、最終グラフトコポリマー粒子サイズは、すべての粒子が重合に同等に加わると仮定して、重合反応混合物中のマクロモノマーの初期粒子サイズおよびエチレン性不飽和モノマーの濃度に直接的に比例する。好ましくは、マクロモノマー粒子は、ＨＰＬＣ型紫外線検出器が装備されたＭａｔｅｃ　ＣＨＤＦ２０００粒子サイズ分析機を用いるＣａｐｉｌｌａｒｙ　Ｈｙｄｒｏｄｙｎａｍｉｃ　Ｆｒａｃｔｉｏｎａｔｉｏｎ技術によって測定して、好ましくは約５０ｎｍから約５００ｎｍ、より好ましくは約８０ｎｍから約２００ｎｍの重量平均粒子サイズを有する。

【００３６】
マクロモノマー水性エマルジョンは一種以上の乳化剤も含んでよい。乳化剤の種類と量は、好ましくは、所望の粒子サイズをもたらすように選択される。適する乳化剤には、乳化重合プロセスによってマクロモノマーを調製する際に使用のために前に開示したものが挙げられる。好ましい乳化剤は、例えば、ラウリル硫酸ナトリウム、ドデシルベンゼンスルホン酸ナトリウム、ノニルフェノールおよび脂肪アルコールの硫酸化誘導体およびエトキ

シル化誘導体などのアニオン界面活性剤である。マクロモノマーの全重量を基準にした乳化剤の全レベルは、好ましくは約０．２重量％から約５重量％、より好ましくは約０．５重量％から約２重量％である。

【００３７】

本発明において有用なモノマー組成物は、少なくとも一種のエチレン性不飽和モノマーを含有する。モノマー組成物は、すべて（すなわち１００％）のモノマーを含んでよいか、あるいは有機溶媒および／または水に溶解または分散したモノマーを含んでよい。好ましくは、モノマー組成物中のモノマーのレベルは、モノマー組成物の全重量を基準にして約５０重量％から１００重量％、より好ましくは約６０％から約９０重量％、最も好ましくは約７０重量％から約８０重量％である。モノマー組成物中に存在してよい有機溶媒の例には、C_6からC_{14}アルカンが挙げられる。モノマー組成物中の有機溶媒は、モノマー組成物の全重量を基準にして３０重量％以下、より好ましくは５重量％以下である。

【００３８】

水および／または有機溶媒に加えて、モノマー組成物は、任意に、例えば、ヒドロキシ、アミド、アルデヒド、ウレイド、ポリエーテル、グリシジルアルキル、ケト官能基またはそれらの組み合わせを含むモノマーを含むモノマーなどの官能基を有するモノマーを含んでもよい。これらの他のモノマーは、グラフトコポリマーの全重量を基準にして一般には約０．５重量％から約１５重量％、より好ましくは約１重量％から約３重量％のレベルでモノマー組成物中に存在する。官能性モノマーの例には、例えば、ヒドロキシアルキルアクリレートおよびヒドロキシアルキルメタクリレートのアセトアセトキシエステル（例えば、アセトアセトキシエチルメタクリレート）、ならびにケト含有アミド（例えば、ジアセトンアクリルアミド）などのケト官能性モノマー、アリルアルキルメタクリレートまたはアクリレート、グリシジルアルキルメタクリレートまたはアクリレート、あるいはそれらの組み合わせが挙げられる。こうした官能性モノマーは必要ならば架橋をもたらすことが可能である。

【００３９】

好ましい実施形態において、モノマー組成物中のモノマーは水中で前もって乳化させて、モノマー水性エマルジョンを形成させる。モノマー水性エマルジョンは、好ましくは約１マイクロメートルから約１００マイクロメートル、より好ましくは約５マイクロメートルから約５０マイクロメートルの小滴サイズを有するモノマー小滴を含む。所望のモノマー小滴サイズにモノマーを乳化するために、例えば、前述した乳化剤などの適するいかなる乳化剤も用いてよい。乳化剤が存在するなら、乳化剤のレベルは、モノマー組成物中のモノマーの全重量を基準にして好ましくは約０．２重量％から約２重量％である。

【００４０】

モノマー組成物のエチレン性不飽和モノマーは、好ましくは、得られるコポリマー組成物に所望の特性を提供するように選択される。適するエチレン性不飽和モノマーには、例えば、メチルメタクリレート、エチルメタクリレート、ｎ－ブチルメタクリレート、２－エチルヘキシルメタクリレート、ラウリルメタクリレート、ステアリルメタクリレート、イソボルニルメタクリレートをはじめとするメタクリル酸のC_1からC_{18}ノルマルまたは分岐アルキルエステルなどのメタクリレートエステル；メチルアクリレート、エチルアクリレート、ｎ－ブチルアクリレートおよび２－エチルヘキシルアクリレートをはじめとするアクリル酸のC_1からC_{18}ノルマルまたは分岐アルキルエステルなどのアクリレートエステル；スチレン；メチルスチレン、α－メチルスチレンまたはｔ－ブチルスチレンなどの置換スチレン；アクリロニトリルまたはメタクリロニトリルなどのオレフィン性不飽和ニトリル；塩化ビニル、塩化ビニリデンまたは弗化ビニルなどのオレフィン性不飽和ハロゲン化物；酢酸ビニルなどの有機酸のビニルエステル；Ｎ－ビニルピロリドンなどのＮ－ビニル化合物；アクリルアミド；メタクリルアミド；置換アクリルアミド；置換メタクリルアミド；ヒドロキシエチルメタクリレートなどのヒドロキシアルキルメタクリレート；ヒドロキシアルキルアクリレート；１，３－ブタジエンおよびイソプレンなどのジエン；ビニルエーテル；またはそれらの組み合わせが挙げられる。エチレン性不飽和モノマー

は、本明細書で前述したものなどの酸含有モノマーまたは官能性モノマーであることも可能である。好ましくは、モノマー組成物のエチレン性不飽和モノマーはアミノ基を含まない。

【００４１】

好ましい実施形態において、モノマー組成物は、メチルアクリレート、エチルアクリレート、ｎ－ブチルアクリレートおよび２－エチルヘキシルアクリレートをはじめとするアクリル酸のC_1からC_{18}ノルマルまたは分岐アルキルエステル；スチレン；メチルスチレン、α－メチルスチレンまたはｔ－ブチルスチレンなどの置換スチレン；ブタジエンまたはそれらの組み合わせから選択された一種以上のエチレン性不飽和モノマーを含む。

【００４２】

前述したように、マクロモノマー水性エマルジョンおよびモノマー組成物は組み合わせて重合反応混合物を生じさせ、フリーラジカル開始剤の存在下で重合させて、水性コポリマー組成物を生成させる。本明細書で用いられる「重合反応混合物」という用語は、マクロモノマー水性エマルジョンの少なくとも一部とモノマー組成物の少なくとも一部を組み合わせる時に形成される生成混合物を意味する。重合反応混合物は、重合中に用いられる開始剤または他の一切の添加剤も含有してよい。従って、重合反応混合物は、マクロモノマーおよびモノマー組成物中のモノマーが反応してグラフトコポリマーを生成させるにつれて組成が変化する混合物である。

【００４３】

重合を行うために、マクロモノマー水性エマルジョンおよびモノマー組成物は種々の方法で組み合わせてよい。例えば、マクロモノマー水性エマルジョンおよびモノマー組成物は、重合反応の開始の前に組み合わせて、重合反応混合物を形成してよい。あるいは、モノマー組成物はマクロモノマー水性エマルジョンに徐々にフィードすることができるであろうし、あるいはマクロモノマー水性エマルジョンはモノマー組成物に徐々にフィードすることができるであろう。マクロモノマーエマルジョンおよび／またはモノマー組成物の一部のみを重合の開始前に組み合わせ、残りのモノマー組成物および／またはマクロモノマー水性エマルジョンを重合中にフィードすることも可能である。

【００４４】

開始剤も種々の方法で添加することが可能である。例えば、開始剤は、重合の開始時にマクロモノマー水性エマルジョン、モノマー組成物またはマクロモノマー水性エマルジョンとモノマー組成物の混合物に「一回で」で添加してよい。あるいは、開始剤の全部または一部は、別個のフィードストリームとして、マクロモノマー水性エマルジョンの一部として、モノマー組成物の一部としてまたはこれらの方法のあらゆる組み合わせとして共フィードすることが可能である。

【００４５】

マクロモノマー水性エマルジョン、モノマー組成物および開始剤を組み合わせる好ましい方法は、所望のグラフトコポリマー組成のような要素に応じて決まる。例えば、主鎖に沿ったグラフトとしてのマクロモノマーの分布は、重合の時点でのマクロモノマーとエチレン性不飽和モノマーの両方の濃度によって影響されうる。この点に関して、バッチ式プロセスは重合の始めにマクロモノマーとエチレン性不飽和モノマーの両方の高い濃度を与えるのに対して、半連続プロセスは重合中にエチレン性不飽和モノマーの濃度を低くしておく。従って、マクロモノマー水性エマルジョンおよびモノマー組成物を組み合わせる方法を通して、例えば、ポリマー鎖当たりのマクロモノマーグラフトの数、各鎖中のグラフトの分布およびポリマー主鎖の長さを制御することが可能である。

【００４６】

マクロモノマーおよびエチレン性不飽和モノマーを重合する際に有用な開始剤には、当業者に知られている乳化重合のために適するいかなる開始剤も挙げられる。開始剤の選択は、反応成分（例えば、モノマー、マクロモノマー、水）の一種以上中の開始剤の溶解度、所望の重合温度での半減期（好ましくは約３０分から約１０時間の範囲内の半減期）のような要素に応じて決まる。適する開始剤には、４，４’－アゾビス（４－シアノバレリア

ン酸）などのアゾ化合物、ｔ－ブチルヒドロペルオキシドなどの過酸化物、過硫酸ナトリウム、過硫酸カリウムまたは過硫酸アンモニウム、例えば、メタ亜硫酸水素ナトリウム、亜硫酸水素ナトリウム、ホルムアルデヒドスルホキシル酸ナトリウム、イソアスコルビン酸などの還元剤と組み合わせた過硫酸塩または過酸化物などのレドックス開始剤系またはそれらの組み合わせなどのマクロモノマーの形成に関連して本明細書で前述した開始剤が挙げられる。鉄などの金属助触媒および炭酸水素ナトリウムなどの緩衝剤も開始剤に関連して用いてよい。さらに、原子移動ラジカル重合（Ａｔｏｍ　Ｔｒａｎｓｆｅｒ　Ｒａｄｉｃａｌ　Ｐｏｌｙｍｅｒｉｚａｔｉｏｎ）、またはニトロオキシド介在ラジカル重合（Ｎｉｔｒｏｘｉｄｅ　Ｍｅｄｉａｔｅｄ　Ｒａｄｉｃａｌ　Ｐｏｌｙｍｅｒｉｚａｔｉｏｎ）などの制御型フリーラジカル重合（Ｃｏｎｔｒｏｌｌｅｄ　Ｆｒｅｅ　Ｒａｄｉｃａｌ　Ｐｏｌｙｍｅｒｉｚａｔｉｏｎ）（ＣＦＲＰ）法を用いてよい。好ましい開始剤には、４，４’－アゾビス（４－シアノバレリアン酸）などのアゾ化合物が挙げられる。

【００４７】

用いられる開始剤の量は、所望のコポリマーおよび選択された開始剤などの要素に応じて決まる。モノマーおよびマクロモノマーの全重量を基準にして好ましくは約０．１重量％から約１重量％の開始剤が用いられる。

【００４８】

重合温度は、選択された開始剤の種類および所望の重合速度に応じて決まる。しかし、好ましくは、マクロモノマーおよびエチレン性不飽和モノマーは、室温から約１５０℃、より好ましくは約４０℃から約９５℃の温度で重合される。

【００４９】

重合反応混合物を形成させるために添加されるマクロモノマー水性エマルジョンおよびモノマー組成物の量は、それぞれマクロモノマー水性エマルジョンおよびモノマー組成物中のマクロモノマーおよびエチレン性不飽和モノマーの濃度ならびに所望のコポリマー組成のような要素に応じて決まる。マクロモノマー水性エマルジョンおよびモノマー組成物は、好ましくは約２重量％から約９０重量％、より好ましくは約５重量％から約５０重量％、最も好ましくは約５重量％から約３５重量％のマクロモノマー、および約１０重量％から約９８重量％、より好ましくは約５０重量％から約９５重量％、最も好ましくは約６５重量％から約９５重量％のエチレン性不飽和モノマーを重合単位として含むコポリマーをもたらす量で添加される。

【００５０】

当業者は、従来の乳化重合で用いられる他の成分を本発明の方法で任意に用いてよいことを認めるであろう。例えば、得られたグラフトコポリマーの分子量を減少させるために、任意にｎ－ドデシルメルカプタン、チオフェノール、ブロモトリクロロメタンなどのハロゲン化合物、またはそれらの組み合わせなどの一種以上の連鎖移動剤の存在下で、重合を行ってよい。残留モノマーを減少させるために重合反応の完了時に重合反応混合物に別の開始剤および／または触媒（例えば、チェイス剤）も添加してよい。適する開始剤または触媒には、本明細書で前述した開始剤が挙げられる。さらに、モノマー組成物および重合条件の適切な設計を通して分子量を減少させるために、付加－フラグメンテーションを通したマクロモノマーの連鎖移動能力をある程度利用することが可能である。例えば、Ｅ．Ｒｉｚｚａｒｏら、Ｐｒｏｇ．Ｐａｃｉｆｉｃ　Ｐｏｌｙｍ．Ｓｃｉ．，１９９１、１，７７～８８、Ｇ．Ｍｏａｄら、ＷＯ９６／１５１５７号を参照すること。

【００５１】

好ましくは、本発明のプロセスは、モノマー、または得られた水性コポリマー組成物の中和を必要としない。これらの成分は、好ましくは、中和されない形で残る（例えば、酸官能基が存在する場合、塩基で中和されない）。

【００５２】

マクロモノマーおよびモノマー組成物中のエチレン性不飽和モノマーの重合によって形成される生成水性コポリマー組成物は、好ましくは約３０重量％から約６５重量％、より好ましくは約４０重量％から約６０重量％の固形物レベルを有する。水性コポリマー組成物

は、好ましくは、水不溶性であるとともに約６０ｎｍから約５００ｎｍ、より好ましくは約８０ｎｍから約２００ｎｍの粒子サイズを有するコポリマー粒子を含有する。

【００５３】
形成されたグラフトコポリマーは、好ましくはモノマー組成物からのエチレン性不飽和モノマーを重合単位として含む主鎖、および主鎖にペンダントしたマクロモノマーを含む一個以上の側鎖を有する。好ましくは、各側鎖は、主鎖にグラフトされた一個のマクロモノマーから形成される。マクロモノマー側鎖の重合度は、好ましくは約１０から約１０００の範囲内、より好ましくは約２０から約２００の範囲内であり、ここで重合度は、マクロモノマーを形成させるために用いられるエチレン性不飽和モノマーの重合単位の数として表現される。グラフトコポリマーの全重量平均分子量は、好ましくは約５０，０００から約２，０００，０００、より好ましくは約１００，０００から約１，０００，０００の範囲内である。本明細書で用いられる重量平均分子量はサイズ排除クロマトグラフィーによって決定することが可能である。

【００５４】
水性コポリマー組成物のコポリマー粒子は、例えば、噴霧乾燥または凝集によって単離することが可能である。しかし、コポリマー水性組成物をそのまま使用することが好ましい。

【００５５】
本発明の好ましい実施形態において、重合は二段で行われる。第一段で、マクロモノマーは水性乳化重合プロセスで形成され、第二段で、マクロモノマーはエマルジョン中でエチレン性不飽和モノマーと重合される。効率のために、これらの二段は、好ましくは単一容器内で行われる。例えば、第一段において、マクロモノマー水性エマルジョンは、少なくとも一種の第１のエチレン性不飽和モノマーを水性エマルジョン中で重合して、水不溶性マクロモノマー粒子を形成させることにより生じさせてよい。この第一段重合は、好ましくは、本明細書で前述した遷移金属キレート連鎖移動剤を用いて行われる。マクロモノマー水性エマルジョンを生じさせた後に、第２の乳化重合は、好ましくは、マクロモノマーを少なくとも一種の第２のエチレン性不飽和モノマーと重合させるために同じ容器内で行われる。この第二段は、例えば、モノマー組成物および開始剤をマクロモノマー水性エマルジョンに直接添加する（例えば、一斉に、または徐々のフィードにより）ことにより行ってよい。この実施形態の一つの主要な利点は、マクロモノマーを単離することが不要であり、モノマー組成物および開始剤をマクロモノマー水性エマルジョンに添加することにより単純に第２の重合を実施できることである。

【００５６】
本発明のもう一つの好ましい実施形態において、マクロモノマーおよびエチレン性不飽和モノマーの重合は、酸含有モノマー、酸含有マクロモノマーまたはそれらの組み合わせの存在下で少なくとも部分的に行われる。酸含有モノマーまたは酸含有マクロモノマーは、重合反応混合物にいかなる方式でも添加してよい。好ましくは、酸含有モノマーまたは酸含有マクロモノマーはモノマー組成物中に存在する。酸含有モノマーまたは酸含有マクロモノマーは重合反応混合物に別個のストリームとして添加してもよい。

【００５７】
重合反応混合物に添加される酸含有モノマーまたは酸含有マクロモノマーの量は、重合反応混合物に添加されるモノマーおよびマクロモノマーの全重量を基準にして好ましくは約０．２重量％から約１０重量％、より好ましくは約０．５重量％から約５重量％、最も好ましくは約１重量％から約２重量％である。

【００５８】
この実施形態で用いてよい酸含有モノマーには、本明細書で前述したものなどの酸官能基または酸形成基を保有するエチレン性不飽和モノマーが挙げられる。この実施形態で有用な酸含有マクロモノマーは、フリーラジカル重合プロセスで重合されることが可能である少なくとも一個の末端エチレン性不飽和基を有し、少なくとも一種の酸含有モノマーから形成される任意の低分子量ポリマーである。酸含有マクロモノマー中の酸含有モノマーの

量は、好ましくは約５０重量％から１００重量％、より好ましくは約９０重量％から１００重量％、最も好ましくは約９５重量％から１００重量％である。

【００５９】

酸含有マクロモノマーは、本明細書で前述した技術などの当業者に知られているいかなる技術によっても調製してよい。本発明の好ましい実施形態において、酸含有マクロモノマーは、フリーラジカル開始剤および遷移金属キレート錯体を用いる溶液重合プロセスによって調製される。こうしたプロセスの例は、例えば、参照してここに組み込まれる米国特許第５，７２１，３３０号において開示されている。酸含有マクロモノマーを形成するために用いられる好ましい酸含有モノマーはメタクリル酸などのα－メチルビニルモノマーである。

【００６０】

本発明のもう一つの好ましい実施形態において、疎水性キャビティを有するマクロモレキュール有機化合物は、マクロモノマーおよび／または水性コポリマー組成物を形成させるために用いられる重合媒体中に存在する。好ましくは、マクロモレキュール有機化合物は、ラウリルまたはステアリルアクリレートおよび／またはメタクリレートなどの水溶解度が非常に低いエチレン性不飽和モノマーを共重合する時に用いられる。「低水溶解度」とは、５０ミリリットル／リットル以下の２５℃から５０℃での水溶解度を意味する。例えば、マクロモレキュール有機化合物は、水性コポリマー組成物を形成するために用いられるモノマー組成物、マクロモノマー水性エマルジョンまたは重合反応混合物に添加してよい。例えば、マクロモレキュール有機化合物は、マクロモノマーを形成させるために用いられるエチレン性不飽和モノマーの水性エマルジョンに添加してもよい。疎水性キャビティを有するマクロモレキュール有機化合物を使用するために適する技術は、例えば、参照してここに組み込まれる米国特許第５，５２１，２６６号において開示されている。

【００６１】

疎水性キャビティを有するマクロモレキュール有機化合物は、好ましくは約５：１から約１：５０００、より好ましくは１：１から約１：５００のマクロモレキュール有機化合物対低水溶解性モノマーまたはマクロモノマーのモル比をもたらすために重合反応混合物に添加される。

【００６２】

本発明において有用な疎水性キャビティを有するマクロモレキュール有機化合物には、例えば、シクロデキストリンまたはシクロデキストリン誘導体、シクロイヌロヘキソース、シクロイヌロヘプトースまたはシクロイヌロオクトースなどの疎水性キャビティを有する環式オリゴ糖、カリキサレン、キャビタンド、またはそれらの組み合わせが挙げられる。好ましくは、マクロモレキュール有機化合物は、β－シクロデキストリン、より好ましくはメチル－β－シクロデキストリンである。

【００６３】

水溶解性が低いモノマーには、例えば、第一アルケン、スチレンおよびアルキル置換スチレン；α－メチルスチレン；ビニルトルエン；ビニル２－エチルヘキサノエート、ビニルネオデカノエートなどのC_4からC_{30}カルボン酸のビニルエステル；塩化ビニル；塩化ビニリデン；オクチルアクリルアミドおよびマレイン酸アミドなどのＮ－アルキル置換（メタ）アクリルアミド；ステアリルビニルエーテルなどの（C_3からC_{30}）アルキル基を有するビニルアルキルエーテルまたはビニルアリールエーテル；メチルメタクリレート、エチル（メタ）アクリレート、ブチル（メタ）アクリレート、２－エチルヘキシル（メタ）アクリレート、ベンジル（メタ）アクリレート、ラウリル（メタ）アクリレート、オレイル（メタ）アクリレート、パルミチル（メタ）アクリレート、ステアリル（メタ）アクリレートなどの（メタ）アクリル酸の（C_1からC_{30}）アルキルエステル；脂肪酸および脂肪アルコールから誘導されたものなどの（メタ）アクリル酸の不飽和ビニルエステル；ペンタエリトリトールトリアクリレートなどの多官能性モノマー；コレステロールから誘導されたモノマー、またはそれらの組み合わせが挙げられる。

【００６４】

本発明のもう一つの態様において、本明細書で前述したように好ましくは本発明の方法によって製造される水性コポリマー組成物が提供される。水性コポリマー組成物は、好ましくは櫛形コポリマー粒子であるグラフトコポリマーの水不溶性粒子を含有する。櫛形コポリマー粒子は、好ましくは約５０ｎｍから約５００ｎｍ、より好ましくは約８０ｎｍから約２００ｎｍの重量平均粒子サイズを有する。

【００６５】

グラフトコポリマーの粒子は、コポリマーの全重量を基準にして、好ましくは約２重量％から約９０重量％、より好ましくは約５重量％から約５０重量％のマクロモノマーの重合単位を含み、ここでマクロモノマーは、好ましくは、マクロモノマー水性エマルジョン中に存在する水不溶性マクロモノマーについて本明細書で前述したような組成を有する。グラフトコポリマー粒子は、コポリマーの全重量を基準にして、好ましくは約１０重量％から約９８重量％、より好ましくは約５０重量％から約９５重量％の少なくとも一種のエチレン性不飽和モノマーの重合単位も含む。エチレン性不飽和モノマーは、本明細書で前述したようにモノマー組成物中で有用なものなどの、コポリマー粒子に所望の特性を与えるいかなるエチレン性不飽和モノマーであってもよい。

【００６６】

好ましくは、グラフトコポリマーの主鎖は直鎖である。組成的には、コポリマーの主鎖は、好ましくはモノマー組成物から誘導されたエチレン性不飽和モノマーの重合単位を含む。主鎖は、コポリマーの全モルを基準にして、マクロモノマー水性エマルジョンから誘導された好ましくは２０モル％未満、より好ましくは１０モル％未満の重合されたマクロモノマーを含む。

【００６７】

グラフトコポリマーの側鎖は、好ましくはマクロモノマーの重合単位を含む。本発明の好ましい実施形態において、各側鎖は一個のマクロモノマーを含む。さらに、側鎖は、側鎖の全重量を基準にして、モノマー組成物から誘導された５重量％未満、より好ましくは１重量％未満の重合されたエチレン性不飽和モノマーを含む。

【００６８】

グラフトコポリマーの全体的な重量平均分子量は、約５０，０００から約２，０００，０００、より好ましくは約１００，０００から約１，０００，０００である。

【００６９】

本発明の好ましい実施形態において、水不溶性コポリマー粒子は、グラフトコポリマーの全重量を基準にして約０．２重量％から約１０重量％、より好ましくは約０．５重量％から約５重量％、最も好ましくは約１重量％から約２重量％の酸含有マクロモノマーをさらに含む。酸含有マクロモノマーは、好ましくは本明細書で前述した組成を有する。

【００７０】

決して理論に縛られるつもりではないけれども、酸含有マクロモノマーが水不溶性グラフトコポリマー粒子の表面に結合され、安定性を提供することが考えられる。本明細書で用いられる「結合」によって、酸含有マクロモノマーが粒子中のポリマー鎖に何らかの方式（例えば、共有、水素結合、イオン）で結合されることが考えられる。好ましくは、酸含有マクロモノマーは粒子中のポリマー鎖に共有結合される。酸含有マクロモノマーが粒子に安定性を提供し、製造された水性コポリマー組成物が予想外の改善された剪断安定性、凍解安定性、および配合物中の添加剤への安定性、ならびに重合中の凝塊の減少を示すことが見出された。酸含有モノマーを用いて改善された安定性を達成できるけれども、これらの利点は、酸含有マクロモノマーを用いる時に最も効果的である。

【００７１】

コポリマー粒子に加えて水性コポリマー組成物は、好ましくは約１０重量％未満、より好ましくは約１重量％未満の有機溶媒を含有する。最も好ましい実施形態において、水性コポリマー組成物は有機溶媒を含有しない。

【００７２】

水性コポリマー組成物を調製するために本発明の方法を用いる利点は、得られたコポリマ

ー組成物が、例えば、モノマー組成物から誘導されたエチレン性不飽和モノマーのホモポリマーまたはマクロモノマー水性エマルジョンから誘導されたマクロモノマーのホモポリマーなどのホモポリマーを低レベルでしか含有しないことである。水性コポリマー組成物は、グラフトコポリマーの全重量を基準にして、好ましくは約３０重量％未満、より好ましくは約２０重量％未満のマクロモノマーのホモポリマーを含有する。水性コポリマー組成物は、好ましくは約３０重量％未満、より好ましくは約２０重量％未満のエチレン性不飽和モノマーのホモポリマーを含有する。

【００７３】

本発明の方法によって製造される水性コポリマー組成物は様々な用途で有用である。例えば、水性コポリマー組成物は、塗料、木材塗料またはインキ、紙塗料、織物および不織布の結合剤および仕上剤、接着剤、マスティック、床磨き剤、皮塗料、プラスチック、プラスチック添加剤、石油添加剤、熱可塑性エラストマーまたはそれらの組み合わせを含む建築用塗料または工業用塗料中で用いてよい。

【００７４】

（実施例）

本発明の幾つかの実施形態を以下の実施例中で今から詳細に記載する。表１に示した以下の略号を実施例において用いる。

【表１】

表1: 略号

略号	
A-16-22	ポリステップ(Polystep)A-16-22、イリノイ州ノースフィールド(Northfield,Ilinois)のステパン社(Stepan Company)によって22%固形物として供給されるアニオン界面活性剤。
BA	ブチルアクリレート
BD	ブタジエン
BMA	ブチルメタクリレート
CoBF	Co(II)-(2,3-ジオキシイミノブタン-BF$_2$)$_2$
CVA	4,4-アゾビス(4-シアノバレリアン酸)
Fe	水中の0.15%硫酸第一鉄
DBS	ドデシルベンゼンスルホン酸塩
GC	ガスクロマトグラフ
SEC	サイズ排除クロマトグラフィー
HPLC	高速液体クロマトグラフィー
Init.	開始剤
IR	赤外分光分析
LCCC	臨界条件下の液体クロマトグラフィー
MAA	メタクリル酸
MMA	メチルメタクリレート
Mn	数平均分子量
NaMBS	ピロ亜硫酸ナトリウム
NaPS	過硫酸ナトリウム
nDDM	ドデシルメルカプタン
OT-100	エーロゾル(Aerosol)OT-100、ニュージャージー州モリスタウン(Morristown, New Jersey)のサイテック・インダストリーズ社(Cytec Industries Inc.)によって100%活性種として供給されるアニオン界面活性剤
PMAA-MM	ポリメタクリル酸マクロモノマー
PMMA	メチルメタクリレートホモポリマー
PMMA-MM	ポリメチルメタクリレートマクロモノマー
ポリ-(BA-g-BMA)	BMA側鎖を有するBAのグラフトコポリマー
ポリ-(BA-g-MMA)	MMA側鎖を有するBAのグラフトコポリマー
ポリ-(BD-g-MMA)	MMA側鎖を有するBDのグラフトコポリマー
ワコー(Wako)VA-044	2,2'-アゾビス[2-(2-イミダゾリン2-2イル)プロパン]ジヒドロクロリド

【００７５】

実施例において、標準法を用いる未反応モノマーのＧＣ分析によってモノマーの転化率を決定した。マクロモノマーおよびコポリマー組成物に関する固形分重量％は重量分析によって決定した。マクロモノマーおよびコポリマー組成物の粒子サイズは、ＨＰＬＣ型紫外線検出器が装備されたＭａｔｅｃ　ＣＨＤＦ２０００粒子サイズ分析機を用いて得た。

【００７６】

特に注記がないかぎり、分子量分布が狭い５８０から７，５００，０００の範囲のピーク平均分子量を有するポリマーラボラトリーズ社（Ｐｏｌｙｍｅｒ　Ｌａｂｏｒａｔｏｒｉｅｓ）からのポリスチレン標準（ＰＳ－１）を用いてＳＥＣによってマクロモノマーの数平均分子量を測定した。ポリスチレンからＰＭＭＡへの換算は、Ｍａｒｋ－Ｈｏｕｗｉｎｋ定数を用いて行った。上述したようなＳＥＣを用いてコポリマー組成物の数平均分子量および重量平均分子量を評価した。

【００７７】

比較例１．０

従来の連鎖移動剤を用いる水性乳化重合プロセスによって低分子量ＭＭＡポリマーを調製

した。以下の手順に従って、メカニカルスターラー、温度制御装置、コンデンサ、モノマーフィードラインおよび窒素入口が付いた２リットルの四つ口丸底反応フラスコ内で行った重合を行った。４８３．７ｇの脱イオン水、２．０ｇのＡ－１６－２２および５２重量％メチル－β－シクロデキストリンを含有する水溶液１．５５ｇを反応フラスコに添加して界面活性剤溶液を生じさせた。１２５ｇの脱イオン水、３ｇのＡ－１６－２２、３０５ｇのＭＡＡおよび５ｇのｎＤＤＭを含むモノマーエマルジョンを別個に調製した。さらに、７２．３ｇの脱イオン水に１．５６ｇのＮａＢＳを溶解することにより開始剤溶液を調製した。界面活性剤溶液を８０℃に加熱し、その後、全開始剤溶液の６０％を反応フラスコに添加した。その後、モノマーエマルジョンおよび残りの開始剤溶液を６０分にわたりフィードした。フィード期間の終わりに、反応混合物をさらに３０分にわたり８０℃に維持し、その後、冷却し濾過した。得られた低分子量ＭＭＡエマルジョンは３１．０重量％の固形物を含んでいた。ＭＭＡポリマーの数平均分子量（Ｍｎ）は２１７００であった。

【００７８】

実施例１．１から１．８－乳化重合によるＰＭＭＡ－ＭＭの調製

比較例１．０に記載されたのと同じ装置を用いて実施例１．１から１．８で乳化重合プロセスによってＭＭＡマクロモノマー（ＰＭＭＡ－ＭＭ）を調製した。実施例１．１から１．８で用いた水、界面活性剤、ＭＭＡ、連鎖移動剤（ＣＴＡ）および開始剤の具体的な量を表２に示している。これらの原料を以下の手順に従って添加した。反応フラスコとは異なるフラスコ内で、窒素パージ下でＭＭＡに連鎖移動剤を溶解することによりモノマー溶液を調製した。脱イオン水および界面活性剤（ＯＴ－１００）を室温で反応フラスコに導入して水界面活性剤溶液を生じさせた。水界面活性剤溶液を混合し、窒素パージ下で攪拌しながら８０℃に加熱した。８０℃の反応温度に達するとともに界面活性剤が完全に溶解すると、開始剤（ＣＶＡ）を水界面活性剤溶液に１分にわたり攪拌しながら添加して、開始剤を溶解させた。開始剤の溶解後に、モノマー溶液の２０重量％を攪拌しながら反応フラスコに添加した。この初期投入後に、残りのモノマー溶液を１から２時間にわたり攪拌しながらフィードして、反応混合物を生じさせた。フィード期間の終わりに、反応混合物をさらに１から３時間にわたり８０℃に維持した。その後、反応混合物を室温に冷却し、フィルタクロスに通して一切の凝塊を除去した。

【００７９】

一般に、得られたマクロモノマーエマルジョンは、マクロモノマーの全重量を基準にして５重量％未満の凝塊を含んでおり、モノマーの転化率は、添加したモノマーの全重量を基準にして９９重量％を上回った。マクロモノマーごとのＭｎ、固形分重量％および粒子サイズを表２に報告している。

【表２】

表2:PMMA-MMの調製

実施例	H_2O (g)	界面活性剤 (g)$^{(3)}$	MMA (g)	CTA ppm$^{(1)}$	開始剤 (g)$^{(2)}$	粒子サイズ (nm)	Mn	固形分重量%
1.1	720	3.6	324	40	3.6	165	2430	32.0
1.2	720	3.6	324	8.7	3.6	126	12612	31.0
1.3	720	3.6	324	10.9	3.6	158	9656	31.0
1.4	720	3.6	324	80.6	3.6	231	1386	30.3
1.5	720	3.6	324	21.8	3.6	201	4416	29.1
1.6	720	3.6	324	10.7	3.6	169	7931	30.5
1.7	720	3.6	360	11.9	3.6	155	10185	32.0
1.8	1440	7.2	720	15.2	7.2	167	7237	32.0

（１）モノマーの全モルを基準にした連鎖移動剤（ＣｏＢＦ）のｐｐｍモル

（２）開始剤の７５重量％水溶液としてアルドリッチ（Ａｌｄｒｉｃｈ）によって供給されるＣＶＡ

（３）ＯＴ－１００

【００８０】

実施例２：溶液重合によるＰＭＡＡ－ＭＭの調製

メカニカルスターラー、コンデンサ、温度制御装置、開始剤フィードラインおよび窒素入口が付いた2リットルのバッフル付きフランジフラスコ内で水溶液重合プロセスによってMAAマクロモノマー（ＰＭＡＡ－ＭＭ）を調製した。０．０18ｇのＣｏＢＦを添加した後、装置を３０分にわたり窒素でパージした。１０８０ｇの脱イオン水をフラスコに投入し、窒素パージ下で５５℃に加熱した。５１０ｍｌのＭＡＡおよび０．０１ｇのＣｏＢＦを含むモノマー混合物を窒素下で別個に調製した。脱イオン水が５５℃の温度に達した時、１．９４ｇの開始剤（Ｗａｋｏ　ＶＡ－０４４）を反応フラスコに添加した。開始剤の添加後に、モノマー混合物を攪拌しながら６０分にわたり反応フラスコに添加した。その後、モノマー混合物フィードの完了後に、温度を２時間にわたり５５℃に保持した。反応フラスコを室温に冷却すると、ＭＡＡ－ＭＭ（実施例２．１）をロータリーエバポレーションによって乾燥ポリマーとして単離した。ポリマー鎖のメチル基およびメチレン基に対するビニル末端基の積分に基づくプロトン核磁気共鳴によって、ＭＡＡ－ＭＭの数平均分子量（Ｍｎ）が４０３０であると測定された。

【００８１】

実施例３：バッチ式乳化重合プロセスによるポリー（ＢＡ－ｇ－ＭＭＡ）グラフトコポリマーの調製

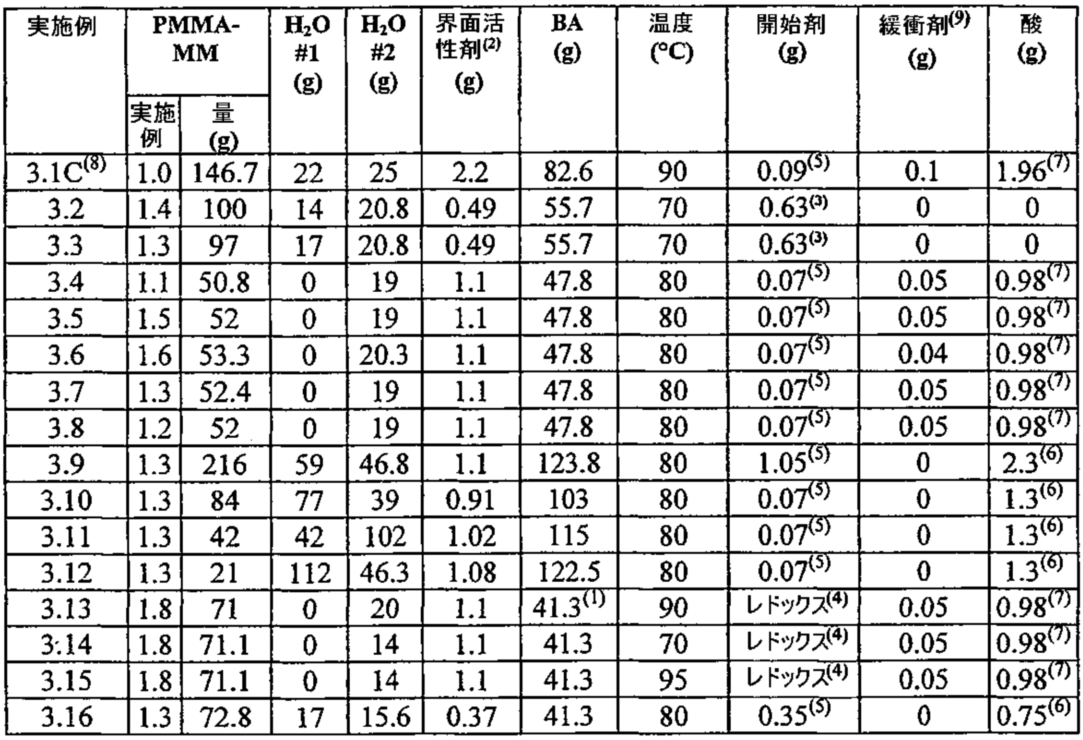
メカニカルスターラー、コンデンサ、温度制御装置、開始剤フィードラインおよび窒素入口が付いた１リットルの四つ口丸底反応フラスコ内でバッチ式乳化重合プロセスによって、比較例３．０Ｃおよび実施例３．１から３．１５のグラフトコポリマーを調製した。用いたＰＭＭＡ－ＭＭ（エマルジョンとして）、水、界面活性剤、酸含有モノマー（表３で「酸」と印付けされたもの）、ＢＡ、開始剤および緩衝剤の具体的な量を表３に示している。これらの原料を以下の手順に従って添加した。脱イオン水（表３の$Ｈ_2$Ｏ＃１）および表３に示した実施例から得たＰＭＭＡ－ＭＭエマルジョン（「ＰＭＭＡ－ＭＭ」欄で「Ｅｘ」で印付けされた下位欄）を室温で反応フラスコに導入した。脱イオン水（表３の$Ｈ_2$Ｏ＃２）、界面活性剤、酸含有モノマーおよびＢＡのモノマーエマルジョンを調製した。実施例３．１３のモノマーエマルジョンは０．１３ｇのｎＤＤＭをさらに含んでいた。モノマーエマルジョンを攪拌しながら室温で反応フラスコに導入して、反応混合物を生じさせた。２０分の攪拌後に、反応混合物を表３に示した反応温度に加熱した。

【００８２】

一旦反応温度に達すると、以下の手順に従って開始剤および任意に緩衝剤を攪拌しながら反応フラスコに導入した。実施例３．１Ｃ、３．２、３．３および３．４から３．８については、表３に記載した緩衝剤と開始剤の両方を反応フラスコに一回で添加した。実施例３．９から３．１２および３．１６については、開始剤溶液の２０重量％を反応フラスコに一回で添加し、残りを１から２時間にわたってフィードした。レドックス開始剤で調製した実施例（３．１３から３．１５）については、ＮａＰＳおよびＮａＭＢＳの三分の一を反応フラスコに一回で添加し、残りを１から２時間にわたってフィードした。また、レドックス開始剤系に関して、ＮａＰＳおよびＮａＭＢＳのフィードの始めにＦｅおよび$Ｎａ_2ＣＯ_3$のすべてを反応フラスコに添加した。開始剤および緩衝剤を添加した後、反応混合物を１から２時間にわたり反応温度に維持した。得られたコポリマー組成物の転化率および他の特性を実施例１０に記載したように分析した。標準ＧＣ分析によって決定されたＢＡの転化率は、投入したＢＡの全重量を基準にして９９重量％より大きかった。

【表３】

表3:バッチ式プロセスによって調製されたポリ-(BA-g-MMA)グラフトコポリマーの調製



実施例	PMMA-MM		H₂O #1 (g)	H₂O #2 (g)	界面活性剤(2) (g)	BA (g)	温度 (°C)	開始剤 (g)	緩衝剤(9) (g)	酸 (g)
	実施例	量 (g)								
3.1C(8)	1.0	146.7	22	25	2.2	82.6	90	0.09(5)	0.1	1.96(7)
3.2	1.4	100	14	20.8	0.49	55.7	70	0.63(3)	0	0
3.3	1.3	97	17	20.8	0.49	55.7	70	0.63(3)	0	0
3.4	1.1	50.8	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.5	1.5	52	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.6	1.6	53.3	0	20.3	1.1	47.8	80	0.07(5)	0.04	0.98(7)
3.7	1.3	52.4	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.8	1.2	52	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.9	1.3	216	59	46.8	1.1	123.8	80	1.05(5)	0	2.3(6)
3.10	1.3	84	77	39	0.91	103	80	0.07(5)	0	1.3(6)
3.11	1.3	42	42	102	1.02	115	80	0.07(5)	0	1.3(6)
3.12	1.3	21	112	46.3	1.08	122.5	80	0.07(5)	0	1.3(6)
3.13	1.8	71	0	20	1.1	41.3(1)	90	レドックス(4)	0.05	0.98(7)
3:14	1.8	71.1	0	14	1.1	41.3	70	レドックス(4)	0.05	0.98(7)
3.15	1.8	71.1	0	14	1.1	41.3	95	レドックス(4)	0.05	0.98(7)
3.16	1.3	72.8	17	15.6	0.37	41.3	80	0.35(5)	0	0.75(6)

（１）０．１３ｇのｎＤＤＭをモノマーエマルジョンに添加した。

（２）Ａ－１６－２２で調製された実施例３．１２を除き、分子当たり１から４０個のエチレンオキシド基を有するエトキシル化Ｃ$_{6}$からＣ$_{18}$アルキルエーテルスルフェート（水中で３０％の活性種）。

（３）エルフ・アトケム（Ｅｌｆ　Ａｔｏｃｈｅｍ）によって供給されるルパゾール（Ｌｕｐｅｒｓｏｌ）１１

（４）レドックス開始剤系は、水３ｇ中のＮａＰＳ０．０７ｇ、水３ｇ中のＮａＭＢＳ０．０６ｇおよびＦｅ０．７ｇを含んでいた。

（５）５から２０ｇの水に溶解したＮａＰＳ

（６）ＭＡＡ

（７）ＰＭＡＡ－ＭＭ（実施例２．１の方法で調製されたもの）

（８）末端エチレン性不飽和基のないＰＭＭＡで調製された比較例

（９）５ｇの水に溶解した炭酸ナトリウム

【００８３】

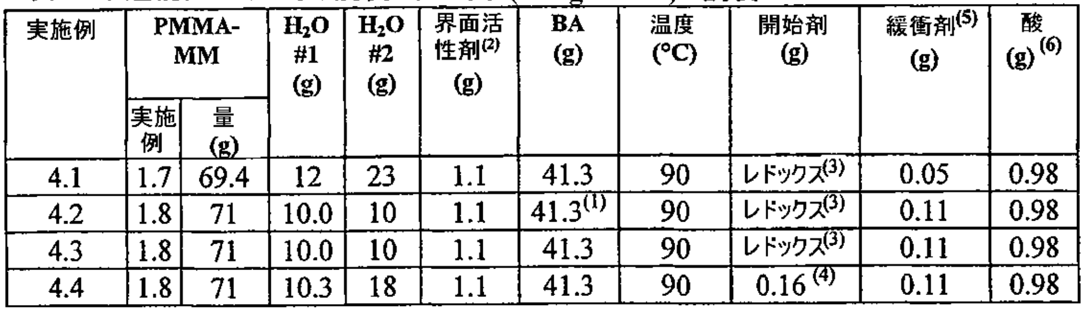
実施例４：半連続プロセスによるポリー（ＢＡ－ｇ－ＭＭＡ）の調製

実施例４．１から４．５において、メカニカルスターラー、温度制御装置、開始剤フィードラインおよび窒素入口が付いた１リットルの四つ口丸底反応フラスコ内で半連続乳化重合プロセスによってグラフトコポリマーを調製した。実施例４．１から４．４で用いたＰＭＭＡ－ＭＭ（エマルジョンとして）、水、界面活性剤、ＢＡ、酸含有モノマーおよび開始剤の具体的な量を表４に示している。これらの原料を以下の手順に従って添加した。脱イオン水（表４のＨ$_2$Ｏ＃２）、界面活性剤およびＢＡのモノマーエマルジョンを別個のフラスコ内で調製した。実施例４．２のモノマーエマルジョンは０．１３ｇのｎＤＤＭをさらに含んでいた。脱イオン水（表４のＨ$_2$Ｏ＃１）、酸含有モノマーおよび表４に示した実施例から得たＰＭＭＡ－ＭＭ（「ＰＭＭＡ－ＭＭ」欄で「Ｅｘ」で印付けされた下位欄）を室温で反応フラスコに導入して、反応混合物を生じさせた。窒素パージ下で撹拌しつつ、反応混合物を表４に示した反応温度に加熱した。反応温度に達すると、以下の手順に従って開始剤および緩衝剤（必要ならば）を撹拌しながら反応フラスコに導入した。実

施例４．１から４．３（レドックス開始剤で調製されたもの）については、ＮａＰＳおよびＮａＭＢＳの三分の一、およびＦｅおよびＮａ$_2$ＣＯ$_3$のすべてを反応フラスコに一回で添加した。その後、残りのＮａＰＳおよびＮａＭＢＳを９０分にわたりモノマーエマルジョンと共フィードした。実施例４．４においては、ＮａＰＳの三分の一、およびＮａ$_2$ＣＯ$_3$のすべてを反応フラスコに一回で添加し、その後、モノマーエマルジョンを残りのＮａＰＳと９０分にわたり共フィードした。フィードが完了すると、反応混合物を１から２時間にわたって反応温度に維持した。得られたコポリマー組成物の転化率および他の特性を実施例１０に記載したように分析した。標準ＧＣ法によって決定されたＢＡの転化率は、投入したＢＡの全重量を基準にして９９重量％より大きかった。

【表４】

表4：半連続プロセスにより調製されたポリ-(BA-g-MMA)の調製



実施例	PMMA-MM		H_2O #1 (g)	H_2O #2 (g)	界面活性剤(2) (g)	BA (g)	温度 (°C)	開始剤 (g)	緩衝剤(5) (g)	酸 (g)(6)
	実施例	量 (g)								
4.1	1.7	69.4	12	23	1.1	41.3	90	レドックス(3)	0.05	0.98
4.2	1.8	71	10.0	10	1.1	41.3(1)	90	レドックス(3)	0.11	0.98
4.3	1.8	71	10.0	10	1.1	41.3	90	レドックス(3)	0.11	0.98
4.4	1.8	71	10.3	18	1.1	41.3	90	0.16 (4)	0.11	0.98

（１）０．１３ｇのｎＤＤＭをモノマーエマルジョンに添加した。

（２）分子当たり１から４０個のエチレンオキシド基を有するエトキシル化Ｃ$_6$からＣ$_{18}$アルキルエーテルスルフェート（水中で３０％の活性種）

（３）レドックス開始剤系は、水６ｇ中のＮａＰＳ０．１６ｇ、水６ｇ中のＮａＭＢＳ０．１４ｇおよびＦｅ０．７ｇを含む。

（４）１０ｇの水に溶解したＮａＰＳ

（５）３ｇの水に溶解した炭酸ナトリウム

（６）ＰＭＡＡ－ＭＭ（実施例２．１の方法で調製されたもの）

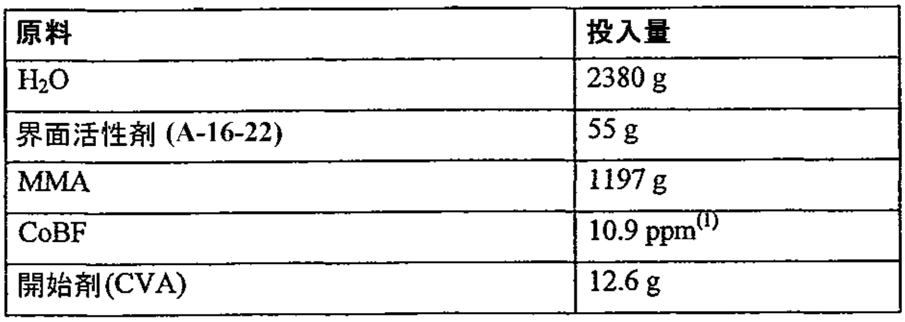
【００８４】

実施例５：ポリー（ＢＤ－ｇ－ＭＭＡ）グラフトコポリマーの調製

本発明の方法に従って、ＢＤの主鎖およびＭＭＡの側鎖を有するグラフトコポリマーを調製した。グラフトコポリマーを二段で調製した。第一段において、表５ａに示した以下の量の原料を表２の対応する原料に代えて用いたことを除き、実施例１で用いた手順に従ってＰＭＭＡ－ＭＭを調製した。

【表５】

表5a: BMAマクロモノマーの調製に際して用いた原料



原料	投入量
H_2O	2380 g
界面活性剤 (A-16-22)	55 g
MMA	1197 g
CoBF	10.9 ppm(1)
開始剤(CVA)	12.6 g

（１）ＭＭＡモノマーの全モルを基準にして

【００８５】

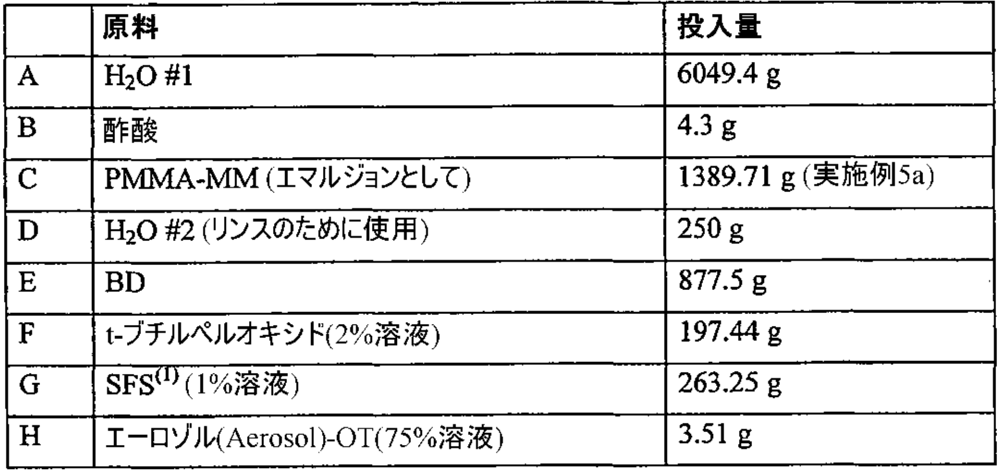
得られたＰＭＭＡ－ＭＭのＭｎは１０，２００であった。

第二段において、メカニカルスターラー、温度制御装置およびフィードラインが付いた鋼

製加圧反応器内でグラフトポリー（ＢＤ－ｇ－ＭＭＡ）を調製した。表５ｂで示した原料ＡからＤを室温で反応器に投入した。その後、反応器を密封し、攪拌しながら真空をかけて、反応圧力を１５インチＨｇに下げた。表５ｂのブタジエン（Ｅ）を反応器にポンプで迅速に送り、１０分にわたり攪拌した。攪拌後に、反応混合物を６０℃に３０分で加熱した。反応器の温度が６０℃に安定化された後に、表５ｂの原料Ｆ、ＧおよびＨを７時間にわたりポンプで反応器に徐々に送った。フィードの完了後に、反応混合物を６０℃で６０分にわたり保持した。

【表６】

表:5b ポリ-(BD-g-MMA)グラフトコポリマーの調製に際して用いた原料



	原料	投入量
A	H_2O #1	6049.4 g
B	酢酸	4.3 g
C	PMMA-MM (エマルジョンとして)	1389.71 g (実施例5a)
D	H_2O #2 (リンスのために使用)	250 g
E	BD	877.5 g
F	t-ブチルペルオキシド(2%溶液)	197.44 g
G	SFS$^{(1)}$ (1%溶液)	263.25 g
H	エーロゾル(Aerosol)-OT(75%溶液)	3.51 g

（１）ホルムアルデヒドスルホキシル酸ナトリウム

【００８６】

テトラヒドロフラン中のグラフトコポリマーの^{1}Ｈ　ＮＭＲ分析によると、ＢＤ対ＭＭＡの重量％比が６５．２対３４．８であることが示された。ＨＰＬＣによる未反応ＰＭＭＡ－ＭＭの分析によると、添加されたＰＭＭＡ－ＭＭの全重量を基準にして約４４重量％のＰＭＭＡ－ＭＭの組み込みが示された。ＨＰＬＣは、主としてＢＤ／ＭＭＡグラフトコポリマーピークを示した（ＩＲによって検証した）。示差走査熱分析は、それぞれ－７９．８℃および１１０．４℃で２つの相転移を示した。グラフトコポリマー組成物は、１５重量％の固形物含有率および１０７ｎｍの重量平均粒子サイズをもっていた。

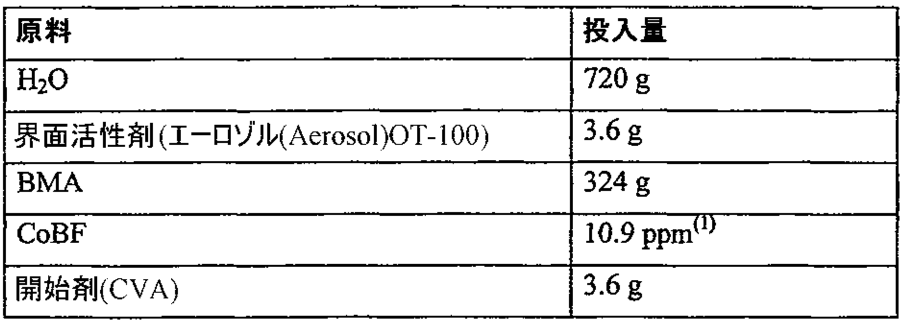
【００８７】

実施例６：ポリー（ＢＡ－ｇ－ＢＭＡ）グラフトコポリマーの調製

本発明の方法に従って、ＢＡの主鎖およびＢＭＡの側鎖を有するグラフトコポリマーを調製した。グラフトコポリマーを二段で調製した。第一段において、表６ａに示した以下の量の原料を表２の対応する原料に代えて用いたことを除き、実施例１で用いた手順に従ってブチルメタクリレートマクロモノマーを調製した。

【表７】

表6a: BMAマクロモノマーの調製に際して用いた原料



原料	投入量
H_2O	720 g
界面活性剤(エーロゾル(Aerosol)OT-100)	3.6 g
BMA	324 g
CoBF	10.9 ppm$^{(1)}$
開始剤(CVA)	3.6 g

（１）ＢＭＡモノマーの全モルを基準にして

【００８８】

得られたＢＭＡマクロモノマーのＭｎは８９００であった。

第二段において、表６ｂに示した以下の量の原料を表３の対応する原料に代えて用い、８５℃の反応温度を用いたことを除き、実施例３で記載した手順を用いてグラフトポリー（ＢＡ－ｇ－ＢＭＡ）を調製した。

【表８】

表6b: ポリ-(BA-g-BMA)グラフトコポリマーの調製に際して用いた原料

原料	投入量
PBMA-MM (エマルジョンとして)	84.1 g (実施例6a)
H_2O #2	15 g
界面活性剤$^{(2)}$	1.1 g
BA	41.3 g
開始剤	レドックス$^{(1)}$
酸(PMAA-MM)	0.98 g (実施例2.1)

（１）レドックス開始剤系は、水３ｇ中のＮａＰＳ０．０７ｇ、水３ｇ中のＮａＭＢＳ０．０６ｇ、水３ｇ中のＮａ$_2$ＣＯ$_3$ ０．０５ｇおよびＦｅ０．７ｇであった。

（２）分子当たり１から４０個のエチレンオキシド基を有するエトキシル化Ｃ$_6$からＣ$_{18}$アルキルエーテルスルフェート（水中で３０％の活性種）

【００８９】

形成されたグラフトコポリマーは、６３．５重量％のＢＡ、３５重量％のＰＢＭＡ－ＭＭおよび１．５重量％のＰＭＡＡ－ＭＭを含んでいた。

【００９０】

実施例７：ポリー（スチレンーｇ－ＭＭＡ）グラフトコポリマーの調製

本発明の方法に従って、スチレンの主鎖およびＰＭＭＡ－ＭＭの側鎖を有するグラフトコポリマーを調製した。グラフトコポリマーを二段で調製した。マクロモノマーＰＭＭＡ－ＭＭ（実施例１．８から得たもの）をグラフトポリー（スチレンーｇ－ＭＭＡ）の合成に際して用いた。表７に示した以下の量の原料を表３の対応する原料に代えて用い、８５℃の反応温度を用いたことを除き、実施例３で記載した手順を用いてグラフトポリー（スチレンーｇ－ＭＭＡ）を調製した。

【表９】

表７：ポリ-(スチレン-g-MMA)グラフトコポリマーの調製に際して用いた原料

原料	投入量
PMMA-MM (エマルジョンとして)	84.1 g (実施例1.8)
H_2O #2	15 g
界面活性剤$^{(2)}$	1.1 g
スチレン	41.3 g
開始剤	レドックス$^{(1)}$
酸(pMAA-MM)	0.98 g (実施例2.1)

（１）レドックス開始剤系は、水３ｇ中のＮａＰＳ０．０７ｇ、水３ｇ中のＮａＭＢＳ０．０６ｇ、水３ｇ中のＮａ$_2$ＣＯ$_3$ ０．０５ｇおよびＦｅ０．７ｇを含む。

（２）分子当たり１から４０個のエチレンオキシド基を有するエトキシル化C_6からC_{18}アルキルエーテルスルフェート（水中で３０％の活性種）。

【００９１】

形成されたグラフトコポリマーは、６３．５重量％のスチレン、３５重量％のＰＭＭＡ－ＭＭおよび１．５重量％のＰＭＡＡ－ＭＭを含んでいた。

【００９２】

実施例８：単一容器合成手順によるポリ（ＢＡ－ｇ－ＭＭＡ）の調製

本発明の方法に従って、ＢＡの主鎖およびＭＭＡの側鎖を有するグラフトコポリマーを二段の水性乳化重合において単一容器内で調製した。第一段でＰＭＭＡ－ＭＭを調製し、第二段でＰＭＭＡ－ＭＭをＢＡと共重合した。

【００９３】

メカニカルスターラー、温度制御装置、コンデンサ、モノマーフィードラインおよび窒素入口が付いた５リットルの四つ口丸底反応フラスコ内でＰＭＭＡ－ＭＭを調製した。反応フラスコに６８０ｇの脱イオン水および１５．７ｇのＡ－１６－２２を投入して水界面活性剤溶液を生じさせた。水界面活性剤溶液を攪拌しながら窒素パージ下で８０℃に加熱した。３．６ｇの４，４－アゾビス（４－シアノバレリアン酸）を攪拌しながら反応フラスコに８０℃で添加した。二分後に、１８ｇのＭＭＡを攪拌しながら反応フラスコに添加した。３４２ｇのＭＭＡおよび０．０２ｇのＣｏＢＦを含有するモノマー混合物を別個に調製し、２０分にわたりモノマー混合物中で窒素を泡立たせることにより脱気した。モノマー混合物の２０重量％部分を１８ｇのＭＭＡの添加から１０分後に反応フラスコに添加した。温度を８０℃に維持しつつ、モノマー混合物の残りを攪拌しながら１２０分にわたりフィードした。モノマー混合物フィードの終わりに、フラスコ内の反応混合物の温度を６０分にわたり８０℃にしておき、その後４０℃に冷却した。得られたマクロモノマー水性エマルジョンを以下に記載するように第二段において同じ容器内で反応させた。

【００９４】

第二段において、２２６ｇの脱イオン水、分子当たり１から４０個のエチレンオキシド基を有するエトキシル化C_6からC_{18}アルキルエーテルスルフェート（水中で３０％の活性種）１６．５２ｇ、６５８ｇのブチルアクリレートを含有するモノマーエマルジョンを調製した。さらに、７５．４ｇの水中の１０．２ｇのＰＭＡＡ－ＭＭを別個に調製した。モノマーエマルジョンおよびＰＭＡＡ－ＭＭ溶液を４０℃で反応フラスコに添加し、得られた反応混合物を２０分にわたり攪拌し、その後、８５℃に加熱した。２５ｇの水に溶解した１．０６ｇの過硫酸ナトリウムおよび２５ｇの水に溶解した０．４７ｇの炭酸ナトリウムを８５℃で反応フラスコに一回で添加し、その後、２０ｇの脱イオン水でリンスした。開始剤および緩衝剤の投入後に、反応混合物を攪拌しながら６０分にわたり８５℃に維持した。反応混合物を４０℃に冷却後に、水中の$FeSO_4$の０．１５％溶液１３．７２ｇを攪拌しながら添加し、その後、ｔ－ブチルペルオキシドおよびイソアスコルビン酸（それぞれ水１５ｇ中の０．７０ｇおよび０．３４ｇ）を添加した。同量のｔ－ブチルペルオキシドおよびイソアスコルビン酸の二回目の添加を一回目から１５分後に添加した。反応混合物を４０℃の温度で３０分にわたり攪拌しながら保持した。

【００９５】

得られたコポリマー組成物を室温に冷却し、フィルタクロスに通して一切の凝塊を除去した。得られたグラフトコポリマーは、６４重量％のブチルアクリレート、３５重量％のメチルメタクリレートおよび１重量％のＰＭＡＡ－ＭＭを含んでいた。コポリマー組成物は、投入したＰＭＭＡ－ＭＭの全重量を基準にして７６重量％のＰＭＭＡ－ＭＭの組み込みを有していた。

【００９６】

実施例９

コポリマー組成物の特性

固形分重量％、粒子サイズ、重量平均分子量、数平均分子量およびマクロモノマーの組み込み％を決定するために、前の実施例で調製したグラフトコポリマー組成物を種々の分析

技術によって特性分析した。

【００９７】

未反応マクロモノマーの量の決定を、以下の手順を用いるＨＰＬＣ分析によって行った。コポリマー組成物をＴＨＦに溶解し、よく分離されたピークが未反応マクロモノマーに関して観察されるようにペンシルバニア州ベルフォンテ（Ｂｅｌｌｆｏｎｔｅ，ＰＡ）のスペルコ社（Ｓｕｐｅｌｃｏ）によって供給されるＬＣ－１８カラムでの傾斜溶離によって分析した。合成において用いたのと同じマクロモノマーの既知標準を用いて検出器応答を較正することにより定量化を行った。特性分析の結果を以下の表８に報告している。

【表１０】

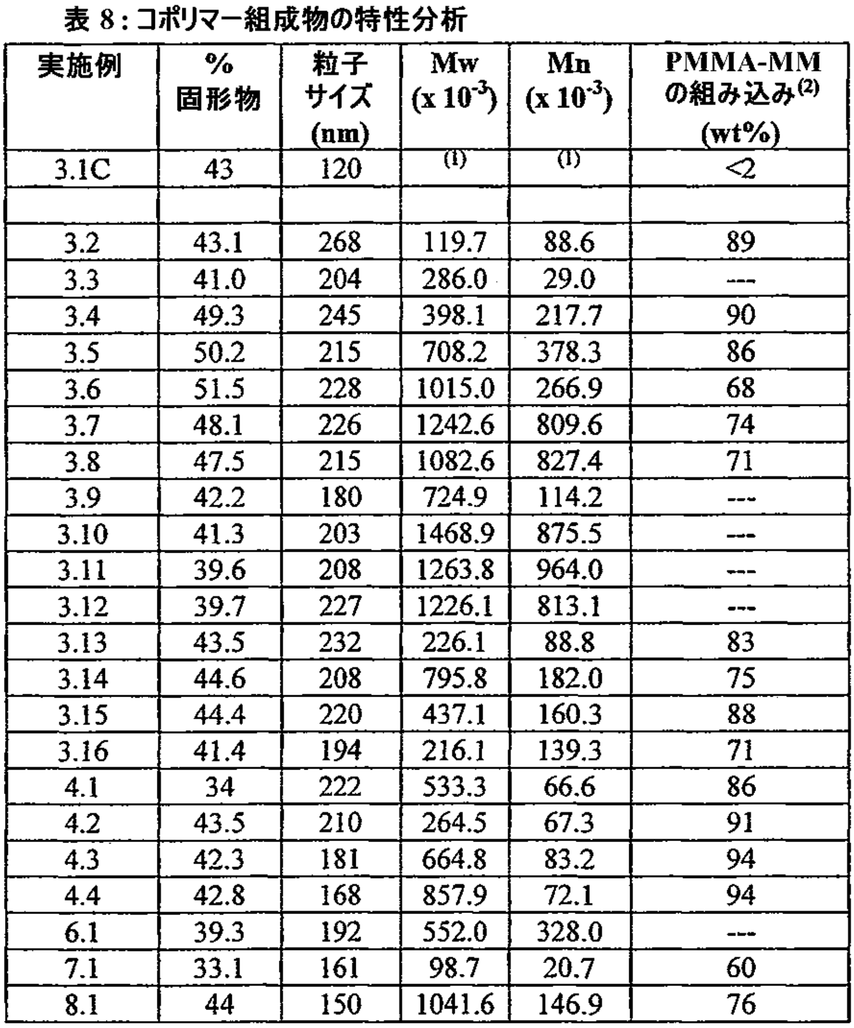


表 8: コポリマー組成物の特性分析

実施例	% 固形物	粒子サイズ (nm)	Mw ($x 10^{-3}$)	Mn ($x 10^{-3}$)	PMMA-MM の組み込み$^{(2)}$ (wt%)
3.1C	43	120	$^{(1)}$	$^{(1)}$	<2
3.2	43.1	268	119.7	88.6	89
3.3	41.0	204	286.0	29.0	---
3.4	49.3	245	398.1	217.7	90
3.5	50.2	215	708.2	378.3	86
3.6	51.5	228	1015.0	266.9	68
3.7	48.1	226	1242.6	809.6	74
3.8	47.5	215	1082.6	827.4	71
3.9	42.2	180	724.9	114.2	---
3.10	41.3	203	1468.9	875.5	---
3.11	39.6	208	1263.8	964.0	---
3.12	39.7	227	1226.1	813.1	---
3.13	43.5	232	226.1	88.8	83
3.14	44.6	208	795.8	182.0	75
3.15	44.4	220	437.1	160.3	88
3.16	41.4	194	216.1	139.3	71
4.1	34	222	533.3	66.6	86
4.2	43.5	210	264.5	67.3	91
4.3	42.3	181	664.8	83.2	94
4.4	42.8	168	857.9	72.1	94
6.1	39.3	192	552.0	328.0	---
7.1	33.1	161	98.7	20.7	60
8.1	44	150	1041.6	146.9	76

（１）実施例１．０Ｃに従って調製されたポリマーが共重合しなかったことを示唆する、下方分子量がマクロモノマーの分子量に対応する双峰分子量分布。

（２）反応容器に添加されたマクロモノマーの全重量を基準にして。サンプルの一部（実施例３．３、３．９、３．１０、３．１１、３．１２、６．１）はＰＭＭＡ－ＭＭの組み込みを分析しなかった。

【００９８】

実施例１０：実施例３．１６の分析

ポリマー分子当たりのグラフトの平均数を決定するとともにグラフトコポリマーが生じていることを示すために、二次元ＨＰＬＣ分析を実施例３．１６について行った。二次元ＨＰＬＣは、錯体ポリマー材料の分離について従来のＨＰＬＣと比べて遙かにより高い解像度を提供する。この分析で用いた方法は、「従来の制御型ラジカルおよびアニオン重合を介したマクロモノマーの共重合によって得られたグラフトコポリマーの二次元クロマトグラフ分析」（２Ｄ Ｃｈｒｏｍａｔｏｇｒａｐｈｉｃ Ａｎａｌｙｓｉｓ ｏｆ Ｇｒａ ft Copolymers Obtained by Copolymerization of Macromonomers Via Conventional, Controlled Radial, And Anionic Polymerizations）、Muller, Axel H. E.らによる、Polym. Prep., Am. Chem. Soc., Div. Polym. Chem., ４０（２）、１４０～１４１頁、１９９９に記載された方法に似ていた。この文献は、参照してここに組み込まれる。ＬＣＣＣを第一次元で用い、ＧＰＣを第二次元で用いた。第１の分析からのカットを第２の技術によって逐次分析し、適切なソフトウェアによって、二次元でのデータのプロットを作製した。コポリマー上のＭＭＡグラフトの全分子量を決定できるように、ＰＢＡに関する臨界条件およびＰＭＭＡに関するサイズ排除条件下でＬＣＣＣ分析を行った。この値から（各側鎖が一個のマクロモノマーを含んでいたと仮定して）コポリマー当たりの側鎖の数を計算した。コポリマーの組成を決定するためにもＬＣＣＣを用いた。コポリマーの全分子量を推定するために、ＳＥＣを用いる第二次元での分析を用いた。ＬＣＣＣ次元のためにＰＭＭＡおよびＧＰＣ次元のためにＰＢＡの標準を用いて、測定された分子量を較正した。得られた二次元クロマトグラムによると、主コポリマーピーク（概算で＞７０％）が示され、それは、ＬＣＣＣデータから、約１１０，０００の全ＰＭＭＡ分子量（Ｍｎ）を含んでいた。ＰＭＭＡマクロモノマーに関する９６００のＭｎ値を用いて、ポリマー鎖当たりの平均のグラフト数を約１１．５と推定した。第二次元から、このピークの全体としての分子量が５８０，０００であると推定された。二次元クロマトグラムによると、二つの他のコポリマーピーク系列を検出したが、ＰＢＡホモポリマーは検出されなかったことが示された。二次元ＨＰＬＣデータから計算された主コポリマーピークの全体としての組成は、ＢＡ約８５重量％およびＭＭＡ１５重量％であった。この組成は、（マクロモノマーの約７０％のみがコポリマーに転化されたことを考慮して、ＮＭＲ組成分析から計算された）ＢＡ７２重量％およびＭＭＡ２８重量％の予想組成とは異なるが、コポリマー系およびコポリマー系の分析の複雑さを考慮に入れると妥当である。

【００９９】

実施例１１：グラフトコポリマー組成物の剪断安定性の評価

前の実施例で製造した幾つかのグラフトコポリマー組成物で剪断安定性試験を行った。グラフトコポリマー組成物の一滴を人差し指の上に置き、親指と人差し指との間で組成物を擦ることにより剪断安定性を試験した。凝塊を生成せずに水蒸発によって乾くまで擦ることができたならコポリマー組成物は合格であり、数回擦った後に凝集し、粘りつくようになったなら不合格であった。試験したコポリマー組成物のすべてが静的条件下でコロイド的に安定であった。結果を以下の表９で報告している。

【表１１】

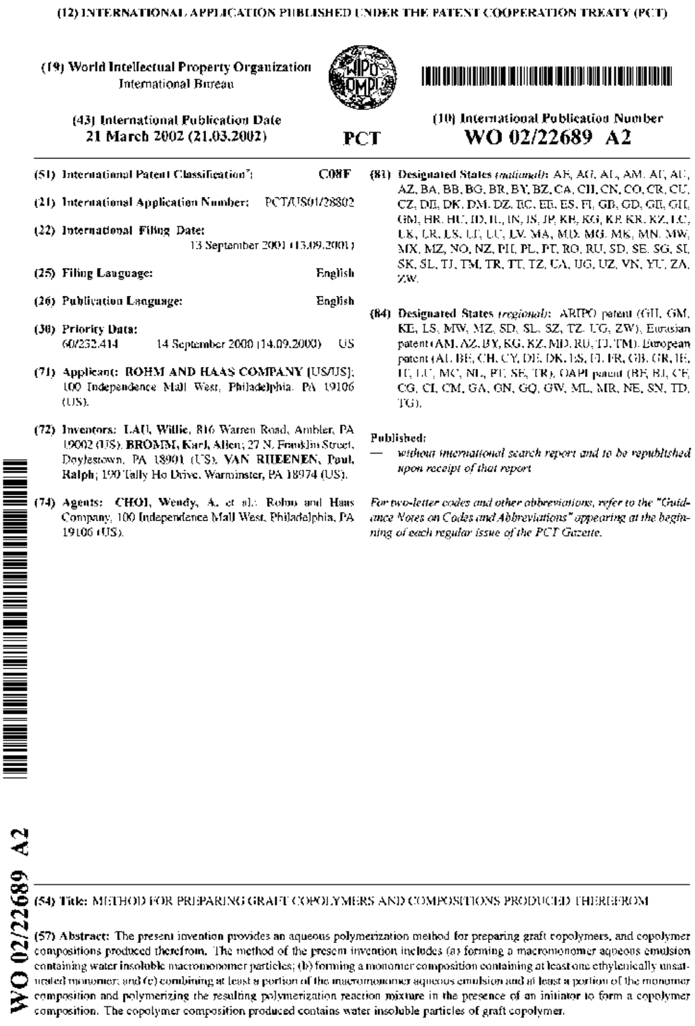
表9: グラフトコポリマー組成物に関する指擦り試験結果

実施例	安定化酸	指擦り試験
3.4	pMAA-MM	合格
3.5	pMAA-MM	合格
3.6	pMAA-MM	合格
3.7	pMAA-MM	合格
3.8	pMAA-MM	合格
3.9	MAA	不合格
3.10	MAA	不合格
3.11	MAA	不合格
3.12	MAA	不合格
4.1	pMAA-MM	合格
4.2	pMAA-MM	合格
4.3	pMAA-MM	合格
4.4	pMAA-MM	合格
8.1	pMAA-MM	合格

【０１００】

表９のデータは、酸含有マクロモノマーを用いて調製されたグラフトコポリマー組成物が酸モノマーを用いて調製されたグラフトコポリマーと比較して驚くほどに良好な剪断安定性を有していたことを示している。ユニオン・カーバイド社（Ｕｎｉｏｎ　Ｃａｒｂｉｄｅ）によって供給される非イオン界面活性剤である登録商標トリトン（Ｔｒｉｔｏｎ）Ｘ－４０５などの界面活性剤をコポリマー組成物に添加するなどによって、酸含有マクロモノマーを使用せずに良好な剪断安定性を得ることができることも発見された。

【国際公開パンフレット】



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 March 2002 (21.03.2002)

PCT

(10) International Publication Number
WO 02/22689 A2

(51) International Patent Classification⁷: **C08F**

(21) International Application Number: PCT/US01/28802

(22) International Filing Date: 13 September 2001 (13.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/232,414 14 September 2000 (14.09.2000) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/22689 A2

(54) Title: METHOD FOR PREPARING GRAFT COPOLYMERS AND COMPOSITIONS PRODUCED THEREFROM

(57) Abstract: The present invention provides an aqueous polymerization method for preparing graft copolymers, and copolymer compositions produced therefrom. The method of the present invention includes (a) forming a macromonomer aqueous emulsion containing water insoluble macromonomer particles; (b) forming a monomer composition containing at least one ethylenically unsaturated monomer; and (c) combining at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition and polymerizing the resulting polymerization reaction mixture in the presence of an initiator to form a copolymer composition. The copolymer composition produced contains water insoluble particles of graft copolymer.

METHOD FOR PREPARING GRAFT COPOLYMERS AND COMPOSITIONS PRODUCED THEREFROM

Field of Invention

This invention relates to a method for making graft copolymers using an aqueous emulsion polymerization process, and copolymer compositions produced therefrom. More particularly, this invention relates to an aqueous emulsion polymerization process for polymerizing at least one macromonomer and at least one ethylenically unsaturated monomer to form a copolymer composition containing graft copolymers.

Background of the Invention

"Graft copolymers" as used herein are macromolecules formed when polymer or copolymer chains are chemically attached as side chains to a polymeric backbone. Generally, the side chains are of a different polymeric composition than the backbone chain. Because graft copolymers often chemically combine unlike polymeric segments in one molecule, these copolymers have unique properties compared to the corresponding random analogues. These properties include, for example, mechanical film properties resulting from thermodynamically driven microphase separation of the polymer, and decreased melt viscosities resulting in part from the branched structure of the graft copolymer. With respect to the latter, reduced melt viscosities can advantageously improve processability of the polymer. *See e.g.*, Hong-Quan Xie and Shi-Biao Zhou, J. Macromol. Sci.-Chem., A27(4), 491-507 (1990); Sebastian Roos, Axel H.E. Müller, Marita Kaufmann, Werner Siol and Clenens Auschra, "Applications of Anionic Polymerization Research", R.P. Quirk, Ed., ACS Symp. Ser. 696, 208 (1998).

The term "comb copolymer," as used herein, is a type of graft copolymer, where the polymeric backbone of the graft copolymer is linear, and each side chain of the graft copolymer is formed by a "macromonomer" that is grafted to the polymer backbone. "Macromonomers" are low molecular weight polymers having at least one functional group at the end of the polymer chain that can further polymerize with others monomers to yield comb copolymers. *See e.g.*, Kawakami in the "Encyclopedia of Polymer Science and Engineering", Vol. 9, pp. 195-204, John Wiley & Sons, New York, 1987. The term "linear," as used herein, is meant to include polymers where minor amounts of branching has occurred through hydrogen abstraction that is normally observed in free radical polymerizations. The comb copolymers are commonly prepared by the free radical copolymerization of macromonomer with conventional monomer (e.g., ethylenically unsaturated monomers).

Comb copolymers prepared with water-insoluble macromonomers have been predominantly prepared using bulk and solution polymerization techniques. However, such processes undesirably use solvent or monomer as the medium in which the polymerization is conducted. Thus, efforts recently have focused on developing methods for preparing comb copolymers via an aqueous emulsion process.

One example, U.S. Patent No. 5,247,040 to Amick et al., ("Amick"), discloses a two stage emulsion polymerization process for producing graft copolymers. In the first stage, a macromonomer is produced by polymerizing ethylenically unsaturated monomer in the presence of a mercapto-olefin compound. In the second stage, the resulting macromonomer is polymerized in an aqueous emulsion with a second ethylenically unsaturated monomer. The Amick process, although having many advantages, produces a graft copolymer having linkages, located between the side chains and backbone, that are susceptible to hydrolysis under certain conditions. These linkages result from using a mercapto-olefin compound having an ester functionality in the preparation of the macromonomer.

U.S. Patent No. 5,264,530 to Darmon et al. ("Darmon") discloses an emulsion or suspension free radical polymerization process where one or more monomer species is polymerized in the presence of a macromonomer that is used as a chain transfer agent. As the macromonomer is being used as a chain transfer agent, the macromonomer is predominately incorporated into the polymer chain at the ends.

U.S. Patent No. 5,804,632 to Haddleton et al. ("Haddleton") discloses an aqueous polymer emulsion process that includes preparing, in the presence of a cobalt chelate complex, a low molecular weight polymer having acid functional groups, and subsequently polymerizing at least one olefinically unsaturated monomer in the presence of the low molecular weight polymer to form a hydrophobic polymer. The low molecular weight polymer in Haddleton is taught to contain a sufficient concentration of acid to render the low molecular weight polymer, as is, or upon neutralization of the acid groups, partially or more preferably fully dissolvable in an aqueous medium. Although Haddleton discloses that some degree of grafting may occur, Haddleton focuses on processes where it is believed that the hydrophobic polymer particles are encapsulated by the low molecular weight polymer in the form of an "inverted core-shell" latex, or where the low molecular weight polymer serves simply as a seed for the polymerization to form the hydrophobic polymer. Thus, Haddleton does not disclose a process to produce graft copolymers of a desired structure such as comb copolymers. It is also believed that using the Haddleton process undesirably results in a substantial amount of low molecular weight polymer remaining unreacted in the water phase.

Publication WO 99/03905 to Huybrechts et al. ("Huybrechts") discloses an anionically stabilized graft copolymer composition that is prepared by emulsion polymerizing acid containing macromonomer and amino functional monomer. The copolymer composition prepared contains from 0.5 to 30 weight percent amino functional monomer in the polymer backbone, and at least 5 weight percent acid functional monomer in the macromonomer that is neutralized with an amine. However, it would be desirable to provide an aqueous emulsion polymerization process for preparing alternative graft copolymer compositions that do not require neutralization.

The present invention seeks to provide a robust emulsion polymerization process for preparing graft copolymers that are preferably resistant to hydrolysis. The present invention also seeks to provide an emulsion polymerization process that preferably provides control over such parameters as polymerization kinetics, polymer structure, conversion, incorporation of macromonomer and particle size.

Summary of Invention

In one aspect of the present invention, a method of making a graft copolymer is provided that includes forming a macromonomer aqueous emulsion containing water-insoluble particles of macromonomer and forming a monomer composition containing ethylenically unsaturated monomer. The macromonomer contains polymerized units of a first ethylenically unsaturated monomer and further has a degree of polymerization of from 10 to 1000, at least one terminal ethylenically unsaturated group, less than 5 weight percent acid-containing monomer as polymerized, and less than 1 mole percent of mercapto-olefin compounds as polymerized. At least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition are combined to form a polymerization to form the graft copolymer composition contains from 10 to 1000 polymerized units of a first ethylenically unsaturated monomer, less than 1 mole percent of polymerized mercapto-olefin compounds, and less than 5 weight percent polymerized acid-containing monomer. In a preferred embodiment, the copolymer composition further contains from 0.2 weight percent to 10 weight percent of an acid containing macromonomer, based on the total weight of the copolymer.

Detailed Description

The present invention provides an aqueous polymerization process for preparing graft copolymers, and more preferably comb copolymers. The present invention also provides novel copolymer compositions produced from the aqueous polymerization process.

The process of the present invention includes (a) forming a macromonomer aqueous emulsion containing one or more water-insoluble particles of macromonomer; (b) forming a monomer composition containing ethylenically unsaturated monomer; and (c) combining at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition to form a polymerization reaction mixture. The macromonomer and ethylenically unsaturated monomer are polymerized in the presence of an initiator to form graft copolymer particles.

The macromonomer, present in the macromonomer aqueous emulsion as water insoluble particles, is any low molecular weight water-insoluble polymer or copolymer having at least one terminal ethylenically unsaturated group that is capable of being polymerized in a free radical polymerization process. By "water-insoluble" it is meant having a water solubility of no greater than 150 millimoles/liter at 25°C to 50°C. By "low molecular weight" it is meant that the macromonomer has a degree of polymerization preferably from about 10 to about 1000, and more preferably from about 20 to about 200. By "degree of polymerization" it is meant the number of polymerized monomer units present in the macromonomer.

The macromonomer contains, as polymerized units, at least one type of ethylenically unsaturated monomer. Preferably, the ethylenically unsaturated monomer is selected to impart low or no water solubility to the macromonomer as previously described herein.

Suitable ethylenically unsaturated monomers for use in preparing macromonomer include for example methacrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of methacrylic acid, including methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, lauryl methacrylate, stearyl methacrylate; acrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of acrylic acid, including methyl acrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate; styrene; substituted styrenes, such as methyl styrene, α-methyl styrene or t-butyl styrene; olefinically unsaturated nitriles, such as acrylonitrile or methacrylonitrile; olefinically unsaturated halides, such as vinyl chloride, vinylidene chloride or vinyl fluoride; vinyl esters of organic acids, such as vinyl acetate; N-vinyl compounds such as N-vinyl pyrrolidone; acrylamide; methacrylamide; substituted acrylamides; substituted methacrylamides; hydroxyalkylmethacrylates such as hydroxyethylmethacrylate; hydroxyalkylacrylates; basic substituted (meth)acrylates and (meth)acrylamides, such as amine-substituted methacrylates including dimethylaminoethyl methacrylate, tertiary-butylaminoethyl methacrylate and dimethylaminopropyl methacrylamide and the likes; dienes such as 1,3-butadiene and isoprene; vinyl ethers; or combinations thereof. The term "(meth)" as used herein means that the "meth" is optionally present. For example, "(meth)acrylate" means methacrylate or acrylate.

The ethylenically unsaturated monomer can also be a functional monomer including for example monomers containing hydroxy, amido, aldehyde, ureido, polyether, glycidylalkyl, keto functional groups or combinations thereof. These functional monomers are generally present in the macromonomer at a level of from about 0.5 weight percent to about 15 weight percent and more preferably from about 1 weight percent to about 3 weight percent, based on the total weight of the graft copolymer. Examples of functional monomers include ketofunctional monomers such as the acetoacetoxy esters of hydroxyalkyl acrylates and methacrylates (e.g., acetoacetoxyethyl methacrylate) and keto-containing amides (e.g., diacetone acrylamide); allyl alkyl methacrylates or acrylates; glycidylalkyl methacrylates or acrylates; or combinations thereof. Such functional monomer can provide crosslinking if desired.

The macromonomer also contains as polymerized units less than about 10 weight percent, preferably less than about 5 weight percent, more preferably less than 2 weight percent and most preferably less than about 1 weight percent acid containing monomer, based on the total weight of the macromonomer. In a most preferred embodiment, the macromonomer contains no acid containing monomer. By "acid containing monomer" it is meant any ethylenically unsaturated monomer that contains one or more acid functional groups or functional groups that are capable of forming an acid (e.g., an anhydride such as methacrylic anhydride or tertiary butyl methacrylate). Examples of acid containing monomers include, for example, carboxylic acid bearing ethylenically unsaturated monomers such as acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid; acryloxypropionic acid and (meth)acryloxypropionic acid; sulphonic acid-bearing monomers, such as styrene sulfonic acid, sodium vinyl sulfonate, sulfoethyl acrylate, sulfoethyl methacrylate, ethylmethacrylate-2-sulphonic acid, or 2-acrylamido-2-methylpropane sulphonic acid; phosphoethylmethacrylate; the corresponding salts of the acid containing monomer; or combinations thereof.

The macromonomer also contains, as polymerized, less than about 1 mole percent, preferably less than about 0.5 mole percent, and more preferably no mercapto-olefin compounds, based on the total weight of the macromonomer. These mercapto-olefin compounds are those as described in U.S. Patent No. 5,247,000 to Amick, which is incorporated herein by reference in its entirety. The mercapto-olefin compounds described in Amick have ester functional groups, which are susceptible to hydrolysis.

In a preferred embodiment of the present invention, the macromonomer is composed of at least about 20 weight percent, more preferably from about 50 weight percent to about 100 weight percent, and most preferably from about 80 to about 100 weight percent of at least one α-methyl vinyl monomer, a non α-methyl vinyl monomer terminated with a α-methyl vinyl monomer, or combinations thereof. In a most preferred embodiment of the present invention the macromonomer contains as polymerized units from about 90 weight percent to about 100 weight percent α-methyl vinyl monomers, non α-methyl vinyl monomers terminated with α-methyl vinyl monomers, or combinations thereof, based on the total weight of the macromonomer. Suitable α-methyl vinyl monomers include, for example, methacrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of methacrylic acid, including methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, isobornyl methacrylate, lauryl methacrylate, or stearyl methacrylate; hydroxyalkyl methacrylates such as hydroxyethyl methacrylate; glycidylmethacrylate; phenyl methacrylate; methacrylamide; methacrylonitrile; or combinations thereof. An example of a non α-methyl vinyl monomer terminated with an α-methyl vinyl monomer includes styrene terminated by α-methyl styrene.

One skilled in the art will recognize that there are many ways to prepare the macromonomer useful in the present invention. For example, the macromonomer may be prepared by a high temperature (e.g., at least about 150°C) continuous process such as disclosed in U.S. Patent No. 5,710,227 or EP-A-1,010,706, published June 21, 2000, the disclosures of which are hereby incorporated by reference in their entireties. In a preferred continuous process, a reaction mixture of ethylenically unsaturated monomers are passed through a heated zone having a temperature of at least about 150°C, and more preferably at least about 275°C. The heated zone may also be maintained at a pressure above atmospheric pressure (e.g., greater than about 30 bar). The reaction mixture of monomers may also optionally contain a solvent such as water, acetone, methanol, isopropanol, propionic acid, acetic acid, dimethylformamide, dimethylsulfoxide, methylethylketone, or combinations thereof.

The macromonomer useful in the present invention may also be prepared by polymerizing ethylenically unsaturated monomers in the presence of a free radical initiator and a catalytic metal chelate chain transfer agent (e.g., a transition metal chelate). Such a polymerization may be carried out by a solution, bulk, suspension, or emulsion polymerization process. Suitable methods for preparing the macromonomer using a catalytic metal chelate chain transfer agent are disclosed in for example U.S. Patent Nos. 4,526,945, 4,680,354, 4,886,861, 5,028,677, 5,362,826, 5,721,330, and 5,756,605; European publications EP-A-0199,436, and EP-A-0196783; and PCT publications WO 87/03605, WO 96/15158, and WO 97/34934, the disclosures of which are hereby incorporated by reference in their entireties.

Preferably, the macromonomer useful in the present invention is prepared by an aqueous emulsion free radical polymerization process using a transition metal chelate complex. Preferably, the transition metal chelate complex is a cobalt (II) or (III) chelate complex such as, for example, dioxime complexes of cobalt, cobalt II porphyrin complexes, or cobalt II chelates of vicinal iminohydroxyimino compounds, dihydroxyimino compounds, diazadihydroxy-iminodialkyldecadienes, or diazadihydroxyiminodialkylundecadienes, or combinations thereof. These complexes may optionally include bridging groups such as BF_2, and may also be optionally coordinated with ligands such as water, alcohols, ketones, and nitrogen bases such as pyridine. Additional suitable transition metal complexes are disclosed in for example U.S. Patent Nos. 4,694,054; 5,770,665; 5,962,609; and 5,602,220, the disclosures of which are hereby incorporated by reference in their entireties. A preferred cobalt chelate complex useful in the present invention is Co II (2,3-dioxyiminobutane-BF_2)$_2$, the Co III analogue of the aforementioned compound, or combinations thereof. The spatial arrangements of such complexes are disclosed in for example EP-A-199436 and U.S. Patent No. 5,756,605.

In preparing macromonomer by an aqueous emulsion polymerization process using a transition metal chelate chain transfer agent, at least one ethylenically unsaturated monomer is polymerized in the presence of a free radical initiator and the transition metal chelate according to conventional aqueous emulsion polymerization techniques. Preferably, the ethylenically unsaturated monomer is an α-methyl vinyl monomer as previously described herein.

The polymerization to form the macromonomer is preferably conducted at a temperature of from about 20°C to about 150°C, and more preferably from about 40°C to about 95°C. The solids level at the completion of the polymerization is typically from about 5 weight percent to about 65 weight percent, and more preferably from about 30 weight percent to about 50 weight percent, based on the total weight of the aqueous emulsion.

The concentration of initiator and transition metal chelate chain transfer agent used during the polymerization process is preferably chosen to obtain the desired degree of polymerization of the macromonomer. Preferably, the concentration of initiator is from about 0.2 weight percent to about 3 weight percent, and more preferably from about 0.5 weight percent to about 1.5 weight percent, based on the total weight of monomer. Preferably, the concentration of transition metal chelate chain transfer agent is from about 5 ppm to about 200 ppm, and more preferably from about 10 ppm to about 100 ppm, based on the total moles of monomer used to form the macromonomer.

The ethylenically unsaturated monomer, initiator, and transition metal chelate chain transfer agent may be added in any manner known to those skilled in the art to carry out the polymerization. For example, the monomer, initiator and transition metal chelate may all be present in the aqueous emulsion at the start of the polymerization process (i.e., a batch process). Alternatively, one or more of the components may be gradually fed to an aqueous solution (i.e., a continuous or semi-batch process). For example, it may be desired to gradually feed the entire or a portion of the initiator, monomer, and/or transition metal chelate to a solution containing water and surfactant. In a preferred embodiment, at least a portion of the monomer and transition metal chelate are gradually fed during the polymerization, with the remainder of the monomer and transition metal chelate being present in the aqueous emulsion at the start of the polymerization. In this embodiment, the monomer may be fed as is, or suspended or emulsified in an aqueous solution prior to being fed.

Any suitable free radical initiator may be used to prepare the macromonomer. The initiator is preferably selected based on such parameters as its solubility in one or more of the other components (e.g., monomers, water); half life at the desired polymerization temperature (preferably a half life within the range of from about 30 minutes to about 10 hours), and stability in the presence of the transition metal chelate. Suitable initiators include for example azo compounds such as 2,2'-azobis (isobutyronitrile), 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis [2-methyl-N-(1,1-bis(hydroxymethyl)-2-(hydroxyethyl)]-propionamide, and 2,2'-azobis [2-methyl-N-(2-hydroxyethyl)]-propionamide; peroxides such as t-butyl hydroperoxide, benzoyl peroxide; sodium, potassium, or ammonium persulphate or combinations thereof. Redox initiator systems may also be used, such as for example persulphate or peroxide in combination with a reducing agent such as sodium metabisulphite, sodium bisulfite, sodium formaldehyde sulfoxylate, isoascorbic acid, or combinations thereof. Metal promoters, such as iron, may also optionally be used in such redox initiator systems. Also, buffers, such as sodium bicarbonate may be used as part of the initiator system.

An emulsifier is also preferably present during the aqueous emulsion polymerization process to prepare the macromonomer. Any emulsifier may be used that is effective in emulsifying the monomers such as for example anionic, cationic, or nonionic emulsifiers. In a preferred embodiment, the emulsifier is anionic such as for example sodium, potassium, or ammonium salts of dialkylsulphosuccinates; sodium, potassium, or ammonium salts of sulphated oils; sodium, potassium, or ammonium salts of alkyl sulphonic acids, such as sodium dodecyl benzene sulfonate; sodium, potassium, or ammonium salts of alkyl sulphates, such as sodium lauryl sulfate; ethoxylated alkyl ether sulfates; alkali metal salts of sulphonic acids; C_{12} to C_{24} fatty alcohols, ethoxylated fatty acids or fatty amides; sodium, potassium, or ammonium salts of fatty acids, such as Na stearate and Na oleate; or combinations thereof. The amount of emulsifier in the aqueous emulsion is preferably from about 0.05 weight percent to about 10 weight percent, and more preferably from about 0.3 weight percent to about 3 weight percent, based on the total weight of the monomers.

The macromonomer thus prepared is emulsion polymerized with ethylenically unsaturated monomer to form a copolymer composition containing graft copolymer particles. The polymerization is carried out by providing the macromonomer as water insoluble particles in a macromonomer aqueous emulsion and the ethylenically unsaturated monomer in a monomer composition. At least a portion of the macromonomer aqueous emulsion is combined with at least a portion of the monomer composition to form a polymerization reaction mixture that is polymerized in the presence of an initiator.

Although in no way intending to be bound in theory, it is believed that by providing the macromonomer in the form of water insoluble macromonomer particles in an aqueous emulsion, and the ethylenically unsaturated monomer in a separate monomer composition, upon combination, the ethylenically unsaturated monomer diffuses into the macromonomer particles where the polymerization occurs. Preferably, the diffusion of the ethylenically unsaturated monomer into the macromonomer particles is evidenced by swelling of the macromonomer particles.

The macromonomer aqueous emulsion useful in the present invention may be formed in any manner known to those skilled in the art. For example, the macromonomer, produced by any known method, may be isolated as a solid (e.g., spray dried) and emulsified in water. Also, for example, the macromonomer, if prepared via an emulsion or aqueous based polymerization process, may be used as is, or diluted with water or concentrated to a desired solids level.

In a preferred embodiment of the present invention, the macromonomer aqueous emulsion is formed from the emulsion polymerization of an ethylenically unsaturated monomer in the presence of a transition metal chelate chain transfer agent as described previously herein. This embodiment is preferred for numerous reasons. For example, the macromonomer polymerization can be readily controlled to produce a desired particle size distribution (preferably narrow, e.g., polydispersity less than 2). Also, for example, additional processing steps, such as isolating the macromonomer as a solid, can be avoided, leading to better process economics. In addition, the macromonomer, macromonomer aqueous emulsion and the graft copolymer can be prepared by consecutive steps in a single reactor which is desirable in a commercial manufacturing facility.

The macromonomer aqueous emulsion useful in the present invention contains from about 20 weight percent to about 60 weight percent, and more preferably from about 30 weight percent to about 50 weight percent of at least one water insoluble macromonomer, based on the total weight of macromonomer aqueous emulsion. The macromonomer aqueous emulsion may also contain mixtures of macromonomer. Preferably, the macromonomer aqueous emulsion contains less than about 5 weight percent and more preferably less than about 1 weight percent of ethylenically unsaturated monomer, based on the total weight of macromonomer aqueous emulsion.

The water insoluble macromonomer particles have a particle size to form graft copolymer of the desired particle size. For example, the final graft copolymer particles size is directly proportional to the initial particle size of the macromonomer and the concentration of ethylenically unsaturated monomers in the polymerization reaction mixture, assuming all the particles participate equally in the polymerization. Preferably, the macromonomer particles have a weight average particle size of from about 50 nm to about 500 nm, and more preferably from about 80 nm to about 200 nm as measured by Capillary Hydrodynamic Fractionation technique using a Matec CHDF 2000 particle size analyzer equipped with a HPLC type Ultra-violet detector.

The macromonomer aqueous emulsion may also include one or more emulsifying agents. The type and amount of emulsifying agent is preferably selected in a manner to produce the desired particle size. Suitable emulsifying agents include those previously disclosed for use in preparing the macromonomer by an emulsion polymerization process. Preferred emulsifying agents are anionic surfactants such as, for example, sodium lauryl sulfate, sodium dodecylbenzene sulfonate, sulfated and ethoxylated derivatives of nonylphenols and fatty alcohols. The total level of emulsifying agent, based on the total weight of macromonomer is preferably from about 0.2 weight percent to about 5 weight percent and more preferably from about 0.5 weight percent to about 2 weight percent.

The monomer composition useful in the present invention contains at least one kind of ethylenically unsaturated monomer. The monomer composition may contain all (i.e., 100%) monomer, or contain monomer dissolved or dispersed in an organic solvent and/or water. Preferably, the level of monomer in the monomer composition is from about 50 weight percent to 100 weight percent, more preferably from about 60 weight percent to about 90 weight percent, and most preferably from about 70 weight percent to about 80 weight percent, based on the total weight of the monomer composition. Examples of organic solvents that may be present in the monomer composition include C_6 to C_{14} alkanes. The organic solvent in the monomer composition will be no more than 30 weight percent, and more preferably no more than 5 weight percent, based on the total weight of the monomer composition.

In addition to water and/or organic solvent, the monomer composition may also optionally contain monomers containing functional groups, such as, for example, monomers containing hydroxy, amido, aldehyde, ureido, polyether, glycidylalkyl, keto groups or combinations thereof. These other monomers are generally present in the monomer composition at a level of from about 0.5 weight percent to about 15 weight percent, and more preferably from about 1 weight percent to about 3 weight percent based on the total weight of the graft copolymer. Examples of functional monomers include ketofunctional monomers such as the acetoacetoxy esters of hydroxyalkyl acrylates and methacrylates (e.g., acetoacetoxyethyl methacrylate) and keto-containing amides (e.g., diacetone acrylamide); allyl alkyl methacrylates or acrylates; glycidylalkyl methacrylates or acrylates; or combinations thereof. Such functional monomer can provide crosslinking if desired.

In a preferred embodiment, the monomers in the monomer composition are preemulsified in water to form a monomer aqueous emulsion. Preferably, the monomer aqueous emulsion contains monomer droplets having a droplet size from about 1 micron to about 100 microns, and more preferably from about 5 micron to about 50 microns. Any suitable emulsifying agent may be used, for example those previously described, to emulsify the monomer to the desired monomer droplet size. Preferably, the level of emulsifying agent, if present, will be from about 0.2 weight percent to about 2 weight percent based on the total weight of monomer in the monomer composition.

The ethylenically unsaturated monomer of the monomer composition is preferably selected to provide the desired properties in the resulting copolymer composition. Suitable ethylenically unsaturated monomers include for example methacrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of methacrylic acid, including methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, stearyl methacrylate, isobornyl methacrylate; acrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of acrylic acid, including methyl acrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate; styrene; substituted styrenes, such as methyl styrene, α-methyl styrene or t-butyl styrene; olefinically unsaturated nitriles, such as acrylonitrile or methacrylonitrile; olefinically unsaturated halides, such as vinyl chloride, vinylidene chloride or vinyl fluoride; vinyl esters of organic acids, such as vinyl acetate; N-vinyl compounds such as N-vinyl pyrrolidone; acrylamide; methacrylamide; substituted acrylamides; substituted methacrylamides; hydroxyalkylmethacrylates such as hydroxyethylmethacrylate; hydroxyalkylacrylates; dienes such as 1,3-butadiene and isoprene; vinyl ethers; or combinations thereof. The ethylenically unsaturated monomer can also be an acid containing monomer or a functional monomer, such as those previously described herein. Preferably, the ethylenically unsaturated monomer of the monomer composition does not contain amino groups.

In a preferred embodiment, the monomer composition includes one or more ethylenically unsaturated monomers selected from C_1 to C_{18} normal or branched alkyl esters of acrylic acid, including methyl acrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate; styrene; substituted styrenes, such as methyl styrene, α-methyl styrene or t-butyl styrene; butadiene or combinations thereof.

As previously mentioned, the macromonomer aqueous emulsion and monomer composition are combined to form a polymerization reaction mixture, and polymerized in the presence of a free radical initiator to form an aqueous copolymer composition. The term "polymerization reaction mixture," as used herein, refers to the resulting mixture formed when at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition are combined. The polymerization reaction mixture may also contain initiator or any other additive used during the polymerization. Thus, the polymerization reaction mixture is a mixture that changes in composition as the macromonomer and monomer in the monomer composition are reacted to form graft copolymer.

The macromonomer aqueous emulsion and monomer composition may be combined in various ways to carry out the polymerization. For example, the macromonomer aqueous emulsion and the monomer composition may be combined prior to the start of the polymerization reaction to form the polymerization reaction mixture. Alternatively, the monomer composition could be gradually fed into the macromonomer aqueous emulsion, or the macromonomer aqueous emulsion could be gradually fed into the monomer composition. It is also possible that only a portion of the macromonomer aqueous emulsion and/or monomer composition be combined prior to the start of the polymerization with the remaining monomer composition and/or macromonomer aqueous emulsion being fed during the polymerization.

The initiator can also be added in various ways. For example, the initiator may be added in "one shot" to the macromonomer aqueous emulsion, the monomer composition, or a mixture of the macromonomer aqueous emulsion and the monomer composition at the start of the polymerization. Alternatively, all or a portion of the initiator can be cofed as a separate feed stream, as part of the macromonomer aqueous emulsion, as part of the monomer composition, or any combination of these methods.

The preferred method of combining the macromonomer aqueous emulsion, the monomer composition, and initiator will depend on such factors as the desired graft copolymer composition. For example, the distribution of the macromonomer as a graft along the backbone can be affected by the concentrations of both the macromonomer and the ethylenically unsaturated monomers at the time of the polymerization. In this regard, a batch process will afford high concentration of both the macromonomer and the ethylenically unsaturated monomers at the onset of the polymerization whereas a semi-continuous process will keep the ethylenically unsaturated monomer concentration low during the polymerization. Thus, through the method in which the macromonomer aqueous emulsion and monomer composition are combined, it is possible to control, for example, the number of macromonomer grafts per polymer chain, the distribution of graft in each chain, and the length of the polymer backbone.

Initiators useful in polymerizing the macromonomer and ethylenically unsaturated monomer include any suitable initiator for emulsion polymerizations known to those skilled in the art. The selection of the initiator will depend on such factors as the initiator's solubility in one or more of the reaction components (e.g. monomer, macromonomer, water); and half life at the desired polymerization temperature (preferably a half life within the range of from about 30 minutes to about 10 hours). Suitable initiators include those previously described herein in connection with forming the macromonomer, such as azo compounds such as 4,4'-azobis(4-cyanovaleric acid), peroxides such as t-butyl hydroperoxide; sodium, potassium, or ammonium persulfate; redox initiator systems such as, for example, persulphate or peroxide in combination with a reducing agent such as sodium metabisulfite, sodium bisulfite, sodium formaldehyde sulfoxylate, isoascorbic acid; or combinations thereof. Metal promoters, such as iron; and buffers, such as sodium bicarbonate, may also be used in combination with the initiator. Additionally, Controlled Free Radical Polymerization (CFRP) methods such as Atom Transfer Radical Polymerization; or Nitroxide Mediated Radical Polymerization may be used. Preferred initiators include azo compounds such as 4,4'-azobis(4-cyanovaleric acid).

The amount of initiator used will depend on such factors as the copolymer desired and the initiator selected. Preferably, from about 0.1 weight percent to about 1 weight percent initiator is used, based on the total weight of monomer and macromonomer.

The polymerization temperature will depend on the type of initiator chosen and desired polymerization rates. Preferably, however, the macromonomer and ethylenically unsaturated monomer are polymerized at a temperature of from about room temperature to about 150°C, and more preferably from about 40°C to about 95°C.

The amount of macromonomer aqueous emulsion and monomer composition added to form the polymerization reaction mixture will depend on such factors as the concentrations of macromonomer and ethylenically unsaturated monomer in the macromonomer aqueous emulsion and monomer composition, respectively, and the desired copolymer composition. Preferably, the macromonomer aqueous emulsion and monomer composition are added in amounts to provide a copolymer containing as polymerized units of from about 2 weight percent to about 90 weight percent, more preferably from about 5 weight percent to about 50 weight percent, and most preferably from about 5 weight percent to about 35 weight percent macromonomer, and from about 10 weight percent to about 98 weight percent, more preferably from about 50 weight percent to about 95 weight percent and most preferably from about 65 weight percent to about 95 weight percent ethylenically unsaturated monomer.

One skilled in the art will recognize that other components used in conventional emulsion polymerizations may optionally be used in the method of the present invention. For example, to reduce the molecular weight of the resulting graft copolymer, the polymerization may optionally be conducted in the presence of one or more chain transfer agents, such as n-dodecyl mercaptan, thiophenol; halogen compounds such as bromotrichloromethane; or combinations thereof. Also, additional initiator and/or catalyst may be added to the polymerization reaction mixture at the completion of the polymerization reaction to reduce any residual monomer, (e.g., chasing agents). Suitable initiators or catalysts include those initiators previously described herein. In addition, the chain transfer capacity of a macromonomer through addition-fragmentation can be utilized in part to reduce molecular weight through appropriate design of monomer compositions and polymerization conditions. *See e.g.*, E. Rizzardo, et. al., Prog. Pacific Polym. Sci., 1991, 1, 77-88; G. Moad, et. al., WO 96/15157.

Preferably, the process of the present invention does not require neutralization of the monomer, or resulting aqueous copolymer composition. These components preferably remain in unneutralized form (e.g., no neutralization with a base if acid functional groups are present).

The resulting aqueous copolymer composition formed by polymerization of the macromonomer and the ethylenically unsaturated monomer in the monomer composition preferably has a solids level of from about 30 weight percent to about 65 weight percent and more preferably from about 40 weight percent to about 60 weight percent. The aqueous copolymer composition preferably contains copolymer particles that are water insoluble and have a particle size of from about 60 nm to about 500 nm, and more preferably from about 80 nm to about 200 nm.

The graft copolymer formed preferably has a backbone containing, as polymerized units, the ethylenically unsaturated monomer from the monomer composition, and one or more side chains, pendent from the backbone, containing the macromonomer. Preferably, each side chain is formed from one macromonomer grafted to the backbone. The degree of polymerization of the macromonomer side chains is preferably in the range of from about 10 to about 1000, and more preferably in the range of from about 20 to about 200, where the degree of polymerization is expressed as the number of polymerized units of ethylenically unsaturated monomer used to form the macromonomer. The total weight average molecular weight of the graft copolymer is preferably in the range of from about 50,000 to about 2,000,000, and more preferably from about 100,000 to about 1,000,000. Weight average molecular weights as used herein can be determined by size exclusion chromatography.

The copolymer particles of the aqueous copolymer composition can be isolated, for example, by spray drying or coagulation. However, it is preferable to use the copolymer aqueous composition as is.

In a preferred embodiment of the present invention, the polymerization is conducted in two stages. In the first stage, the macromonomer is formed in an aqueous emulsion polymerization process, and in the second stage the macromonomer is polymerized with the ethylenically unsaturated monomer in an emulsion. For efficiency, preferably these two stages are conducted in a single vessel. For example, in the first stage, the macromonomer aqueous emulsion may be formed by polymerizing in an aqueous emulsion at least one first ethylenically unsaturated monomer to form water insoluble macromonomer particles. This first stage polymerization is preferably conducted using a transition metal chelate chain transfer agent as previously described herein. After forming the macromonomer aqueous emulsion, a second emulsion polymerization is preferably performed in the same vessel to polymerize the macromonomer with at least one second ethylenically unsaturated monomer. This second stage may be conducted for example by directly adding (e.g., all at once or by a gradual feed) the monomer composition and initiator to the macromonomer aqueous emulsion. One main advantage of this embodiment is that the macromonomer does not have to be isolated, and the second polymerization can take place simply by adding the monomer composition and initiator to the macromonomer aqueous emulsion.

In another preferred embodiment of the present invention, the polymerization of the macromonomer and ethylenically unsaturated monomer is at least partially performed in the presence of an acid containing monomer, acid containing macromonomer, or combinations thereof. The acid containing monomer or acid containing macromonomer may be added in any manner to the polymerization reaction mixture. Preferably, the acid containing monomer or acid containing macromonomer is present in the monomer composition. The acid containing monomer or acid containing macromonomer may also be added as a separate stream to the polymerization reaction mixture.

The amount of acid containing monomer or acid containing macromonomer added to the polymerization reaction mixture is preferably from about 0.2 weight percent to about 10 weight percent, more preferably from about 0.5 weight percent to about 5 weight percent, and most preferably from about 1 weight percent to about 2 weight percent, based on the total weight of monomer and macromonomer added to the polymerization reaction mixture.

Acid containing monomers which may be used in this embodiment include ethylenically unsaturated monomers bearing acid functional or acid forming groups such as those previously described herein. The acid containing macromonomer useful in this embodiment is any low molecular weight polymer having at least one terminal ethylenically unsaturated group that is capable of being polymerized in a free radical polymerization process, and that is formed from at least one kind of acid containing monomer. Preferably, the amount of acid containing monomer in the acid containing macromonomer is from about 50 weight percent to 100 weight percent, more preferably from about 90 weight percent to 100 weight percent, and most preferably from about 95 weight percent to 100 weight percent.

The acid containing macromonomer may be prepared according to any technique known to those skilled in the art such as those previously described herein. In a preferred embodiment of the present invention, the acid containing macromonomer is prepared by a solution polymerization process using a free radical initiator and transition metal chelate complex. An example of such a process is disclosed in for example U.S. Patent No. 5,721,330, which is incorporated by reference in its entirety. Preferred acid containing monomers used to form the acid containing macromonomer are α-methyl vinyl monomers such as methacrylic acid.

In another preferred embodiment of the present invention, a macromolecular organic compound having a hydrophobic cavity is present in the polymerization medium used to form the macromonomer and/or aqueous copolymer composition. Preferably, the macromolecular organic compound is used when copolymerizing ethylenically unsaturated monomers with very low water solubility such as lauryl or stearyl acrylates and/or methacrylates. By "low water solubility" it is meant a water solubility at 25°C to 50°C of no greater than 50 millimoles/liter. For example, the macromolecular organic compound may be added to the monomer composition, the macromonomer aqueous emulsion, or the polymerization reaction mixture used to form the aqueous copolymer composition. Also, for example the macromolecular organic compound may be added to an aqueous emulsion of ethylenically unsaturated monomer used to form the macromonomer. Suitable techniques for using a macromolecular organic compound having a hydrophobic cavity are disclosed in, for example, U.S. Patent No. 5,521,266, the disclosure of which is hereby incorporated by reference in its entirety.

Preferably, the macromolecular organic compound having a hydrophobic cavity is added to the polymerization reaction mixture to provide a molar ratio of macromolecular organic compound to low water solubility monomer or macromonomer of from about 5:1 to about 1:5000 and more preferably from about 1:1 to about 1:500.

Macromolecular organic compounds having a hydrophobic cavity useful in the present invention include for example cyclodextrin or cyclodextrin derivatives; cyclic oligosaccharides having a hydrophobic cavity such as cycloinulohexose, cycloinuloheptose, or cycloinulooctose; calyxarenes; cavitands; or combinations thereof. Preferably, the macromolecular organic compound is ß-cyclodextrin, more preferably methyl-ß-cyclodextrin.

Monomers having low water solubility include for example primary alkenes; styrene and alkylsubstituted styrene; α-methyl styrene; vinyltoluene; vinyl esters of C_4 to C_{30} carboxylic acids, such as vinyl 2-ethylhexanoate, vinyl neodecanoate; vinyl chloride; vinylidene chloride; N-alkyl substituted (meth)acrylamide such as octyl acrylamide and maleic acid amide; vinyl alkyl or aryl ethers with (C_3 -C_{30}) alkyl groups such as stearyl vinyl ether; (C_1 -C_{30}) alkyl esters of (meth)acrylic acid, such as methyl methacrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate; unsaturated vinyl esters of (meth)acrylic acid such as those derived from fatty acids and fatty alcohols; multifunctional monomers such as pentaerythritol triacrylate; monomers derived from cholesterol or combinations thereof.

In another aspect of the present invention an aqueous copolymer composition is provided that is preferably produced by the method of the present invention as previously described herein. The aqueous copolymer composition contains water insoluble particles of graft copolymer that are preferably comb copolymer particles. The comb copolymer particles preferably have a weight average particle size of from about 50 nm to about 500 nm, and more preferably from about 80 nm to about 200 nm.

Preferably, the particles of graft copolymer contain from about 2 weight percent to about 90 weight percent, and more preferably from about 5 weight percent to about 50 weight percent polymerized units of a macromonomer, based on the total weight of the copolymer, where the macromonomer preferably has a composition as previously described herein for the water insoluble macromonomer present in the macromonomer aqueous emulsion. The graft copolymer particles also preferably contain from about 10 weight percent to about 98 weight percent, and more preferably from about 50 weight percent to about 95 weight percent polymerized units of at least one ethylenically unsaturated monomer, based on the total weight of the copolymer. The ethylenically unsaturated monomer may be any ethylenically unsaturated monomer that provides desirable properties in the copolymer particles, such as those useful in the monomer composition as previously described herein.

Preferably, the backbone of the graft copolymer is linear. Compositionally, the backbone of the copolymer preferably contains polymerized units of the ethylenically unsaturated monomer derived from the monomer composition. Preferably, the backbone contains less than 20 mole percent, and more preferably less than 10 mole percent of polymerized macromonomer derived from the macromonomer aqueous emulsion based on the total moles of the copolymer.

The side chains of the graft copolymer preferably contain polymerized units of the macromonomer. In a preferred embodiment of the present invention, each side chain comprises one macromonomer. Additionally, the side chains contain less than 5 weight percent and more preferably less than 1 weight percent of the polymerized ethylenically unsaturated monomer derived from the monomer composition, based on the total weight of the side chains.

Preferably, the overall weight average molecular weight of the graft copolymer is from about 50,000 to about 2,000,000, and more preferably from about 100,000 to about 1,000,000.

In a preferred embodiment of the present invention, the water insoluble copolymer particles further contain from about 0.2 weight percent to about 10 weight percent, more preferably from about 0.5 weight percent to about 5 weight percent, and most preferably from about 1 weight percent to about 2 weight percent of an acid containing macromonomer, based on the total weight of the graft copolymer. The acid containing macromonomer preferably has a composition as previously described herein.

Although in no way intending to be bound by theory, it is believed that the acid containing macromonomer is attached to the surface of the water insoluble graft copolymer particles and provides stability. By "attached," as used herein, it is believed that the acid containing macromonomer is bound in some manner (e.g., covalent, hydrogen bonding, ionic) to a polymer chain in the particle. Preferably, the acid containing macromonomer is covalently bound to a polymer chain in the particle. It has been found that the acid containing macromonomer provides stability to the particles such that the aqueous copolymer composition produced exhibits unexpected improved shear stability; freeze thaw stability; and stability to additives in formulations, as well as reduction of coagulums during the polymerization. Although improved stability can be achieved using acid containing monomer, these benefits are most dramatic when an acid containing macromonomer is used.

The aqueous copolymer composition in addition to the copolymer particles preferably contains less than about 10 weight percent, and more preferably less than about 1 weight percent of organic solvent. In a most preferred embodiment, the aqueous copolymer composition contains no organic solvent.

An advantage of using the method of the present invention to prepare the aqueous copolymer composition is that the resulting copolymer composition contains low levels of homopolymer, such as for example homopolymer of ethylenically unsaturated monomer derived from the monomer composition or homopolymer of macromonomer derived from the macromonomer aqueous emulsion. Preferably the aqueous copolymer composition contains less than about 30 weight percent and more preferably less than about 20 weight percent of homopolymer of macromonomer, based on the total weight of the graft copolymer. Preferably also the aqueous copolymer composition contains less than about 30 weight percent and more preferably less than about 20 weight percent of homopolymer of ethylenically unsaturated monomer.

The aqueous copolymer compositions produced by the method of the present invention are useful in a variety of applications. For example, the aqueous copolymer compositions may be used in architectural and industrial coatings including paints, wood coatings, or inks; paper coatings; textile and nonwoven binders and finishes; adhesives; mastics; floor polishes; leather coatings; plastics; plastic additives; petroleum additives; thermoplastic elastomers or combinations thereof.

EXAMPLES

Some embodiments of the invention will now be described in detail in the following Examples. The following abbreviations shown in Table 1 are used in the examples:

Table I: Abbreviations

Abbreviation	
A-16-22	Polystep A-16-22, anionic surfactant, supplied as 22% solids by Stepan Company, located in Northfield, Illinois.
BA	Butyl acrylate
BD	Butadiene
BMA	Butyl methacrylate
CoBF	Co(II)-(2,3-dioxyiminobutane-BF$_2$)$_2$
CVA	4,4-azobis(4-cyanovaleric acid)
Fe	0.15% Ferrous sulfate in water
DBS	Dodecyl benzene sulfonate
GC	Gas chromatograph
SEC	Size exclusion chromatography
HPLC	High performance liquid chromatography
Init.	Initiator
IR	Infrared spectroscopy
LCCC	Liquid chromatography under critical conditions
MAA	Methacrylic acid
MMA	Methyl methacrylate
Mn	Number average molecular weight
NaMBS	Sodium metabisulfite
NaPS	Sodium persulfate
nDDM	Dodecyl mercaptan
OT-100	Aerosol OT-100, anionic surfactant, supplied as 100% active by Cytec Industries Inc., located in Morristown, New Jersey.
PMAA-MM	Poly-methacrylic acid macromonomer
PMMA	Methyl methacrylate homopolymer
PMMA-MM	Poly-methyl methacrylate macromonomer
Poly-(BA-g-BMA)	Graft copolymer of BA with BMA side chains
Poly-(BA-g-MMA)	Graft copolymer of BA with MMA side chains
Poly-(BD-g-MMA)	Graft copolymer of BD with MMA side chains
Wako VA-044	2,2'-azobis[2-(2-imidazolin2-2yl)propane] dihydrochloride

In the Examples, monomer conversion was determined by GC analysis of unreacted monomer using standard methods. Weight percent solids for the macromonomer and copolymer compositions were determined by gravimetric analysis. Particle size of the macromonomer and copolymer compositions were obtained using a Matec CHDF 2000 particle size analyzer equipped with a HPLC type Ultra-violet detector.

Except where noted differently, macromonomer was measured for number average molecular weight by SEC using a polystyrene standard from Polymer Laboratories (PS-1) having a peak average molecular weight ranging from 580 to 7,500,000 with narrow molecular weight distribution. Conversions from polystyrene to PMMA were made using Mark-Houwink constants. Copolymer compositions were evaluated for number average molecular weight and weight average molecular weight using SEC as described above.

Comparative Example 1.0

Low molecular weight MMA polymer was prepared by an aqueous emulsion polymerization process using a conventional chain transfer agent. The polymerization was conducted in a 2-liter, four neck round bottom reaction flask equipped with a mechanical stirrer, temperature control device, condenser, monomer feed line and a nitrogen inlet according to the following procedure. To the reaction flask were added 483.7 grams of deionized water, 2.0 grams of A-16-22, and 1.55 grams of an aqueous solution containing 52 wt% methyl-ß-cyclodextrin to form a surfactant solution. A monomer emulsion containing 125g of deionized water, 3g of A-16-22, 305g of MMA and 5g of nDDM was prepared separately. Additionally, an initiator solution was prepared by dissolving 1.56g of NaBS in 72.3 g of deionized water. The surfactant solution was heated to 80°C after which 60% of the total initiator solution was added to the reaction flask. The monomer emulsion and the remaining initiator solution were then fed over a period of 60 minutes. At the end of the feed period, the reaction mixture was maintained at 80°C for an additional 30 minutes, followed by cooling and filtering. The resulting low molecular weight MMA emulsion contained 31.0 wt% solids. The MMA polymer had a number average molecular weight (Mn) of 21700.

Examples 1.1 to 1.8 -- Preparation of PMMA-MM by Emulsion Polymerization

MMA macromonomer (PMMA-MM) was prepared by emulsion polymerization processes in Examples 1.1 to 1.8 using the same equipment described in Comparative Example 1.0. The specific amounts of water, surfactant, MMA, chain transfer agent (CTA), and initiator used in Examples 1.1 to 1.8 are shown in Table 2. These ingredients were added according to the following procedure. In a different flask from the reaction flask, a monomer solution was prepared by dissolving the chain transfer agent in MMA under a nitrogen purge. Deionized water and surfactant (OT-100) were introduced into the reaction flask at room temperature to form a water surfactant solution. The water surfactant solution was mixed and heated to 80°C with stirring under a nitrogen purge. Upon reaching a temperature of 80°C, and upon complete dissolution of the surfactant, the initiator (CVA) was added to the water surfactant solution with stirring for 1 minute to permit the initiator to dissolve. After dissolution of the initiator, 20 percent by weight of the monomer solution was added to the reaction flask with stirring. Following this initial charge, the remaining monomer solution was fed over a period of 1 to 2 hours, with stirring, to form a reaction mixture. At the end of the feed period, the reaction mixture was maintained at 80°C for an additional 1 to 3 hours. The reaction mixture was then cooled to room temperature and passed through a filter cloth to remove any coagulum.

Generally, the resulting macromonomer emulsion contained less than 5 weight percent coagulum based on the total weight of macromonomer, and the conversion of monomer was over 99 weight percent, based on the total weight of monomer added. The Mn, weight percent solids and particle size for each macromonomer are reported in Table 2.

Table 2: Preparation of PMMA-MM

Example	H_2O (g)	Surfactant (g) [3]	MMA (g)	CTA ppm[1]	Initiator (g) [2]	Part. Size (nm)	Mn	Wt % Solids
1.1	720	3.6	324	40	3.6	165	2430	32.0
1.2	720	3.6	324	8.7	3.6	126	12612	31.0
1.3	720	3.6	324	10.9	3.6	158	9656	31.0
1.4	720	3.6	324	80.6	3.6	231	1386	30.3
1.5	720	3.6	324	21.8	3.6	201	4416	29.1
1.6	720	3.6	324	10.7	3.6	169	7931	30.5
1.7	720	3.6	360	11.9	3.6	155	10185	32.0
1.8	1440	7.2	720	15.2	7.2	167	7237	32.0

[1] ppm moles of chain transfer agent (CoBF) based on total moles of monomer.
[2] CVA, supplied by Aldrich as a 75 weight percent aqueous solution of initiator.
[3] OT-100.

Example 2: Preparation of PMAA-MM By Solution Polymerization

An MAA macromonomer (PMAA-MM) was prepared by an aqueous solution polymerization process in a 2-liter baffled flange flask equipped with a mechanical stirrer, condenser, temperature control device, initiator feed lines and a nitrogen inlet. The apparatus was purged with nitrogen for 30 minutes after 0.018 g of CoBF was added. Deionized water, 1080 g, was charged to the flask and heated to 55°C under a nitrogen purge. A monomer mixture containing 510 ml of MAA and 0.01 g of CoBF was prepared separately under nitrogen. When the deionized water reached a temperature of 55°C, 1.94 g of initiator (Wako VA-044) was added to the reaction flask. Following the addition of the initiator, the monomer mixture was added over a period of 60 minutes to the reaction flask with stirring. The temperature was then held at 55°C for 2 hours following completion of the monomer mixture feed. Upon cooling the reaction flask to room temperature, the MAA-MM (Example 2.1) was isolated as dried polymer by rotary evaporation. The number average molecular weight (Mn) of the MAA-MM was determined by proton nuclear magnetic resonance to be 4030 based on the integration of the vinyl end group with respect to the methyl and methylene groups of the polymer chain.

Example 3: Preparation of Poly-(BA-g-MMA) Graft Copolymers by Batch Emulsion Polymerization Process

Comparative Example 3.0C and Examples 3.1 to 3.15 graft copolymers were prepared by a batch emulsion polymerization process in a 1-liter, four neck round bottom reaction flask equipped with a mechanical stirrer, condenser, temperature control device, initiator feed lines and a nitrogen inlet. The specific amounts of PMMA-MM (as emulsion), water, surfactant, acid containing monomer (marked "acid" in Table 3), BA, initiator, and buffer used are shown in Table 3. These ingredients were added according to the following procedure. Deionized water (H_2O #1 in Table 3) and PMMA-MM emulsion obtained from the example indicated in Table 3 (sub-column marked "Ex" under the "PMMA-MM" column) were introduced into the reaction flask at room temperature. A monomer emulsion of deionized water (H_2O #2 in Table 3), surfactant, acid containing monomer, and BA was prepared. The monomer emulsion in Example 3.13 additionally contained 0.13 g of nDDM. The monomer emulsion was introduced into the reaction flask at room temperature with stirring to form a reaction mixture. After stirring for 20 minutes, the reaction mixture was heated to the reaction temperature indicated in Table 3.

Once the reaction temperature was reached, an initiator and optionally a buffer were introduced into the reaction flask with stirring according to the following procedures. For examples 3.1C; 3.2; 3.3 and 3.4 to 3.8, both the buffer and initiator listed in Table 3 were added as a single shot to the reaction flask. For examples 3.9 to 3.12 and 3.16, 20% by weight of the initiator solution was added in one shot to the reaction flask, with the remainder being fed over 1 to 2 hours. For the examples prepared with a redox initiator (3.13 to 3.15), one third of the NaPS and NaMBS were added in one shot to the reaction flask, with the remainder fed over, 1 to 2 hours. Also, for the redox initiator system, all of the Fe and Na_2CO_3 were added to the reaction flask at the beginning of the NaPS and NaMBS feeds. After the initiator and buffer were added, the reaction mixture was maintained at the reaction temperature for a period of 1 to 2 hours. The resulting copolymer composition was analyzed for conversion and other properties as described in Example 10. The conversion of BA, as determined by standard GC methods, was greater than 99 weight percent based on the total weight of BA charged.

Table 3: Preparation of Poly-(BA-g-MMA) Graft Copolymers Prepared by Batch Process

Example	PMMA-MM		H_2O #1 (g)	H_2O #2 (g)	Surf.(2) (g)	BA (g)	Temp. (°C)	Init. (g)	Buffer(9) (g)	Acid (g)
	Ex	Amt. (g)								
3.1C(8)	1.0	146.7	22	25	2.2	82.6	90	0.09(5)	0.1	1.96(7)
3.2	1.4	100	14	20.8	0.49	55.7	70	0.63(3)	0	0
3.3	1.3	97	17	20.8	0.49	55.7	70	0.63(3)	0	0
3.4	1.1	50.8	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.5	1.5	52	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.6	1.6	53.3	0	20.3	1.1	47.8	80	0.07(5)	0.04	0.98(7)
3.7	1.3	52.4	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.8	1.2	52	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.9	1.3	216	59	46.8	1.1	123.8	80	1.05(5)	0	2.3(6)
3.10	1.3	84	77	39	0.91	103	80	0.07(5)	0	1.3(6)
3.11	1.3	42	42	102	1.02	115	80	0.07(3)	0	1.3(6)
3.12	1.3	21	112	46.3	1.08	122.5	80	0.07(5)	0	1.3(6)
3.13	1.8	71	0	20	1.1	41.3(1)	90	Redox(4)	0.05	0.98(7)
3.14	1.8	71.1	0	14	1.1	41.3	70	Redox(4)	0.05	0.98(7)
3.15	1.8	71.1	0	14	1.1	41.3	95	Redox(4)	0.05	0.98(7)
3.16	1.3	72.8	17	15.6	0.37	41.3	80	0.35(5)	0	0.75(6)

(1) 0.13 g nDDM was added to the monomer emulsion.

(2) Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water), except for Example 3.12 which was prepared with A-16-22 .

(3) Lupersol 11 supplied by Elf Atochem.

(4) Redox initiator system contained 0.07g NaPS in 3g water; 0.06g NaMBS in 3g water; and 0.7g Fe.

(5) NaPS dissolved in 5-20 g of water.

(6) MAA

(7) PMAA-MM (prepared by method of Example 2.1)

(8) Comparative prepared with PMMA having no terminal ethylenically unsaturated groups.

(9) Sodium carbonate dissolved in 5g of water.

Example 4: Preparation of Poly-(BA-g-MMA) by Semi-continuous Process

In Examples 4.1 to 4.5, graft copolymers were prepared by a semi-continuous emulsion polymerization process in a 1-liter round bottom flask with four neck equipped with a mechanical stirrer, temperature control device, initiator feed lines and a nitrogen inlet. The specific amounts of PMMA-MM (as emulsion), water, surfactant, BA, acid containing monomer, and initiator used in Examples 4.1 to 4.4 are shown in Table 4. These ingredients were added according to the following procedure. A monomer emulsion of deionized water (H_2O #2 in Table 4), surfactant, and BA was prepared in a separate flask. The monomer emulsion in Example 4.2 additionally contained 0.13 g of nDDM. Deionized water (H_2O #1 in Table 4), acid containing monomer, and PMMA-MM obtained from the example indicated in Table 4 (sub-column marked "Ex" under the "PMMA-MM" column) were introduced into the reaction flask at room temperature to form a reaction mixture. The reaction mixture was heated to the reaction temperature indicated in Table 4 while stirring under a nitrogen purge. Upon reaching the reaction temperature, an initiator and buffer (if desired) were introduced into the reaction flask with stirring according to the following procedures. For examples 4.1 to 4.3 (prepared with a redox initiator), one third of the NaPS and NaMBS, and all of the Fe and Na_2CO_3 were added in one shot to the reaction flask. The remaining NaPS and NaMBS was then cofed with the monomer emulsion over a 90 minute period. In Example 4.4, one third of the NaPS, and all of the Na_2CO_3 were added in one shot to the reaction flask, followed by cofeeding the monomer emulsion with the remaining NaPS over a 90 minute period. Upon completion of the feeds, the reaction mixture was maintained at the reaction temperature for a period of 1 to 2 hours. The resulting copolymer composition was analyzed for conversion and other properties as described in Example 10. The conversion of BA, determined by standard GC methods, was greater than 99 weight percent based on the total weight of BA charged.

Table 4: Preparation of Poly-(BA-g-MMA) Prepared by Semi-Continuous Process

Example	PMMA-MM		H_2O #1 (g)	H_2O #2 (g)	Surf.[2] (g)	BA (g)	Temp. (°C)	Init. (g)	Buffer[5] (g)	Acid (g)[6]
	Ex	Amt. (g)								
4.1	1.7	69.4	12	23	1.1	41.3	90	Redox[3]	0.05	0.98
4.2	1.8	71	10.0	10	1.1	41.3[1]	90	Redox[3]	0.11	0.98
4.3	1.8	71	10.0	10	1.1	41.3	90	Redox[3]	0.11	0.98
4.4	1.8	71	10.3	18	1.1	41.3	90	0.16[4]	0.11	0.98

[1] 0.13 g nDDM was added to the monomer emulsion.

[2] Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water).

[3] Redox initiator system include 0.16g NaPS in 6g water; 0.14g NaMBS in 6g water; and 0.7g Fe.

[4] NaPS dissolved in 10g of water.

[5] Sodium carbonate dissolved in 3g of water.

[6] PMAA-MM (prepared by method of Example 2.1)

Example 5: Preparation of Poly-(BD-g-MMA) graft copolymers

A graft copolymer having a backbone of BD and side chains of MMA was prepared in accordance with the method of the present invention. The graft copolymer was prepared in two stages. In the first stage, PMMA-MM was prepared in accordance with the procedure used in Example 1, except that the following amounts of ingredients shown in Table 5a were used to replace the corresponding ingredients in Table 2:

Table 5a: Ingredients used in Preparation of BMA Macromonomer

Ingredient	Amount Charged
H_2O	2380 g
Surfactant (A-16-22)	55 g
MMA	1197 g
CoBF	10.9 ppm[1]
Initiator (CVA)	12.6 g

[1] Based on total moles of MMA monomer.

The resulting PMMA-MM had an Mn of 10,200.

In the second stage, a graft poly-(BD-g-MMA) was prepared in a steel pressure reactor equipped with a mechanical stirrer, temperature control device, and feed lines. Ingredients A through D, shown in Table 5b, were charged to the reactor at room temperature. The reactor was then sealed and vacuum was applied, with stirring, to reduce the reactor pressure to 15 inches of Hg. Butadiene (E) in Table 5b was quickly pumped into the reactor and stirred for

10 minutes. Following stirring the reaction mixture was heated to 60°C for 30 minutes. After the reactor temperature stabilized to 60°C, ingredients F, G, and H in Table 5b were gradually pumped into the reactor over a period of 7 hours. Following completion of the feeds, the reaction mixture was held for 60 minutes at 60 °C.

Table 5b: Ingredients used in Preparation of Poly-(BD-g-MMA) Graft Copolymer

	Ingredient	**Amount Charged**
A	H_2O #1	6049.4 g
B	Acetic acid	4.3 g
C	PMMA-MM (as emulsion)	1389.71 g (Example 5a)
D	H_2O #2 (use for rinsing)	250 g
E	BD	877.5 g
F	t-butyl peroxide (2% solution)	197.44 g
G	SFS(1) (1% solution)	263.25 g
H	Aerosol-OT (75% solution)	3.51 g

(1) Sodium formaldehyde sulfoxylate

^{1}H NMR analysis of the graft copolymer in tetrahydrofuran showed a weight percent ratio of BD to MMA of 65.2 to 34.8. Analysis of the unreacted PMMA-MM by HPLC showed an incorporation of PMMA-MM of about 44 wt% based on the total weight of PMMA-MM added. HPLC showed a predominant BD/MMA graft copolymer peak (verified by IR). Differential scanning calorimetry showed two phase transitions at -79.8° and 110.4°C, respectively. The graft copolymer composition had a solids content of 15 wt% and weight average particle size of 107 nm.

Example 6: Preparation of Poly-(BA-g-BMA) Graft Copolymer

A graft copolymer having a backbone of BA and side chains of BMA was prepared in accordance with the method of the present invention. The graft copolymer was prepared in two stages. In the first stage, butyl methacrylate macromonomer was prepared in accordance with the procedure used in Example 1, except that the following amounts of ingredients shown in Table 6a were used to replace the corresponding ingredients in Table 2:

Table 6a: Ingredients used in Preparation of BMA Macromonomer

Ingredient	Amount Charged
H_2O	720 g
Surfactant (Aerosol OT-100)	3.6 g
BMA	324 g
CoBF	10.9 ppm(1)
Initiator (CVA)	3.6 g

(1) Based on total moles of BMA monomer

The resulting BMA macromonomer had an Mn of 8900.

In the second stage, a graft poly-(BA-g-BMA) was prepared using the procedure described in Example 3, except that the following amounts of ingredients shown in Table 6b were used to replace the corresponding ingredients in Table 3, and a reaction temperature of 85°C was used.

Table 6b: Ingredients used in Preparation of Poly-(BA-g-BMA) Graft Copolymer

Ingredient	Amount Charged
PBMA-MM (as emulsion)	84.1 g (Example 6a)
H_2O #2	15 g
Surfactant(2)	1.1 g
BA	41.3 g
Initiator	Redox(1)
Acid (PMAA-MM)	0.98 g (Example 2.1)

(1) Redox initiator system was 0.07g NaPS in 3g water; 0.06g NaMBS in 3g water; 0.05g Na_2CO_3 in 3g water and 0.7g Fe.

(2) Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water).

The graft copolymer formed contained 63.5 weight percent BA, 35 weight percent of PBMA-MM and 1.5 weight percent of PMAA-MM.

Example 7: Preparation of Poly-(Styrene-g-MMA) Graft Copolymer

A graft copolymer having a backbone of styrene and side chains of PMMA-MM was prepared in accordance with the method of the present invention. The graft copolymer was prepared in two stages. Macromonomer PMMA-MM (obtained from Example 1.8) was used in the synthesis of the graft Poly-(Styrene-g-MMA). The graft Poly-(Styrene-g-MMA) was prepared using the procedure described in Example 3 except that the following amounts of ingredients shown in Table 7 were used to replace the corresponding ingredients in Table 3, and a reaction temperature of 85°C was used.

Table 7: Ingredients used in Preparation of Poly-(Styrene-g-MMA) Graft Copolymer

Ingredient	Amount Charged
PMMA-MM (as emulsion)	84.1 g (Example 1.8)
H_2O #2	15 g
Surfactant[2]	1.1 g
Styrene	41.3 g
Initiator	Redox[1]
Acid (pMAA-MM)	0.98 g (Example 2.1)

[1] Redox initiator system include 0.07g NaPS in 3g water; 0.06g NaMBS in 3g water; 0.05g Na_2CO_3 in 3g water and 0.7g Fe.

[2] Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water).

The graft copolymer formed contained 63.5 weight percent styrene, 35 weight percent of PMMA-MM and 1.5 weight percent of PMAA-MM.

Example 8: Preparation of Poly-(BA-g-MMA) by a Single Vessel Synthesis Procedure

A graft copolymer having a backbone of BA and side chains of MMA was prepared in accordance with the method of the present invention in a single vessel in two aqueous emulsion polymerization stages. In the first stage, PMMA-MM was prepared and in the second stage the PMMA-MM was copolymerized with BA.

The PMMA-MM was prepared in a four neck, 5-liter round bottom reaction flask equipped with a mechanical stirrer, temperature control device, condenser, monomer feed line and a nitrogen inlet. The reaction flask was charged with 680 g of deionized water and 15.7 g of A-16-22 to form a water surfactant solution. The water surfactant solution was heated with stirring to 80°C under a nitrogen purge. At 80°C, 3.6 g of 4,4-azobis(4-cyanovaleric acid) was added with stirring to the reaction flask. Two minutes later, 18 g of MMA was added to the reaction flask with stirring. A monomer mixture containing 342 g of MMA and 0.02 g of CoBF was prepared separately and degassed by bubbling nitrogen in the monomer mixture for 20 minutes. A 20% by weight portion of the monomer mixture was added to the reaction flask 10 minutes after adding the 18 g of MMA. The remainder of the monomer mixture was fed over 120 minutes with stirring while maintaining the temperature at 80°C. At the end of the monomer mixture feed, the temperature of the reaction mixture in the flask was kept at 80°C for 60 minutes and then cooled to 40°C. The resulting macromonomer aqueous emulsion was reacted in the same vessel in a second stage as described below.

In the second stage, a monomer emulsion containing 226 g of deionized water, 16.52 g of an ethoxylated C_6 to C_{18} alkyl ether sulfate (30 wt% active) having from 1 to 40 ethylene oxide groups per molecule (30% active in water), 658 g of butyl acrylate was prepared. In addition, 10.2 g of PMAA-MM, in 75.4 g of water was prepared separately. The monomer emulsion and the PMAA-MM solution were added to the reaction flask at 40°C, and the resulting reaction mixture was stirred for 20 minutes, followed by heating to 85°C. At 85°C, 1.06 g of sodium persulfate dissolved in 25 g of water and 0.47 g of sodium carbonate dissolved in 25 g of were added to the reaction flask in a single shot, followed with 20 g of deionized water rinse. Following the charges of initiator and buffer, the reaction mixture was maintained with stirring at 85°C for 60 minutes. After cooling the reaction mixture to 40°C, 13.72 g of a 0.15% solution of $FeSO_4$ in water was added with stirring, followed by additions of t-butyl peroxide and isoascorbic acid (0.70 g and 0.34 g each in 15 g of water, respectively). A second addition of t-butyl peroxide and isoascorbic acid in the same amounts were added 15 minutes after the first one. The reaction mixture was held with stirring for 30 minutes at a temperature of 40°C.

The resulting copolymer composition was cooled to room temperature and passed through a filter cloth to remove any coagulum. The resulting graft copolymer contained 64 weight percent of butyl acrylate, 35 weight percent of methyl methacrylate and 1 weight percent of PMAA-MM. The copolymer composition had an incorporation of PMMA-MM of 76 weight percent based on the total weight of PMMA-MM charged.

Example 9: Characterization of Copolymer Compositions

Graft copolymer compositions prepared in the previous examples were characterized by various analytical techniques to determine wt% solids, particle size, weight average molecular weight, number average molecular weight, and percent incorporation of macromonomer.

Determination of the amount of unreacted macromonomer was carried out by HPLC analysis using the following procedure. The copolymer compositions were dissolved in THF and analyzed by gradient elution on an LC-18 column supplied by Supelco, located in

Bellefonte, PA such that a well-isolated peak was observed for the unreacted macromonomer. Quantification was carried out by calibrating the detector response using known standards of the same macromonomer employed in the synthesis. The results of the characterization are reported in Table 8 below.

Table 8: Characterization Of Copolymer Compositions

Example	% Solids	Particle Size (nm)	Mw (x 10^{-3})	Mn (x 10^{-3})	PMMA-MM Incorp. (2) (wt%)
3.1C	43	120	(1)	(1)	<2
3.2	43.1	268	119.7	88.6	89
3.3	41.0	204	286.0	29.0	---
3.4	49.3	245	398.1	217.7	90
3.5	50.2	215	708.2	378.3	86
3.6	51.5	228	1015.0	266.9	68
3.7	48.1	226	1242.6	809.6	74
3.8	47.5	215	1082.6	827.4	71
3.9	42.2	180	724.9	114.2	---
3.10	41.3	203	1468.9	875.5	---
3.11	39.6	208	1263.8	964.0	---
3.12	39.7	227	1226.1	813.1	---
3.13	43.5	232	226.1	88.8	83
3.14	44.6	208	795.8	182.0	75
3.15	44.4	220	437.1	160.3	88
3.16	41.4	194	216.1	139.3	71
4.1	34	222	533.3	66.6	86
4.2	43.5	210	264.5	67.3	91
4.3	42.3	181	664.8	83.2	94
4.4	42.8	168	857.9	72.1	94
6.1	39.3	192	552.0	328.0	---
7.1	33.1	161	98.7	20.7	60
8.1	44	150	1041.6	146.9	76

(1) Bimodal molecular weight distribution with the lower molecular weight corresponding to the molecular weight of the macromonomer, indicating that the polymer prepared according to Example 1.0C did not copolymerize.

(2) Based on the total weight of macromonomer added to reaction vessel. Some of the samples (Example 3.3, 3.9, 3.10, 3.11, 3.12, 6.1) were not analyzed for PMMA-MM incorporation.

Example 10: Analysis of Example 3.16

A two-dimensional HPLC analysis was carried out on Example 3.16 to determine the average number of grafts per polymer molecule and to show that a graft copolymer is formed.

Two-dimensional HPLC provides much greater resolution compared to conventional HPLC for the separation of complex polymer materials. The method used in this analysis was similar to that described in "2D Chromatographic Analysis Of Graft Copolymers Obtained By Copolymerization Of Macromonomers Via Conventional, Controlled Radical, And Anionic Polymerizations" by Müller, Axel H. E et al., Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 40(2), pages 140-141, 1999, which is hereby incorporated by reference in its entirety. LCCC was used in one dimension and GPC was used in the second dimension; cuts from the first analysis were sequentially analyzed by the second technique, and appropriate software constructed a plot of the data in two dimensions. The LCCC analysis was run under critical conditions for PBA, and size exclusion conditions for PMMA so that the total molecular weight of the MMA grafts on the copolymer could be determined. From this value, (assuming each side chain contained one macromonomer) the number of side chains per copolymer was calculated. Also, LCCC was used to determine the composition of the copolymer. The analysis in the second dimension using SEC was used to estimate the total molecular weights of the copolymer. The molecular weights measured were calibrated using standards of PMMA for the LCCC dimension and PBA for the GPC dimension. The resulting two-dimensional chromatogram showed a major copolymer peak (roughly estimated at >70%) which, from the LCCC data, contained a total PMMA molecular weight (Mn) of about 110,000. Using the Mn value of 9600 for the PMMA macromonomer, an average number of grafts per polymer chain was estimated at about 11.5. From the second dimension the overall molecular weight of this peak was estimated to be 580,000. The two-dimensional chromatogram showed two other series of copolymer peaks, but no PBA homopolymer was detected. The overall composition of the major copolymer peak calculated from the two-dimensional HPLC data was about 85wt% BA and 15wt% MMA. This composition varies from the expected composition of 72wt% BA and 28wt% MMA (calculated from an NMR analysis of the composition, taking into account that only about 70% of the macromonomer was converted to copolymer), but is reasonable considering the complexity of the copolymer system and the analysis of it.

Example 11: Evaluation Of Shear Stability Of Graft Copolymer Compositions

Shear stability tests were carried out on several graft copolymer compositions made in the previous examples. Shear stability was tested by placing a drop of the graft copolymer composition on the index finger and rubbing the composition between the thumb and index finger. A copolymer composition passed if it could be rubbed until it dried by water evaporation without the formation of coagulum, and failed if it flocculated after a few rubs and became ropy. All of the copolymer compositions tested were stable colloidally under static conditions. The results are reported in Table 9 below.

Table 9: Finger Rub Test Results for Graft Copolymer Compositions

Example	Stabilized acid	Finger Rub Test
3.4	pMAA-MM	Pass
3.5	pMAA-MM	Pass
3.6	pMAA-MM	Pass
3.7	pMAA-MM	Pass
3.8	pMAA-MM	Pass
3.9	MAA	Fail
3.10	MAA	Fail
3.11	MAA	Fail
3.12	MAA	Fail
4.1	pMAA-MM	Pass
4.2	pMAA-MM	Pass
4.3	pMAA-MM	Pass
4.4	pMAA-MM	Pass
8.1	pMAA-MM	Pass

The data in Table 9 shows that graft copolymer compositions prepared with an acid containing macromonomer had surprisingly good shear stability in comparison to graft copolymer prepared with an acid monomer. It was also discovered that good shear stability could be obtained, without the use of an acid containing macromonomer, such as by adding a surfactant such as Triton™ X-405, a nonionic surfactant supplied by Union Carbide, to the copolymer composition.

What is claimed is:

1. A method of making a graft copolymer comprising:
   (a) forming a macromonomer aqueous emulsion comprising one or more water-insoluble particles of macromonomer, wherein the macromonomer comprises polymerized units of a first ethylenically unsaturated monomer, the macromonomer further having
      (i) a degree of polymerization of from 10 to 1000,
      (ii) at least one terminal ethylenically unsaturated group,
      (iii) less than 5 weight percent polymerized acid-containing monomer, and
      (iv) less than one mole percent of polymerized mercaptan-olefin compounds;
   (b) forming a monomer composition comprising at least one second ethylenically unsaturated monomer; and
   (c) combining at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition to form a polymerization reaction mixture and polymerizing the macromonomer with the second ethylenically unsaturated monomer in the presence of an initiator to produce a copolymer composition comprising graft copolymer particles.

2. The method of Claim 1 wherein the step of forming the macromonomer aqueous emulsion comprises polymerizing in an aqueous emulsion the at least first ethylenically unsaturated monomer in the presence of a transition metal chelate chain transfer agent and a free radical initiator to form the macromonomer particles.

3. The method of Claim 2 wherein the first ethylenically unsaturated monomer is polymerized in the presence of a macromolecular organic compound having a hydrophobic cavity.

4. The method of Claim 1 wherein the monomer composition comprises an aqueous emulsion comprising the at least one second ethylenically unsaturated monomer.

5. The method of Claim 1 wherein the second ethylenically unsaturated monomer diffuses into the macromonomer particles and swells the macromonomer particles.

6. The method of Claim 1 wherein the macromonomer comprises as polymerized units less than 1 weight percent of acid containing monomer.

7. The method of Claim 1 wherein the first ethylenically unsaturated monomer is an α--methyl vinyl monomer, a non α-methyl vinyl monomer terminated with a α-methyl vinyl monomer, or combinations thereof.

8. The method of Claim 7 wherein the first ethylenically unsaturated monomer is methyl methacrylate, ethyl methacrylate, 2-ethylhexyl methacrylate, isobornyl methacrylate, butyl methacrylate, lauryl methacrylate, stearyl methacrylate, styrene terminated by α-methyl styrene, or combinations thereof.

9. The method of Claim 1 wherein the second ethylenically unsaturated monomer is selected from the group consisting of acrylate esters; methacrylate esters; styrene; substituted styrenes; olefinically unsaturated nitriles; olefinically unsaturated halides; vinyl esters of organic acids; N-vinyl compounds; acrylamide; methacrylamide; substituted acrylamides; substituted methacrylamides; hydroxyalkylmethacrylates; hydroxyalkylacrylates; vinyl ethers; dienes and combinations thereof.

10. The method of Claim 9 wherein the second ethylenically unsaturated monomer is selected from the group consisting of C_1 to C_{18} alkyl acrylate, styrene, butadiene, and combinations thereof.

11. The method of Claim 1 wherein the macromonomer and the second ethylenically unsaturated monomer are polymerized in the presence of an acid containing monomer, acid containing macromonomer, or combinations thereof.

12. The method of Claim 11 wherein the macromonomer and the second ethylenically unsaturated monomer are polymerized in the presence of an acid containing macromonomer, the acid containing macromonomer comprising as polymerized units from 50 weight percent to 100 weight percent of an acid containing monomer, based on the total weight of the acid containing macromonomer.

13. The method of Claim 1 wherein the macromonomer and ethylenically unsaturated monomer are polymerized in the presence of a macromolecular organic compound having a hydrophobic cavity.

14. The method of Claim 1 wherein all the macromonomer aqueous emulsion and all the monomer composition are combined prior to beginning the polymerization.

15. The method of Claim 1 wherein the macromonomer and the second ethylenically unsaturated monomer are combined by gradually feeding at least a portion of the monomer composition into the macromonomer aqueous emulsion in the presence of the initiator.

16. A graft copolymer produced by the process of claim 1.

17. A copolymer composition comprising water insoluble graft copolymer particles, wherein the graft copolymer particles comprise:

(a) from 2 weight percent to 90 weight percent of macromonomer, based on the total weight of the copolymer, wherein the macromonomer is water insoluble and comprises from 10 to 1000 polymerized units of at least one first ethylenically unsaturated monomer, less than 1 mole percent of polymerized mercapto-olefin compounds, and less than 5 weight percent polymerized acid-containing monomer; and

(b) from 10 weight percent to 98 weight percent of polymerized units of at least one second ethylenically unsaturated monomer, based on the total weight of the copolymer.

18. The copolymer composition of Claim 17 wherein the macromonomer comprises as polymerized units less than 1 weight percent acid containing monomer, based on the total weight of the macromonomer.

19. The copolymer composition of Claim 18 wherein the copolymer composition further comprises from 0.2 weight percent to 10 weight percent of an acid containing macromonomer, or acid containing monomer based on the total weight of the copolymer.

20. The copolymer composition of Claim 19 wherein the graft copolymer comprises a backbone and one or more side chains, wherein the side chains are pendant from the backbone and comprise the water insoluble macromonomer, and wherein the backbone comprises the polymerized units of the second ethylenically unsaturated monomer.

21. The copolymer composition of Claim 20 wherein the acid containing macromonomer is attached to the surface of the copolymer particles.

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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
21 March 2002 (21.03.2002)

PCT

(10) **International Publication Number**
WO 02/022689 A3

(51) **International Patent Classification^7:** **C08F 290/04**

(21) **International Application Number:** PCT/US01/28802

(22) **International Filing Date:**
13 September 2001 (13.09.2001)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
60/232,414 14 September 2000 (14.09.2000) US

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(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

(88) **Date of publication of the international search report:**
1 August 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/022689 A3

(54) **Title:** METHOD FOR PREPARING GRAFT COPOLYMERS AND COMPOSITIONS PRODUCED THEREFROM

(57) **Abstract:** The present invention provides an aqueous polymerization method for preparing graft copolymers, and copolymer compositions produced therefrom. The method of the present invention includes (a) forming a macromonomer aqueous emulsion containing water insoluble macromonomer particles; (b) forming a monomer composition containing at least one ethylenically unsaturated monomer; and (c) combining at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition and polymerizing the resulting polymerization reaction mixture in the presence of an initiator to form a copolymer composition. The copolymer composition produced contains water insoluble particles of graft copolymer.

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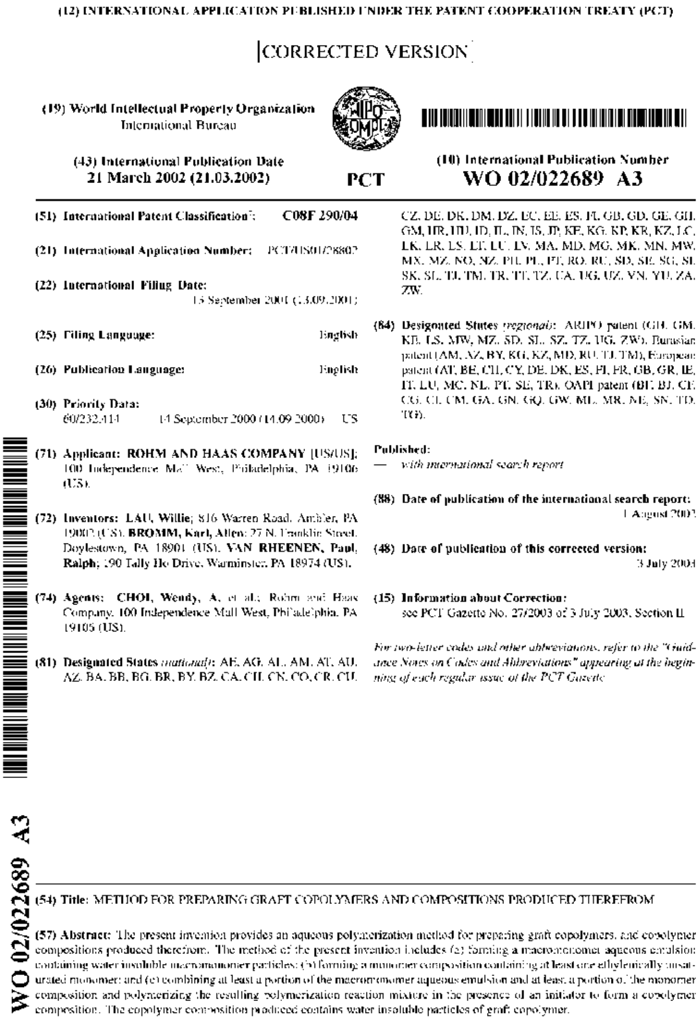

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 March 2002 (21.03.2002)

PCT

(10) International Publication Number
WO 02/022689 A3

(51) International Patent Classification^7: **C08F 290/04**

(21) International Application Number: PCT/US01/28802

(22) International Filing Date: 13 September 2001 (13.09.2001)

(25) Filing Language: English

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

(88) Date of publication of the international search report: 1 August 2002

(48) Date of publication of this corrected version: 3 July 2003

(15) Information about Correction:
see PCT Gazette No. 27/2003 of 3 July 2003, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/022689 A3

(54) Title: METHOD FOR PREPARING GRAFT COPOLYMERS AND COMPOSITIONS PRODUCED THEREFROM

(57) Abstract: The present invention provides an aqueous polymerization method for preparing graft copolymers, and copolymer compositions produced therefrom. The method of the present invention includes (a) forming a macromonomer aqueous emulsion containing water insoluble macromonomer particles; (b) forming a monomer composition containing at least one ethylenically unsaturated monomer; and (c) combining at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition and polymerizing the resulting polymerization reaction mixture in the presence of an initiator to form a copolymer composition. The copolymer composition produced contains water insoluble particles of graft copolymer.

METHOD FOR PREPARING GRAFT COPOLYMERS AND COMPOSITIONS PRODUCED THEREFROM

Field of Invention

This invention relates to a method for making graft copolymers using an aqueous emulsion polymerization process, and copolymer compositions produced therefrom. More particularly, this invention relates to an aqueous emulsion polymerization process for polymerizing at least one macromonomer and at least one ethylenically unsaturated monomer to form a copolymer composition containing graft copolymers.

Background of the Invention

"Graft copolymers" as used herein are macromolecules formed when polymer or copolymer chains are chemically attached as side chains to a polymeric backbone. Generally, the side chains are of a different polymeric composition than the backbone chain. Because graft copolymers often chemically combine unlike polymeric segments in one molecule, these copolymers have unique properties compared to the corresponding random analogues. These properties include, for example, mechanical film properties resulting from thermodynamically driven microphase separation of the polymer, and decreased melt viscosities resulting in part from the branched structure of the graft copolymer. With respect to the latter, reduced melt viscosities can advantageously improve processability of the polymer. *See e.g.*, Hong-Quan Xie and Shi-Biao Zhou, J. Macromol. Sci.-Chem., A27(4), 491-507 (1990); Sebastian Roos, Axel H.E. Müller, Marita Kaufmann, Werner Siol and Clenens Auschra, "Applications of Anionic Polymerization Research", R.P. Quirk, Ed., ACS Symp. Ser. 696, 208 (1998).

The term "comb copolymer," as used herein, is a type of graft copolymer, where the polymeric backbone of the graft copolymer is linear, and each side chain of the graft copolymer is formed by a "macromonomer" that is grafted to the polymer backbone. "Macromonomers" are low molecular weight polymers having at least one functional group at the end of the polymer chain that can further polymerize with others monomers to yield comb copolymers. *See e.g.*, Kawakami in the "Encyclopedia of Polymer Science and Engineering", Vol. 9, pp. 195-204, John Wiley & Sons, New York, 1987. The term "linear," as used herein, is meant to include polymers where minor amounts of branching has occurred through hydrogen abstraction that is normally observed in free radical polymerizations. The comb copolymers are commonly prepared by the free radical copolymerization of macromonomer with conventional monomer (e.g., ethylenically unsaturated monomers).

Comb copolymers prepared with water-insoluble macromonomers have been predominantly prepared using bulk and solution polymerization techniques. However, such processes undesirably use solvent or monomer as the medium in which the polymerization is conducted. Thus, efforts recently have focused on developing methods for preparing comb copolymers via an aqueous emulsion process.

One example, U.S. Patent No. 5,247,040 to Amick et al., ("Amick"), discloses a two stage emulsion polymerization process for producing graft copolymers. In the first stage, a macromonomer is produced by polymerizing ethylenically unsaturated monomer in the presence of a mercapto-olefin compound. In the second stage, the resulting macromonomer is polymerized in an aqueous emulsion with a second ethylenically unsaturated monomer. The Amick process, although having many advantages, produces a graft copolymer having linkages, located between the side chains and backbone, that are susceptible to hydrolysis under certain conditions. These linkages result from using a mercapto-olefin compound having an ester functionality in the preparation of the macromonomer.

U.S. Patent No. 5,264,530 to Darmon et al. ("Darmon") discloses an emulsion or suspension free radical polymerization process where one or more monomer species is polymerized in the presence of a macromonomer that is used as a chain transfer agent. As the macromonomer is being used as a chain transfer agent, the macromonomer is predominately incorporated into the polymer chain at the ends.

U.S. Patent No. 5,804,632 to Haddleton et al. ("Haddleton") discloses an aqueous polymer emulsion process that includes preparing, in the presence of a cobalt chelate complex, a low molecular weight polymer having acid functional groups, and subsequently polymerizing at least one olefinically unsaturated monomer in the presence of the low molecular weight polymer to form a hydrophobic polymer. The low molecular weight polymer in Haddleton is taught to contain a sufficient concentration of acid to render the low molecular weight polymer, as is, or upon neutralization of the acid groups, partially or more preferably fully dissolvable in an aqueous medium. Although Haddleton discloses that some degree of grafting may occur, Haddleton focuses on processes where it is believed that the hydrophobic polymer particles are encapsulated by the low molecular weight polymer in the form of an "inverted core-shell" latex, or where the low molecular weight polymer serves simply as a seed for the polymerization to form the hydrophobic polymer. Thus, Haddleton does not disclose a process to produce graft copolymers of a desired structure such as comb copolymers. It is also believed that using the Haddleton process undesirably results in a substantial amount of low molecular weight polymer remaining unreacted in the water phase.

Publication WO 99/03905 to Huybrechts et al. ("Huybrechts") discloses an anionically stabilized graft copolymer composition that is prepared by emulsion polymerizing acid containing macromonomer and amino functional monomer. The copolymer composition prepared contains from 0.5 to 30 weight percent amino functional monomer in the polymer backbone, and at least 5 weight percent acid functional monomer in the macromonomer that is neutralized with an amine. However, it would be desirable to provide an aqueous emulsion polymerization process for preparing alternative graft copolymer compositions that do not require neutralization.

The present invention seeks to provide a robust emulsion polymerization process for preparing graft copolymers that are preferably resistant to hydrolysis. The present invention also seeks to provide an emulsion polymerization process that preferably provides control over such parameters as polymerization kinetics, polymer structure, conversion, incorporation of macromonomer and particle size.

Summary of Invention

In one aspect of the present invention, a method of making a graft copolymer is provided that includes forming a macromonomer aqueous emulsion containing water-insoluble particles of macromonomer and forming a monomer composition containing ethylenically unsaturated monomer. The macromonomer contains polymerized units of a first ethylenically unsaturated monomer and further has a degree of polymerization of from 10 to 1000, at least one terminal ethylenically unsaturated group, less than 5 weight percent acid-containing monomer as polymerized, and less than 1 mole percent of mercapto-olefin compounds as polymerized. At least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition are combined to form a polymerization reaction mixture, and the macromonomer and the second ethylenically unsaturated monomer therein are polymerized in the presence of an initiator to produce a graft copolymer composition containing graft copolymer particles.

In another aspect of the present invention, a graft copolymer composition is provided that contains water insoluble graft copolymer particles. The copolymer particles contain from 2 weight percent to 90 weight percent water insoluble macromonomer, and from 10 weight percent to 98 weight percent of polymerized units of at least one second ethylenically unsaturated monomer, based on the total weight of the copolymer. The macromonomer used to form the graft copolymer composition contains from 10 to 1000 polymerized units of a first ethylenically unsaturated monomer, less than 1 mole percent of polymerized mercapto-olefin compounds, and less than 5 weight percent polymerized acid-containing monomer. In a preferred embodiment, the copolymer composition further contains from 0.2 weight percent to 10 weight percent of an acid containing macromonomer, based on the total weight of the copolymer.

Detailed Description

The present invention provides an aqueous polymerization process for preparing graft copolymers, and more preferably comb copolymers. The present invention also provides novel copolymer compositions produced from the aqueous polymerization process.

The process of the present invention includes (a) forming a macromonomer aqueous emulsion containing one or more water-insoluble particles of macromonomer; (b) forming a monomer composition containing ethylenically unsaturated monomer; and (c) combining at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition to form a polymerization reaction mixture. The macromonomer and ethylenically unsaturated monomer are polymerized in the presence of an initiator to form graft copolymer particles.

The macromonomer, present in the macromonomer aqueous emulsion as water insoluble particles, is any low molecular weight water-insoluble polymer or copolymer having at least one terminal ethylenically unsaturated group that is capable of being polymerized in a free radical polymerization process. By "water-insoluble" it is meant having a water solubility of no greater than 150 millimoles/liter at 25°C to 50°C. By "low molecular weight" it is meant that the macromonomer has a degree of polymerization preferably from about 10 to about 1000, and more preferably from about 20 to about 200. By "degree of polymerization" it is meant the number of polymerized monomer units present in the macromonomer.

The macromonomer contains, as polymerized units, at least one type of ethylenically unsaturated monomer. Preferably, the ethylenically unsaturated monomer is selected to impart low or no water solubility to the macromonomer as previously described herein.

Suitable ethylenically unsaturated monomers for use in preparing macromonomer include for example methacrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of methacrylic acid, including methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, lauryl methacrylate, stearyl methacrylate; acrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of acrylic acid, including methyl acrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate; styrene; substituted styrenes, such as methyl styrene, α-methyl styrene or t-butyl styrene; olefinically unsaturated nitriles, such as acrylonitrile or methacrylonitrile; olefinically unsaturated halides, such as vinyl chloride, vinylidene chloride or vinyl fluoride; vinyl esters of organic acids, such as vinyl acetate; N-vinyl compounds such as N-vinyl pyrrolidone; acrylamide; methacrylamide; substituted acrylamides; substituted methacrylamides; hydroxyalkylmethacrylates such as hydroxyethylmethacrylate; hydroxyalkylacrylates; basic substituted (meth)acrylates and (meth)acrylamides, such as amine-substituted methacrylates including dimethylaminoethyl methacrylate, tertiary-butylaminoethyl methacrylate and dimethylaminopropyl methacrylamide and the likes; dienes such as 1,3-butadiene and isoprene; vinyl ethers; or combinations thereof. The term "(meth)" as used herein means that the "meth" is optionally present. For example, "(meth)acrylate" means methacrylate or acrylate.

The ethylenically unsaturated monomer can also be a functional monomer including for example monomers containing hydroxy, amido, aldehyde, ureido, polyether, glycidylalkyl, keto functional groups or combinations thereof. These functional monomers are generally present in the macromonomer at a level of from about 0.5 weight percent to about 15 weight percent and more preferably from about 1 weight percent to about 3 weight percent, based on the total weight of the graft copolymer. Examples of functional monomers include ketofunctional monomers such as the acetoacetoxy esters of hydroxyalkyl acrylates and methacrylates (e.g., acetoacetoxyethyl methacrylate) and keto-containing amides (e.g., diacetone acrylamide); allyl alkyl methacrylates or acrylates; glycidylalkyl methacrylates or acrylates; or combinations thereof. Such functional monomer can provide crosslinking if desired.

The macromonomer also contains as polymerized units less than about 10 weight percent, preferably less than about 5 weight percent, more preferably less than 2 weight percent and most preferably less than about 1 weight percent acid containing monomer, based on the total weight of the macromonomer. In a most preferred embodiment, the macromonomer contains no acid containing monomer. By "acid containing monomer" it is meant any ethylenically unsaturated monomer that contains one or more acid functional groups or functional groups that are capable of forming an acid (e.g., an anhydride such as methacrylic anhydride or tertiary butyl methacrylate). Examples of acid containing monomers include, for example, carboxylic acid bearing ethylenically unsaturated monomers such as acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid; acryloxypropionic acid and (meth)acryloxypropionic acid; sulphonic acid-bearing monomers, such as styrene sulfonic acid, sodium vinyl sulfonate, sulfoethyl acrylate, sulfoethyl methacrylate, ethylmethacrylate-2-sulphonic acid, or 2-acrylamido-2-methylpropane sulphonic acid; phosphoethylmethacrylate; the corresponding salts of the acid containing monomer; or combinations thereof.

The macromonomer also contains, as polymerized, less than about 1 mole percent, preferably less than about 0.5 mole percent, and more preferably no mercapto-olefin compounds, based on the total weight of the macromonomer. These mercapto-olefin compounds are those as described in U.S. Patent No. 5,247,000 to Amick, which is incorporated herein by reference in its entirety. The mercapto-olefin compounds described in Amick have ester functional groups, which are susceptible to hydrolysis.

In a preferred embodiment of the present invention, the macromonomer is composed of at least about 20 weight percent, more preferably from about 50 weight percent to about 100 weight percent, and most preferably from about 80 to about 100 weight percent of at least one α-methyl vinyl monomer, a non α-methyl vinyl monomer terminated with a α-methyl vinyl monomer, or combinations thereof. In a most preferred embodiment of the present invention the macromonomer contains as polymerized units from about 90 weight percent to about 100 weight percent α-methyl vinyl monomers, non α-methyl vinyl monomers terminated with α-methyl vinyl monomers, or combinations thereof, based on the total weight of the macromonomer. Suitable α-methyl vinyl monomers include, for example, methacrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of methacrylic acid, including methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, isobornyl methacrylate, lauryl methacrylate, or stearyl methacrylate; hydroxyalkyl methacrylates such as hydroxyethyl methacrylate; glycidylmethacrylate; phenyl methacrylate; methacrylamide; methacrylonitrile; or combinations thereof. An example of a non α-methyl vinyl monomer terminated with an α-methyl vinyl monomer includes styrene terminated by α-methyl styrene.

One skilled in the art will recognize that there are many ways to prepare the macromonomer useful in the present invention. For example, the macromonomer may be prepared by a high temperature (e.g., at least about 150°C) continuous process such as disclosed in U.S. Patent No. 5,710,227 or EP-A-1,010,706, published June 21, 2000, the disclosures of which are hereby incorporated by reference in their entireties. In a preferred continuous process, a reaction mixture of ethylenically unsaturated monomers are passed through a heated zone having a temperature of at least about 150°C, and more preferably at least about 275°C. The heated zone may also be maintained at a pressure above atmospheric pressure (e.g., greater than about 30 bar). The reaction mixture of monomers may also optionally contain a solvent such as water, acetone, methanol, isopropanol, propionic acid, acetic acid, dimethylformamide, dimethylsulfoxide, methylethylketone, or combinations thereof.

The macromonomer useful in the present invention may also be prepared by polymerizing ethylenically unsaturated monomers in the presence of a free radical initiator and a catalytic metal chelate chain transfer agent (e.g., a transition metal chelate). Such a polymerization may be carried out by a solution, bulk, suspension, or emulsion polymerization process. Suitable methods for preparing the macromonomer using a catalytic metal chelate chain transfer agent are disclosed in for example U.S. Patent Nos. 4,526,945, 4,680,354, 4,886,861, 5,028,677, 5,362,826, 5,721,330, and 5,756,605; European publications EP-A-0199,436, and EP-A-0196783; and PCT publications WO 87/03605, WO 96/15158, and WO 97/34934, the disclosures of which are hereby incorporated by reference in their entireties.

Preferably, the macromonomer useful in the present invention is prepared by an aqueous emulsion free radical polymerization process using a transition metal chelate complex. Preferably, the transition metal chelate complex is a cobalt (II) or (III) chelate complex such as, for example, dioxime complexes of cobalt, cobalt II porphyrin complexes, or cobalt II chelates of vicinal iminohydroxyimino compounds, dihydroxyimino compounds, diazadihydroxy-iminodialkyldecadienes, or diazadihydroxyiminodialkylundecadienes, or combinations thereof. These complexes may optionally include bridging groups such as BF_2, and may also be optionally coordinated with ligands such as water, alcohols, ketones, and nitrogen bases such as pyridine. Additional suitable transition metal complexes are disclosed in for example U.S. Patent Nos. 4,694,054; 5,770,665; 5,962,609; and 5,602,220, the disclosures of which are hereby incorporated by reference in their entireties. A preferred cobalt chelate complex useful in the present invention is Co II (2,3-dioxyiminobutane-BF_2)$_2$, the Co III analogue of the aforementioned compound, or combinations thereof. The spatial arrangements of such complexes are disclosed in for example EP-A-199436 and U.S. Patent No. 5,756,605.

In preparing macromonomer by an aqueous emulsion polymerization process using a transition metal chelate chain transfer agent, at least one ethylenically unsaturated monomer is polymerized in the presence of a free radical initiator and the transition metal chelate according to conventional aqueous emulsion polymerization techniques. Preferably, the ethylenically unsaturated monomer is an α-methyl vinyl monomer as previously described herein.

The polymerization to form the macromonomer is preferably conducted at a temperature of from about 20°C to about 150°C, and more preferably from about 40°C to about 95°C. The solids level at the completion of the polymerization is typically from about 5 weight percent to about 65 weight percent, and more preferably from about 30 weight percent to about 50 weight percent, based on the total weight of the aqueous emulsion.

The concentration of initiator and transition metal chelate chain transfer agent used during the polymerization process is preferably chosen to obtain the desired degree of polymerization of the macromonomer. Preferably, the concentration of initiator is from about 0.2 weight percent to about 3 weight percent, and more preferably from about 0.5 weight percent to about 1.5 weight percent, based on the total weight of monomer. Preferably, the concentration of transition metal chelate chain transfer agent is from about 5 ppm to about 200 ppm, and more preferably from about 10 ppm to about 100 ppm, based on the total moles of monomer used to form the macromonomer.

The ethylenically unsaturated monomer, initiator, and transition metal chelate chain transfer agent may be added in any manner known to those skilled in the art to carry out the polymerization. For example, the monomer, initiator and transition metal chelate may all be present in the aqueous emulsion at the start of the polymerization process (i.e., a batch process). Alternatively, one or more of the components may be gradually fed to an aqueous solution (i.e., a continuous or semi-batch process). For example, it may be desired to gradually feed the entire or a portion of the initiator, monomer, and/or transition metal chelate to a solution containing water and surfactant. In a preferred embodiment, at least a portion of the monomer and transition metal chelate are gradually fed during the polymerization, with the remainder of the monomer and transition metal chelate being present in the aqueous emulsion at the start of the polymerization. In this embodiment, the monomer may be fed as is, or suspended or emulsified in an aqueous solution prior to being fed.

Any suitable free radical initiator may be used to prepare the macromonomer. The initiator is preferably selected based on such parameters as its solubility in one or more of the other components (e.g., monomers, water); half life at the desired polymerization temperature (preferably a half life within the range of from about 30 minutes to about 10 hours), and stability in the presence of the transition metal chelate. Suitable initiators include for example azo compounds such as 2,2'-azobis (isobutyronitrile), 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis [2-methyl-N-(1,1-bis(hydroxymethyl)-2-(hydroxyethyl)]-propionamide, and 2,2'-azobis [2-methyl-N-(2-hydroxyethyl)]-propionamide; peroxides such as t-butyl hydroperoxide, benzoyl peroxide; sodium, potassium, or ammonium persulphate or combinations thereof. Redox initiator systems may also be used, such as for example persulphate or peroxide in combination with a reducing agent such as sodium metabisulphite, sodium bisulfite, sodium formaldehyde sulfoxylate, isoascorbic acid, or combinations thereof. Metal promoters, such as iron, may also optionally be used in such redox initiator systems. Also, buffers, such as sodium bicarbonate may be used as part of the initiator system.

An emulsifier is also preferably present during the aqueous emulsion polymerization process to prepare the macromonomer. Any emulsifier may be used that is effective in emulsifying the monomers such as for example anionic, cationic, or nonionic emulsifiers. In a preferred embodiment, the emulsifier is anionic such as for example sodium, potassium, or ammonium salts of dialkylsulphosuccinates; sodium, potassium, or ammonium salts of sulphated oils; sodium, potassium, or ammonium salts of alkyl sulphonic acids, such as sodium dodecyl benzene sulfonate; sodium, potassium, or ammonium salts of alkyl sulphates, such as sodium lauryl sulfate; ethoxylated alkyl ether sulfates; alkali metal salts of sulphonic acids; C_{12} to C_{24} fatty alcohols, ethoxylated fatty acids or fatty amides: sodium, potassium, or ammonium salts of fatty acids, such as Na stearate and Na oleate; or combinations thereof. The amount of emulsifier in the aqueous emulsion is preferably from about 0.05 weight percent to about 10 weight percent, and more preferably from about 0.3 weight percent to about 3 weight percent, based on the total weight of the monomers.

The macromonomer thus prepared is emulsion polymerized with ethylenically unsaturated monomer to form a copolymer composition containing graft copolymer particles. The polymerization is carried out by providing the macromonomer as water insoluble particles in a macromonomer aqueous emulsion and the ethylenically unsaturated monomer in a monomer composition. At least a portion of the macromonomer aqueous emulsion is combined with at least a portion of the monomer composition to form a polymerization reaction mixture that is polymerized in the presence of an initiator.

Although in no way intending to be bound in theory, it is believed that by providing the macromonomer in the form of water insoluble macromonomer particles in an aqueous emulsion, and the ethylenically unsaturated monomer in a separate monomer composition, upon combination, the ethylenically unsaturated monomer diffuses into the macromonomer particles where the polymerization occurs. Preferably, the diffusion of the ethylenically unsaturated monomer into the macromonomer particles is evidenced by swelling of the macromonomer particles.

The macromonomer aqueous emulsion useful in the present invention may be formed in any manner known to those skilled in the art. For example, the macromonomer, produced by any known method, may be isolated as a solid (e.g., spray dried) and emulsified in water. Also, for example, the macromonomer, if prepared via an emulsion or aqueous based polymerization process, may be used as is, or diluted with water or concentrated to a desired solids level.

In a preferred embodiment of the present invention, the macromonomer aqueous emulsion is formed from the emulsion polymerization of an ethylenically unsaturated monomer in the presence of a transition metal chelate chain transfer agent as described previously herein. This embodiment is preferred for numerous reasons. For example, the macromonomer polymerization can be readily controlled to produce a desired particle size distribution (preferably narrow, e.g., polydispersity less than 2). Also, for example, additional processing steps, such as isolating the macromonomer as a solid, can be avoided, leading to better process economics. In addition, the macromonomer, macromonomer aqueous emulsion and the graft copolymer can be prepared by consecutive steps in a single reactor which is desirable in a commercial manufacturing facility.

The macromonomer aqueous emulsion useful in the present invention contains from about 20 weight percent to about 60 weight percent, and more preferably from about 30 weight percent to about 50 weight percent of at least one water insoluble macromonomer, based on the total weight of macromonomer aqueous emulsion. The macromonomer aqueous emulsion may also contain mixtures of macromonomer. Preferably, the macromonomer aqueous emulsion contains less than about 5 weight percent and more preferably less than about 1 weight percent of ethylenically unsaturated monomer, based on the total weight of macromonomer aqueous emulsion.

The water insoluble macromonomer particles have a particle size to form graft copolymer of the desired particle size. For example, the final graft copolymer particles size is directly proportional to the initial particle size of the macromonomer and the concentration of ethylenically unsaturated monomers in the polymerization reaction mixture, assuming all the particles participate equally in the polymerization. Preferably, the macromonomer particles have a weight average particle size of from about 50 nm to about 500 nm, and more preferably from about 80 nm to about 200 nm as measured by Capillary Hydrodynamic Fractionation technique using a Matec CHDF 2000 particle size analyzer equipped with a HPLC type Ultra-violet detector.

The macromonomer aqueous emulsion may also include one or more emulsifying agents. The type and amount of emulsifying agent is preferably selected in a manner to produce the desired particle size. Suitable emulsifying agents include those previously disclosed for use in preparing the macromonomer by an emulsion polymerization process. Preferred emulsifying agents are anionic surfactants such as, for example, sodium lauryl sulfate, sodium dodecylbenzene sulfonate, sulfated and ethoxylated derivatives of nonylphenols and fatty alcohols. The total level of emulsifying agent, based on the total weight of macromonomer is preferably from about 0.2 weight percent to about 5 weight percent and more preferably from about 0.5 weight percent to about 2 weight percent.

The monomer composition useful in the present invention contains at least one kind of ethylenically unsaturated monomer. The monomer composition may contain all (i.e., 100%) monomer, or contain monomer dissolved or dispersed in an organic solvent and/or water. Preferably, the level of monomer in the monomer composition is from about 50 weight percent to 100 weight percent, more preferably from about 60 weight percent to about 90 weight percent, and most preferably from about 70 weight percent to about 80 weight percent, based on the total weight of the monomer composition. Examples of organic solvents that may be present in the monomer composition include C_6 to C_{14} alkanes. The organic solvent in the monomer composition will be no more than 30 weight percent, and more preferably no more than 5 weight percent, based on the total weight of the monomer composition.

In addition to water and/or organic solvent, the monomer composition may also optionally contain monomers containing functional groups, such as, for example, monomers containing hydroxy, amido, aldehyde, ureido, polyether, glycidylalkyl, keto groups or combinations thereof. These other monomers are generally present in the monomer composition at a level of from about 0.5 weight percent to about 15 weight percent, and more preferably from about 1 weight percent to about 3 weight percent based on the total weight of the graft copolymer. Examples of functional monomers include ketofunctional monomers such as the acetoacetoxy esters of hydroxyalkyl acrylates and methacrylates (e.g., acetoacetoxyethyl methacrylate) and keto-containing amides (e.g., diacetone acrylamide); allyl alkyl methacrylates or acrylates; glycidylalkyl methacrylates or acrylates; or combinations thereof. Such functional monomer can provide crosslinking if desired.

In a preferred embodiment, the monomers in the monomer composition are preemulsified in water to form a monomer aqueous emulsion. Preferably, the monomer aqueous emulsion contains monomer droplets having a droplet size from about 1 micron to about 100 microns, and more preferably from about 5 micron to about 50 microns. Any suitable emulsifying agent may be used, for example those previously described, to emulsify the monomer to the desired monomer droplet size. Preferably, the level of emulsifying agent, if present, will be from about 0.2 weight percent to about 2 weight percent based on the total weight of monomer in the monomer composition.

The ethylenically unsaturated monomer of the monomer composition is preferably selected to provide the desired properties in the resulting copolymer composition. Suitable ethylenically unsaturated monomers include for example methacrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of methacrylic acid, including methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, stearyl methacrylate, isobornyl methacrylate; acrylate esters, such as C_1 to C_{18} normal or branched alkyl esters of acrylic acid, including methyl acrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate; styrene; substituted styrenes, such as methyl styrene, α-methyl styrene or t-butyl styrene; olefinically unsaturated nitriles, such as acrylonitrile or methacrylonitrile; olefinically unsaturated halides, such as vinyl chloride, vinylidene chloride or vinyl fluoride; vinyl esters of organic acids, such as vinyl acetate; N-vinyl compounds such as N-vinyl pyrrolidone; acrylamide; methacrylamide; substituted acrylamides; substituted methacrylamides; hydroxyalkylmethacrylates such as hydroxyethylmethacrylate; hydroxyalkylacrylates; dienes such as 1,3-butadiene and isoprene; vinyl ethers; or combinations thereof. The ethylenically unsaturated monomer can also be an acid containing monomer or a functional monomer, such as those previously described herein. Preferably, the ethylenically unsaturated monomer of the monomer composition does not contain amino groups.

In a preferred embodiment, the monomer composition includes one or more ethylenically unsaturated monomers selected from C_1 to C_{18} normal or branched alkyl esters of acrylic acid, including methyl acrylate, ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate; styrene; substituted styrenes, such as methyl styrene, α-methyl styrene or t-butyl styrene; butadiene or combinations thereof.

As previously mentioned, the macromonomer aqueous emulsion and monomer composition are combined to form a polymerization reaction mixture, and polymerized in the presence of a free radical initiator to form an aqueous copolymer composition. The term "polymerization reaction mixture," as used herein, refers to the resulting mixture formed when at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition are combined. The polymerization reaction mixture may also contain initiator or any other additive used during the polymerization. Thus, the polymerization reaction mixture is a mixture that changes in composition as the macromonomer and monomer in the monomer composition are reacted to form graft copolymer.

The macromonomer aqueous emulsion and monomer composition may be combined in various ways to carry out the polymerization. For example, the macromonomer aqueous emulsion and the monomer composition may be combined prior to the start of the polymerization reaction to form the polymerization reaction mixture. Alternatively, the monomer composition could be gradually fed into the macromonomer aqueous emulsion, or the macromonomer aqueous emulsion could be gradually fed into the monomer composition. It is also possible that only a portion of the macromonomer aqueous emulsion and/or monomer composition be combined prior to the start of the polymerization with the remaining monomer composition and/or macromonomer aqueous emulsion being fed during the polymerization.

The initiator can also be added in various ways. For example, the initiator may be added in "one shot" to the macromonomer aqueous emulsion, the monomer composition, or a mixture of the macromonomer aqueous emulsion and the monomer composition at the start of the polymerization. Alternatively, all or a portion of the initiator can be cofed as a separate feed stream, as part of the macromonomer aqueous emulsion, as part of the monomer composition, or any combination of these methods.

The preferred method of combining the macromonomer aqueous emulsion, the monomer composition, and initiator will depend on such factors as the desired graft copolymer composition. For example, the distribution of the macromonomer as a graft along the backbone can be affected by the concentrations of both the macromonomer and the ethylenically unsaturated monomers at the time of the polymerization. In this regard, a batch process will afford high concentration of both the macromonomer and the ethylenically unsaturated monomers at the onset of the polymerization whereas a semi-continuous process will keep the ethylenically unsaturated monomer concentration low during the polymerization. Thus, through the method in which the macromonomer aqueous emulsion and monomer composition are combined, it is possible to control, for example, the number of macromonomer grafts per polymer chain, the distribution of graft in each chain, and the length of the polymer backbone.

Initiators useful in polymerizing the macromonomer and ethylenically unsaturated monomer include any suitable initiator for emulsion polymerizations known to those skilled in the art. The selection of the initiator will depend on such factors as the initiator's solubility in one or more of the reaction components (e.g. monomer, macromonomer, water); and half life at the desired polymerization temperature (preferably a half life within the range of from about 30 minutes to about 10 hours). Suitable initiators include those previously described herein in connection with forming the macromonomer, such as azo compounds such as 4,4'-azobis(4-cyanovaleric acid), peroxides such as t-butyl hydroperoxide; sodium, potassium, or ammonium persulfate; redox initiator systems such as, for example, persulphate or peroxide in combination with a reducing agent such as sodium metabisulfite, sodium bisulfite, sodium formaldehyde sulfoxylate, isoascorbic acid; or combinations thereof. Metal promoters, such as iron; and buffers, such as sodium bicarbonate, may also be used in combination with the initiator. Additionally, Controlled Free Radical Polymerization (CFRP) methods such as Atom Transfer Radical Polymerization; or Nitroxide Mediated Radical Polymerization may be used. Preferred initiators include azo compounds such as 4,4'-azobis(4-cyanovaleric acid).

The amount of initiator used will depend on such factors as the copolymer desired and the initiator selected. Preferably, from about 0.1 weight percent to about 1 weight percent initiator is used, based on the total weight of monomer and macromonomer.

The polymerization temperature will depend on the type of initiator chosen and desired polymerization rates. Preferably, however, the macromonomer and ethylenically unsaturated monomer are polymerized at a temperature of from about room temperature to about 150°C, and more preferably from about 40°C to about 95°C.

The amount of macromonomer aqueous emulsion and monomer composition added to form the polymerization reaction mixture will depend on such factors as the concentrations of macromonomer and ethylenically unsaturated monomer in the macromonomer aqueous emulsion and monomer composition, respectively, and the desired copolymer composition. Preferably, the macromonomer aqueous emulsion and monomer composition are added in amounts to provide a copolymer containing as polymerized units of from about 2 weight percent to about 90 weight percent, more preferably from about 5 weight percent to about 50 weight percent, and most preferably from about 5 weight percent to about 35 weight percent macromonomer, and from about 10 weight percent to about 98 weight percent, more preferably from about 50 weight percent to about 95 weight percent and most preferably from about 65 weight percent to about 95 weight percent ethylenically unsaturated monomer.

One skilled in the art will recognize that other components used in conventional emulsion polymerizations may optionally be used in the method of the present invention. For example, to reduce the molecular weight of the resulting graft copolymer, the polymerization may optionally be conducted in the presence of one or more chain transfer agents, such as n-dodecyl mercaptan, thiophenol; halogen compounds such as bromotrichloromethane; or combinations thereof. Also, additional initiator and/or catalyst may be added to the polymerization reaction mixture at the completion of the polymerization reaction to reduce any residual monomer, (e.g., chasing agents). Suitable initiators or catalysts include those initiators previously described herein. In addition, the chain transfer capacity of a macromonomer through addition-fragmentation can be utilized in part to reduce molecular weight through appropriate design of monomer compositions and polymerization conditions. *See e.g.*, E. Rizzardo, et. al., Prog. Pacific Polym. Sci., 1991, 1, 77-88; G. Moad, et. al., WO 96/15157.

Preferably, the process of the present invention does not require neutralization of the monomer, or resulting aqueous copolymer composition. These components preferably remain in unneutralized form (e.g., no neutralization with a base if acid functional groups are present).

The resulting aqueous copolymer composition formed by polymerization of the macromonomer and the ethylenically unsaturated monomer in the monomer composition preferably has a solids level of from about 30 weight percent to about 65 weight percent and more preferably from about 40 weight percent to about 60 weight percent. The aqueous copolymer composition preferably contains copolymer particles that are water insoluble and have a particle size of from about 60 nm to about 500 nm, and more preferably from about 80 nm to about 200 nm.

The graft copolymer formed preferably has a backbone containing, as polymerized units, the ethylenically unsaturated monomer from the monomer composition, and one or more side chains, pendent from the backbone, containing the macromonomer. Preferably, each side chain is formed from one macromonomer grafted to the backbone. The degree of polymerization of the macromonomer side chains is preferably in the range of from about 10 to about 1000, and more preferably in the range of from about 20 to about 200, where the degree of polymerization is expressed as the number of polymerized units of ethylenically unsaturated monomer used to form the macromonomer. The total weight average molecular weight of the graft copolymer is preferably in the range of from about 50,000 to about 2,000,000, and more preferably from about 100,000 to about 1,000,000. Weight average molecular weights as used herein can be determined by size exclusion chromatography.

The copolymer particles of the aqueous copolymer composition can be isolated, for example, by spray drying or coagulation. However, it is preferable to use the copolymer aqueous composition as is.

In a preferred embodiment of the present invention, the polymerization is conducted in two stages. In the first stage, the macromonomer is formed in an aqueous emulsion polymerization process, and in the second stage the macromonomer is polymerized with the ethylenically unsaturated monomer in an emulsion. For efficiency, preferably these two stages are conducted in a single vessel. For example, in the first stage, the macromonomer aqueous emulsion may be formed by polymerizing in an aqueous emulsion at least one first ethylenically unsaturated monomer to form water insoluble macromonomer particles. This first stage polymerization is preferably conducted using a transition metal chelate chain transfer agent as previously described herein. After forming the macromonomer aqueous emulsion, a second emulsion polymerization is preferably performed in the same vessel to polymerize the macromonomer with at least one second ethylenically unsaturated monomer. This second stage may be conducted for example by directly adding (e.g., all at once or by a gradual feed) the monomer composition and initiator to the macromonomer aqueous emulsion. One main advantage of this embodiment is that the macromonomer does not have to be isolated, and the second polymerization can take place simply by adding the monomer composition and initiator to the macromonomer aqueous emulsion.

In another preferred embodiment of the present invention, the polymerization of the macromonomer and ethylenically unsaturated monomer is at least partially performed in the presence of an acid containing monomer, acid containing macromonomer, or combinations thereof. The acid containing monomer or acid containing macromonomer may be added in any manner to the polymerization reaction mixture. Preferably, the acid containing monomer or acid containing macromonomer is present in the monomer composition. The acid containing monomer or acid containing macromonomer may also be added as a separate stream to the polymerization reaction mixture.

The amount of acid containing monomer or acid containing macromonomer added to the polymerization reaction mixture is preferably from about 0.2 weight percent to about 10 weight percent, more preferably from about 0.5 weight percent to about 5 weight percent, and most preferably from about 1 weight percent to about 2 weight percent, based on the total weight of monomer and macromonomer added to the polymerization reaction mixture.

Acid containing monomers which may be used in this embodiment include ethylenically unsaturated monomers bearing acid functional or acid forming groups such as those previously described herein. The acid containing macromonomer useful in this embodiment is any low molecular weight polymer having at least one terminal ethylenically unsaturated group that is capable of being polymerized in a free radical polymerization process, and that is formed from at least one kind of acid containing monomer. Preferably, the amount of acid containing monomer in the acid containing macromonomer is from about 50 weight percent to 100 weight percent, more preferably from about 90 weight percent to 100 weight percent, and most preferably from about 95 weight percent to 100 weight percent.

The acid containing macromonomer may be prepared according to any technique known to those skilled in the art such as those previously described herein. In a preferred embodiment of the present invention, the acid containing macromonomer is prepared by a solution polymerization process using a free radical initiator and transition metal chelate complex. An example of such a process is disclosed in for example U.S. Patent No. 5,721,330, which is incorporated by reference in its entirety. Preferred acid containing monomers used to form the acid containing macromonomer are α-methyl vinyl monomers such as methacrylic acid.

In another preferred embodiment of the present invention, a macromolecular organic compound having a hydrophobic cavity is present in the polymerization medium used to form the macromonomer and/or aqueous copolymer composition. Preferably, the macromolecular organic compound is used when copolymerizing ethylenically unsaturated monomers with very low water solubility such as lauryl or stearyl acrylates and/or methacrylates. By "low water solubility" it is meant a water solubility at 25°C to 50°C of no greater than 50 millimoles/liter. For example, the macromolecular organic compound may be added to the monomer composition, the macromonomer aqueous emulsion, or the polymerization reaction mixture used to form the aqueous copolymer composition. Also, for example the macromolecular organic compound may be added to an aqueous emulsion of ethylenically unsaturated monomer used to form the macromonomer. Suitable techniques for using a macromolecular organic compound having a hydrophobic cavity are disclosed in, for example, U.S. Patent No. 5,521,266, the disclosure of which is hereby incorporated by reference in its entirety.

Preferably, the macromolecular organic compound having a hydrophobic cavity is added to the polymerization reaction mixture to provide a molar ratio of macromolecular organic compound to low water solubility monomer or macromonomer of from about 5:1 to about 1:5000 and more preferably from about 1:1 to about 1:500.

Macromolecular organic compounds having a hydrophobic cavity useful in the present invention include for example cyclodextrin or cyclodextrin derivatives; cyclic oligosaccharides having a hydrophobic cavity such as cycloinulohexose, cycloinuloheptose, or cycloinulooctose; calyxarenes; cavitands; or combinations thereof. Preferably, the macromolecular organic compound is ß-cyclodextrin, more preferably methyl-ß-cyclodextrin.

Monomers having low water solubility include for example primary alkenes; styrene and alkylsubstituted styrene; α-methyl styrene; vinyltoluene; vinyl esters of C_4 to C_{30} carboxylic acids, such as vinyl 2-ethylhexanoate, vinyl neodecanoate; vinyl chloride; vinylidene chloride; N-alkyl substituted (meth)acrylamide such as octyl acrylamide and maleic acid amide; vinyl alkyl or aryl ethers with (C_3 -C_{30}) alkyl groups such as stearyl vinyl ether; (C_1 -C_{30}) alkyl esters of (meth)acrylic acid, such as methyl methacrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate; unsaturated vinyl esters of (meth)acrylic acid such as those derived from fatty acids and fatty alcohols; multifunctional monomers such as pentaerythritol triacrylate; monomers derived from cholesterol or combinations thereof.

In another aspect of the present invention an aqueous copolymer composition is provided that is preferably produced by the method of the present invention as previously described herein. The aqueous copolymer composition contains water insoluble particles of graft copolymer that are preferably comb copolymer particles. The comb copolymer particles preferably have a weight average particle size of from about 50 nm to about 500 nm, and more preferably from about 80 nm to about 200 nm.

Preferably, the particles of graft copolymer contain from about 2 weight percent to about 90 weight percent, and more preferably from about 5 weight percent to about 50 weight percent polymerized units of a macromonomer, based on the total weight of the copolymer, where the macromonomer preferably has a composition as previously described herein for the water insoluble macromonomer present in the macromonomer aqueous emulsion. The graft copolymer particles also preferably contain from about 10 weight percent to about 98 weight percent, and more preferably from about 50 weight percent to about 95 weight percent polymerized units of at least one ethylenically unsaturated monomer, based on the total weight of the copolymer. The ethylenically unsaturated monomer may be any ethylenically unsaturated monomer that provides desirable properties in the copolymer particles, such as those useful in the monomer composition as previously described herein.

Preferably, the backbone of the graft copolymer is linear. Compositionally, the backbone of the copolymer preferably contains polymerized units of the ethylenically unsaturated monomer derived from the monomer composition. Preferably, the backbone contains less than 20 mole percent, and more preferably less than 10 mole percent of polymerized macromonomer derived from the macromonomer aqueous emulsion based on the total moles of the copolymer.

The side chains of the graft copolymer preferably contain polymerized units of the macromonomer. In a preferred embodiment of the present invention, each side chain comprises one macromonomer. Additionally, the side chains contain less than 5 weight percent and more preferably less than 1 weight percent of the polymerized ethylenically unsaturated monomer derived from the monomer composition, based on the total weight of the side chains.

Preferably, the overall weight average molecular weight of the graft copolymer is from about 50,000 to about 2,000,000, and more preferably from about 100,000 to about 1,000,000.

In a preferred embodiment of the present invention, the water insoluble copolymer particles further contain from about 0.2 weight percent to about 10 weight percent, more preferably from about 0.5 weight percent to about 5 weight percent, and most preferably from about 1 weight percent to about 2 weight percent of an acid containing macromonomer, based on the total weight of the graft copolymer. The acid containing macromonomer preferably has a composition as previously described herein.

Although in no way intending to be bound by theory, it is believed that the acid containing macromonomer is attached to the surface of the water insoluble graft copolymer particles and provides stability. By "attached," as used herein, it is believed that the acid containing macromonomer is bound in some manner (e.g., covalent, hydrogen bonding, ionic) to a polymer chain in the particle. Preferably, the acid containing macromonomer is covalently bound to a polymer chain in the particle. It has been found that the acid containing macromonomer provides stability to the particles such that the aqueous copolymer composition produced exhibits unexpected improved shear stability; freeze thaw stability; and stability to additives in formulations, as well as reduction of coagulums during the polymerization. Although improved stability can be achieved using acid containing monomer, these benefits are most dramatic when an acid containing macromonomer is used.

The aqueous copolymer composition in addition to the copolymer particles preferably contains less than about 10 weight percent, and more preferably less than about 1 weight percent of organic solvent. In a most preferred embodiment, the aqueous copolymer composition contains no organic solvent.

An advantage of using the method of the present invention to prepare the aqueous copolymer composition is that the resulting copolymer composition contains low levels of homopolymer, such as for example homopolymer of ethylenically unsaturated monomer derived from the monomer composition or homopolymer of macromonomer derived from the macromonomer aqueous emulsion. Preferably the aqueous copolymer composition contains less than about 30 weight percent and more preferably less than about 20 weight percent of homopolymer of macromonomer, based on the total weight of the graft copolymer. Preferably also the aqueous copolymer composition contains less than about 30 weight percent and more preferably less than about 20 weight percent of homopolymer of ethylenically unsaturated monomer.

The aqueous copolymer compositions produced by the method of the present invention are useful in a variety of applications. For example, the aqueous copolymer compositions may be used in architectural and industrial coatings including paints, wood coatings, or inks; paper coatings; textile and nonwoven binders and finishes; adhesives; mastics; floor polishes; leather coatings; plastics; plastic additives; petroleum additives; thermoplastic elastomers or combinations thereof.

EXAMPLES

Some embodiments of the invention will now be described in detail in the following Examples. The following abbreviations shown in Table 1 are used in the examples:

Table 1: Abbreviations

Abbreviation	
A-16-22	Polystep A-16-22, anionic surfactant, supplied as 22% solids by Stepan Company, located in Northfield, Illinois.
BA	Butyl acrylate
BD	Butadiene
BMA	Butyl methacrylate
CoBF	Co(II)-(2,3-dioxyiminobutane-BF_2)$_2$
CVA	4,4-azobis(4-cyanovaleric acid)
Fe	0.15% Ferrous sulfate in water
DBS	Dodecyl benzene sulfonate
GC	Gas chromatograph
SEC	Size exclusion chromatography
HPLC	High performance liquid chromatography
Init.	Initiator
IR	Infrared spectroscopy
LCCC	Liquid chromatography under critical conditions
MAA	Methacrylic acid
MMA	Methyl methacrylate
Mn	Number average molecular weight
NaMBS	Sodium metabisulfite
NaPS	Sodium persulfate
nDDM	Dodecyl mercaptan
OT-100	Aerosol OT-100, anionic surfactant, supplied as 100% active by Cytec Industries Inc., located in Morristown, New Jersey.
PMAA-MM	Poly-methacrylic acid macromonomer
PMMA	Methyl methacrylate homopolymer
PMMA-MM	Poly-methyl methacrylate macromonomer
Poly-(BA-g-BMA)	Graft copolymer of BA with BMA side chains
Poly-(BA-g-MMA)	Graft copolymer of BA with MMA side chains
Poly-(BD-g-MMA)	Graft copolymer of BD with MMA side chains
Wako VA-044	2,2'-azobis[2-(2-imidazolin2-2yl)propane] dihydrochloride

In the Examples, monomer conversion was determined by GC analysis of unreacted monomer using standard methods. Weight percent solids for the macromonomer and copolymer compositions were determined by gravimetric analysis. Particle size of the macromonomer and copolymer compositions were obtained using a Matec CHDF 2000 particle size analyzer equipped with a HPLC type Ultra-violet detector.

Except where noted differently, macromonomer was measured for number average molecular weight by SEC using a polystyrene standard from Polymer Laboratories (PS-1) having a peak average molecular weight ranging from 580 to 7.500,000 with narrow molecular weight distribution. Conversions from polystyrene to PMMA were made using Mark-Houwink constants. Copolymer compositions were evaluated for number average molecular weight and weight average molecular weight using SEC as described above.

Comparative Example 1.0

Low molecular weight MMA polymer was prepared by an aqueous emulsion polymerization process using a conventional chain transfer agent. The polymerization was conducted in a 2-liter, four neck round bottom reaction flask equipped with a mechanical stirrer, temperature control device, condenser, monomer feed line and a nitrogen inlet according to the following procedure. To the reaction flask were added 483.7 grams of deionized water, 2.0 grams of A-16-22, and 1.55 grams of an aqueous solution containing 52 wt% methyl-ß-cyclodextrin to form a surfactant solution. A monomer emulsion containing 125g of deionized water, 3g of A-16-22, 305g of MMA and 5g of nDDM was prepared separately. Additionally, an initiator solution was prepared by dissolving 1.56g of NaBS in 72.3 g of deionized water. The surfactant solution was heated to 80°C after which 60% of the total initiator solution was added to the reaction flask. The monomer emulsion and the remaining initiator solution were then fed over a period of 60 minutes. At the end of the feed period, the reaction mixture was maintained at 80°C for an additional 30 minutes, followed by cooling and filtering. The resulting low molecular weight MMA emulsion contained 31.0 wt% solids. The MMA polymer had a number average molecular weight (Mn) of 21700.

Examples 1.1 to 1.8 – Preparation of PMMA-MM by Emulsion Polymerization

MMA macromonomer (PMMA-MM) was prepared by emulsion polymerization processes in Examples 1.1 to 1.8 using the same equipment described in Comparative Example 1.0. The specific amounts of water, surfactant, MMA, chain transfer agent (CTA), and initiator used in Examples 1.1 to 1.8 are shown in Table 2. These ingredients were added according to the following procedure. In a different flask from the reaction flask, a monomer solution was prepared by dissolving the chain transfer agent in MMA under a nitrogen purge. Deionized water and surfactant (OT-100) were introduced into the reaction flask at room temperature to form a water surfactant solution. The water surfactant solution was mixed and heated to 80°C with stirring under a nitrogen purge. Upon reaching a temperature of 80°C, and upon complete dissolution of the surfactant, the initiator (CVA) was added to the water surfactant solution with stirring for 1 minute to permit the initiator to dissolve. After dissolution of the initiator, 20 percent by weight of the monomer solution was added to the reaction flask with stirring. Following this initial charge, the remaining monomer solution was fed over a period of 1 to 2 hours, with stirring, to form a reaction mixture. At the end of the feed period, the reaction mixture was maintained at 80°C for an additional 1 to 3 hours. The reaction mixture was then cooled to room temperature and passed through a filter cloth to remove any coagulum.

Generally, the resulting macromonomer emulsion contained less than 5 weight percent coagulum based on the total weight of macromonomer, and the conversion of monomer was over 99 weight percent, based on the total weight of monomer added. The Mn, weight percent solids and particle size for each macromonomer are reported in Table 2.

Table 2: Preparation of PMMA-MM

Example	H_2O (g)	Surfactant (g)[3]	MMA (g)	CTA ppm[1]	Initiator (g)[2]	Part. Size (nm)	Mn	Wt % Solids
1.1	720	3.6	324	40	3.6	165	2430	32.0
1.2	720	3.6	324	8.7	3.6	126	12612	31.0
1.3	720	3.6	324	10.9	3.6	158	9656	31.0
1.4	720	3.6	324	80.6	3.6	231	1386	30.3
1.5	720	3.6	324	21.8	3.6	201	4416	29.1
1.6	720	3.6	324	10.7	3.6	169	7931	30.5
1.7	720	3.6	360	11.9	3.6	155	10185	32.0
1.8	1440	7.2	720	15.2	7.2	167	7237	32.0

[1] ppm moles of chain transfer agent (CoBF) based on total moles of monomer.

[2] CVA, supplied by Aldrich as a 75 weight percent aqueous solution of initiator.

[3] OT-100.

Example 2: Preparation of PMAA-MM By Solution Polymerization

An MAA macromonomer (PMAA-MM) was prepared by an aqueous solution polymerization process in a 2-liter baffled flange flask equipped with a mechanical stirrer, condenser, temperature control device, initiator feed lines and a nitrogen inlet. The apparatus was purged with nitrogen for 30 minutes after 0.018 g of CoBF was added. Deionized water, 1080 g, was charged to the flask and heated to 55°C under a nitrogen purge. A monomer mixture containing 510 ml of MAA and 0.01 g of CoBF was prepared separately under nitrogen. When the deionized water reached a temperature of 55°C, 1.94 g of initiator (Wako VA-044) was added to the reaction flask. Following the addition of the initiator, the monomer mixture was added over a period of 60 minutes to the reaction flask with stirring. The temperature was then held at 55°C for 2 hours following completion of the monomer mixture feed. Upon cooling the reaction flask to room temperature, the MAA-MM (Example 2.1) was isolated as dried polymer by rotary evaporation. The number average molecular weight (Mn) of the MAA-MM was determined by proton nuclear magnetic resonance to be 4030 based on the integration of the vinyl end group with respect to the methyl and methylene groups of the polymer chain.

Example 3: Preparation of Poly-(BA-g-MMA) Graft Copolymers by Batch Emulsion Polymerization Process

Comparative Example 3.0C and Examples 3.1 to 3.15 graft copolymers were prepared by a batch emulsion polymerization process in a 1-liter, four neck round bottom reaction flask equipped with a mechanical stirrer, condenser, temperature control device, initiator feed lines and a nitrogen inlet. The specific amounts of PMMA-MM (as emulsion), water, surfactant, acid containing monomer (marked "acid" in Table 3), BA, initiator, and buffer used are shown in Table 3. These ingredients were added according to the following procedure. Deionized water (H_2O #1 in Table 3) and PMMA-MM emulsion obtained from the example indicated in Table 3 (sub-column marked "Ex" under the "PMMA-MM" column) were introduced into the reaction flask at room temperature. A monomer emulsion of deionized water (H_2O #2 in Table 3), surfactant, acid containing monomer, and BA was prepared. The monomer emulsion in Example 3.13 additionally contained 0.13 g of nDDM. The monomer emulsion was introduced into the reaction flask at room temperature with stirring to form a reaction mixture. After stirring for 20 minutes, the reaction mixture was heated to the reaction temperature indicated in Table 3.

Once the reaction temperature was reached, an initiator and optionally a buffer were introduced into the reaction flask with stirring according to the following procedures. For examples 3.1C; 3.2; 3.3 and 3.4 to 3.8, both the buffer and initiator listed in Table 3 were added as a single shot to the reaction flask. For examples 3.9 to 3.12 and 3.16, 20% by weight of the initiator solution was added in one shot to the reaction flask, with the remainder being fed over 1 to 2 hours. For the examples prepared with a redox initiator (3.13 to 3.15), one third of the NaPS and NaMBS were added in one shot to the reaction flask, with the remainder fed over 1 to 2 hours. Also, for the redox initiator system, all of the Fe and Na_2CO_3 were added to the reaction flask at the beginning of the NaPS and NaMBS feeds. After the initiator and buffer were added, the reaction mixture was maintained at the reaction temperature for a period of 1 to 2 hours. The resulting copolymer composition was analyzed for conversion and other properties as described in Example 10. The conversion of BA, as determined by standard GC methods, was greater than 99 weight percent based on the total weight of BA charged.

Table 3: Preparation of Poly-(BA-g-MMA) Graft Copolymers Prepared by Batch Process

Example	PMMA-MM		H_2O #1 (g)	H_2O #2 (g)	Surf.(2) (g)	BA (g)	Temp. (°C)	Init. (g)	Buffer(9) (g)	Acid (g)
	Ex	Amt. (g)								
3.1C(8)	1.0	146.7	22	25	2.2	82.6	90	0.09(5)	0.1	1.96(7)
3.2	1.4	100	14	20.8	0.49	55.7	70	0.63(3)	0	0
3.3	1.3	97	17	20.8	0.49	55.7	70	0.63(3)	0	0
3.4	1.1	50.8	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.5	1.5	52	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.6	1.6	53.3	0	20.3	1.1	47.8	80	0.07(5)	0.04	0.98(7)
3.7	1.3	52.4	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.8	1.2	52	0	19	1.1	47.8	80	0.07(5)	0.05	0.98(7)
3.9	1.3	216	59	46.8	1.1	123.8	80	1.05(5)	0	2.3(6)
3.10	1.3	84	77	39	0.91	103	80	0.07(5)	0	1.3(6)
3.11	1.3	42	42	102	1.02	115	80	0.07(5)	0	1.3(6)
3.12	1.3	21	112	46.3	1.08	122.5	80	0.07(5)	0	1.3(6)
3.13	1.8	71	0	20	1.1	41.3(1)	90	Redox(4)	0.05	0.98(7)
3.14	1.8	71.1	0	14	1.1	41.3	70	Redox(4)	0.05	0.98(7)
3.15	1.8	71.1	0	14	1.1	41.3	95	Redox(4)	0.05	0.98(7)
3.16	1.3	72.8	17	15.6	0.37	41.3	80	0.35(5)	0	0.75(6)

(1) 0.13 g nDDM was added to the monomer emulsion.

(2) Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water), except for Example 3.12 which was prepared with A-16-22 .

(3) Lupersol 11 supplied by Elf Atochem.

(4) Redox initiator system contained 0.07g NaPS in 3g water; 0.06g NaMBS in 3g water; and 0.7g Fe.

(5) NaPS dissolved in 5-20 g of water.

(6) MAA

(7) PMAA-MM (prepared by method of Example 2.1)

(8) Comparative prepared with PMMA having no terminal ethylenically unsaturated groups.

(9) Sodium carbonate dissolved in 5g of water.

Example 4: Preparation of Poly-(BA-g-MMA) by Semi-continuous Process

In Examples 4.1 to 4.5, graft copolymers were prepared by a semi-continuous emulsion polymerization process in a 1-liter round bottom flask with four neck equipped with a mechanical stirrer, temperature control device, initiator feed lines and a nitrogen inlet. The specific amounts of PMMA-MM (as emulsion), water, surfactant, BA, acid containing monomer, and initiator used in Examples 4.1 to 4.4 are shown in Table 4. These ingredients were added according to the following procedure. A monomer emulsion of deionized water (H_2O #2 in Table 4), surfactant, and BA was prepared in a separate flask. The monomer emulsion in Example 4.2 additionally contained 0.13 g of nDDM. Deionized water (H_2O #1 in Table 4), acid containing monomer, and PMMA-MM obtained from the example indicated in Table 4 (sub-column marked "Ex" under the "PMMA-MM" column) were introduced into the reaction flask at room temperature to form a reaction mixture. The reaction mixture was heated to the reaction temperature indicated in Table 4 while stirring under a nitrogen purge. Upon reaching the reaction temperature, an initiator and buffer (if desired) were introduced into the reaction flask with stirring according to the following procedures. For examples 4.1 to 4.3 (prepared with a redox initiator), one third of the NaPS and NaMBS, and all of the Fe and Na_2CO_3 were added in one shot to the reaction flask. The remaining NaPS and NaMBS was then cofed with the monomer emulsion over a 90 minute period. In Example 4.4, one third of the NaPS, and all of the Na_2CO_3 were added in one shot to the reaction flask, followed by cofeeding the monomer emulsion with the remaining NaPS over a 90 minute period. Upon completion of the feeds, the reaction mixture was maintained at the reaction temperature for a period of 1 to 2 hours. The resulting copolymer composition was analyzed for conversion and other properties as described in Example 10. The conversion of BA, determined by standard GC methods, was greater than 99 weight percent based on the total weight of BA charged.

Table 4: Preparation of Poly-(BA-g-MMA) Prepared by Semi-Continuous Process

Example	PMMA-MM		H_2O #1 (g)	H_2O #2 (g)	Surf.[2] (g)	BA (g)	Temp. (°C)	Init. (g)	Buffer[5] (g)	Acid (g) [6]
	Ex	Amt. (g)								
4.1	1.7	69.4	12	23	1.1	41.3	90	Redox[3]	0.05	0.98
4.2	1.8	71	10.0	10	1.1	41.3[1]	90	Redox[3]	0.11	0.98
4.3	1.8	71	10.0	10	1.1	41.3	90	Redox[3]	0.11	0.98
4.4	1.8	71	10.3	18	1.1	41.3	90	0.16 [4]	0.11	0.98

[1] 0.13 g nDDM was added to the monomer emulsion.

[2] Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water).

[3] Redox initiator system include 0.16g NaPS in 6g water; 0.14g NaMBS in 6g water; and 0.7g Fe.

[4] NaPS dissolved in 10g of water.

[5] Sodium carbonate dissolved in 3g of water.

[6] PMAA-MM (prepared by method of Example 2.1)

Example 5: Preparation of Poly-(BD-g-MMA) graft copolymers

A graft copolymer having a backbone of BD and side chains of MMA was prepared in accordance with the method of the present invention. The graft copolymer was prepared in two stages. In the first stage, PMMA-MM was prepared in accordance with the procedure used in Example 1. except that the following amounts of ingredients shown in Table 5a were used to replace the corresponding ingredients in Table 2:

Table 5a: Ingredients used in Preparation of BMA Macromonomer

Ingredient	Amount Charged
H_2O	2380 g
Surfactant (A-16-22)	55 g
MMA	1197 g
CoBF	10.9 ppm[1]
Initiator (CVA)	12.6 g

[1] Based on total moles of MMA monomer.

The resulting PMMA-MM had an Mn of 10,200.

In the second stage, a graft poly-(BD-g-MMA) was prepared in a steel pressure reactor equipped with a mechanical stirrer, temperature control device, and feed lines. Ingredients A through D, shown in Table 5b, were charged to the reactor at room temperature. The reactor was then sealed and vacuum was applied, with stirring, to reduce the reactor pressure to 15 inches of Hg. Butadiene (E) in Table 5b was quickly pumped into the reactor and stirred for

10 minutes. Following stirring the reaction mixture was heated to 60°C for 30 minutes. After the reactor temperature stabilized to 60°C, ingredients F, G, and H in Table 5b were gradually pumped into the reactor over a period of 7 hours. Following completion of the feeds, the reaction mixture was held for 60 minutes at 60 °C.

Table 5b: Ingredients used in Preparation of Poly-(BD-g-MMA) Graft Copolymer

	Ingredient	**Amount Charged**
A	H_2O #1	6049.4 g
B	Acetic acid	4.3 g
C	PMMA-MM (as emulsion)	1389.71 g (Example 5a)
D	H_2O #2 (use for rinsing)	250 g
E	BD	877.5 g
F	t-butyl peroxide (2% solution)	197.44 g
G	SFS(1) (1% solution)	263.25 g
H	Aerosol-OT (75% solution)	3.51 g

(1) Sodium formaldehyde sulfoxylate

^1H NMR analysis of the graft copolymer in tetrahydrofuran showed a weight percent ratio of BD to MMA of 65.2 to 34.8. Analysis of the unreacted PMMA-MM by HPLC showed an incorporation of PMMA-MM of about 44 wt% based on the total weight of PMMA-MM added. HPLC showed a predominant BD/MMA graft copolymer peak (verified by IR). Differential scanning calorimetry showed two phase transitions at -79.8° and 110.4°C, respectively. The graft copolymer composition had a solids content of 15 wt% and weight average particle size of 107 nm.

Example 6: Preparation of Poly-(BA-g-BMA) Graft Copolymer

A graft copolymer having a backbone of BA and side chains of BMA was prepared in accordance with the method of the present invention. The graft copolymer was prepared in two stages. In the first stage, butyl methacrylate macromonomer was prepared in accordance with the procedure used in Example 1, except that the following amounts of ingredients shown in Table 6a were used to replace the corresponding ingredients in Table 2:

Table 6a: Ingredients used in Preparation of BMA Macromonomer

Ingredient	Amount Charged
H_2O	720 g
Surfactant (Aerosol OT-100)	3.6 g
BMA	324 g
CoBF	10.9 ppm(1)
Initiator (CVA)	3.6 g

(1) Based on total moles of BMA monomer

The resulting BMA macromonomer had an Mn of 8900.

In the second stage, a graft poly-(BA-g-BMA) was prepared using the procedure described in Example 3, except that the following amounts of ingredients shown in Table 6b were used to replace the corresponding ingredients in Table 3, and a reaction temperature of 85°C was used.

Table 6b: Ingredients used in Preparation of Poly-(BA-g-BMA) Graft Copolymer

Ingredient	Amount Charged
PBMA-MM (as emulsion)	84.1 g (Example 6a)
H_2O #2	15 g
Surfactant(2)	1.1 g
BA	41.3 g
Initiator	Redox(1)
Acid (PMAA-MM)	0.98 g (Example 2.1)

(1) Redox initiator system was 0.07g NaPS in 3g water; 0.06g NaMBS in 3g water; 0.05g Na_2CO_3 in 3g water and 0.7g Fe.

(2) Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water).

The graft copolymer formed contained 63.5 weight percent BA, 35 weight percent of PBMA-MM and 1.5 weight percent of PMAA-MM.

Example 7: Preparation of Poly-(Styrene-g-MMA) Graft Copolymer

A graft copolymer having a backbone of styrene and side chains of PMMA-MM was prepared in accordance with the method of the present invention. The graft copolymer was prepared in two stages. Macromonomer PMMA-MM (obtained from Example 1.8) was used in the synthesis of the graft Poly-(Styrene-g-MMA). The graft Poly-(Styrene-g-MMA) was prepared using the procedure described in Example 3 except that the following amounts of ingredients shown in Table 7 were used to replace the corresponding ingredients in Table 3, and a reaction temperature of 85°C was used.

Table 7: Ingredients used in Preparation of Poly-(Styrene-g-MMA) Graft Copolymer

Ingredient	Amount Charged
PMMA-MM (as emulsion)	84.1 g (Example 1.8)
H_2O #2	15 g
Surfactant(2)	1.1 g
Styrene	41.3 g
Initiator	Redox(1)
Acid (pMAA-MM)	0.98 g (Example 2.1)

(1) Redox initiator system include 0.07g NaPS in 3g water; 0.06g NaMBS in 3g water; 0.05g Na_2CO_3 in 3g water and 0.7g Fe.

(2) Ethoxylated C_6 to C_{18} alkyl ether sulfate having from 1 to 40 ethylene oxide groups per molecule (30% active in water).

The graft copolymer formed contained 63.5 weight percent styrene, 35 weight percent of PMMA-MM and 1.5 weight percent of PMAA-MM.

Example 8: Preparation of Poly-(BA-g-MMA) by a Single Vessel Synthesis Procedure

A graft copolymer having a backbone of BA and side chains of MMA was prepared in accordance with the method of the present invention in a single vessel in two aqueous emulsion polymerization stages. In the first stage, PMMA-MM was prepared and in the second stage the PMMA-MM was copolymerized with BA.

The PMMA-MM was prepared in a four neck, 5-liter round bottom reaction flask equipped with a mechanical stirrer, temperature control device, condenser, monomer feed line and a nitrogen inlet. The reaction flask was charged with 680 g of deionized water and 15.7 g of A-16-22 to form a water surfactant solution. The water surfactant solution was heated with stirring to 80°C under a nitrogen purge. At 80°C, 3.6 g of 4,4-azobis(4-cyanovaleric acid) was added with stirring to the reaction flask. Two minutes later, 18 g of MMA was added to the reaction flask with stirring. A monomer mixture containing 342 g of MMA and 0.02 g of CoBF was prepared separately and degassed by bubbling nitrogen in the monomer mixture for 20 minutes. A 20% by weight portion of the monomer mixture was added to the reaction flask 10 minutes after adding the 18 g of MMA. The remainder of the monomer mixture was fed over 120 minutes with stirring while maintaining the temperature at 80°C. At the end of the monomer mixture feed, the temperature of the reaction mixture in the flask was kept at 80°C for 60 minutes and then cooled to 40°C. The resulting macromonomer aqueous emulsion was reacted in the same vessel in a second stage as described below.

In the second stage, a monomer emulsion containing 226 g of deionized water, 16.52 g of an ethoxylated C_6 to C_{18} alkyl ether sulfate (30 wt% active) having from 1 to 40 ethylene oxide groups per molecule (30% active in water), 658 g of butyl acrylate was prepared. In addition, 10.2 g of PMAA-MM, in 75.4 g of water was prepared separately. The monomer emulsion and the PMAA-MM solution were added to the reaction flask at 40°C, and the resulting reaction mixture was stirred for 20 minutes, followed by heating to 85°C. At 85°C, 1.06 g of sodium persulfate dissolved in 25 g of water and 0.47 g of sodium carbonate dissolved in 25 g of were added to the reaction flask in a single shot, followed with 20 g of deionized water rinse. Following the charges of initiator and buffer, the reaction mixture was maintained with stirring at 85°C for 60 minutes. After cooling the reaction mixture to 40°C, 13.72 g of a 0.15% solution of $FeSO_4$ in water was added with stirring, followed by additions of t-butyl peroxide and isoascorbic acid (0.70 g and 0.34 g each in 15 g of water, respectively). A second addition of t-butyl peroxide and isoascorbic acid in the same amounts were added 15 minutes after the first one. The reaction mixture was held with stirring for 30 minutes at a temperature of 40°C.

The resulting copolymer composition was cooled to room temperature and passed through a filter cloth to remove any coagulum. The resulting graft copolymer contained 64 weight percent of butyl acrylate, 35 weight percent of methyl methacrylate and 1 weight percent of PMAA-MM. The copolymer composition had an incorporation of PMMA-MM of 76 weight percent based on the total weight of PMMA-MM charged.

Example 9: Characterization of Copolymer Compositions

Graft copolymer compositions prepared in the previous examples were characterized by various analytical techniques to determine wt% solids, particle size, weight average molecular weight, number average molecular weight, and percent incorporation of macromonomer.

Determination of the amount of unreacted macromonomer was carried out by HPLC analysis using the following procedure. The copolymer compositions were dissolved in THF and analyzed by gradient elution on an LC-18 column supplied by Supelco, located in

Belletonte, PA such that a well-isolated peak was observed for the unreacted macromonomer. Quantification was carried out by calibrating the detector response using known standards of the same macromonomer employed in the synthesis. The results of the characterization are reported in Table 8 below.

Table 8: Characterization Of Copolymer Compositions

Example	% Solids	Particle Size (nm)	Mw (x 10^{-3})	Mn (x 10^{-3})	PMMA-MM Incorp. (2) (wt%)
3.1C	43	120	(1)	(1)	<2
3.2	43.1	268	119.7	88.6	89
3.3	41.0	204	286.0	29.0	---
3.4	49.3	245	398.1	217.7	90
3.5	50.2	215	708.2	378.3	86
3.6	51.5	228	1015.0	266.9	68
3.7	48.1	226	1242.6	809.6	74
3.8	47.5	215	1082.6	827.4	71
3.9	42.2	180	724.9	114.2	---
3.10	41.3	203	1468.9	875.5	---
3.11	39.6	208	1263.8	964.0	---
3.12	39.7	227	1226.1	813.1	---
3.13	43.5	232	226.1	88.8	83
3.14	44.6	208	795.8	182.0	75
3.15	44.4	220	437.1	160.3	88
3.16	41.4	194	216.1	139.3	71
4.1	34	222	533.3	66.6	86
4.2	43.5	210	264.5	67.3	91
4.3	42.3	181	664.8	83.2	94
4.4	42.8	168	857.9	72.1	94
6.1	39.3	192	552.0	328.0	--
7.1	33.1	161	98.7	20.7	60
8.1	44	150	1041.6	146.9	76

(1) Bimodal molecular weight distribution with the lower molecular weight corresponding to the molecular weight of the macromonomer, indicating that the polymer prepared according to Example 1.0C did not copolymerize.

(2) Based on the total weight of macromonomer added to reaction vessel. Some of the samples (Example 3.3, 3.9, 3.10, 3.11, 3.12, 6.1) were not analyzed for PMMA-MM incorporation.

Example 10: Analysis of Example 3.16

A two-dimensional HPLC analysis was carried out on Example 3.16 to determine the average number of grafts per polymer molecule and to show that a graft copolymer is formed.

Two-dimensional HPLC provides much greater resolution compared to conventional HPLC for the separation of complex polymer materials. The method used in this analysis was similar to that described in "2D Chromatographic Analysis Of Graft Copolymers Obtained By Copolymerization Of Macromonomers Via Conventional, Controlled Radical, And Anionic Polymerizations" by Müller, Axel H. E et al., Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 40(2), pages 140-141, 1999, which is hereby incorporated by reference in its entirety. LCCC was used in one dimension and GPC was used in the second dimension; cuts from the first analysis were sequentially analyzed by the second technique, and appropriate software constructed a plot of the data in two dimensions. The LCCC analysis was run under critical conditions for PBA, and size exclusion conditions for PMMA so that the total molecular weight of the MMA grafts on the copolymer could be determined. From this value, (assuming each side chain contained one macromonomer) the number of side chains per copolymer was calculated. Also, LCCC was used to determine the composition of the copolymer. The analysis in the second dimension using SEC was used to estimate the total molecular weights of the copolymer. The molecular weights measured were calibrated using standards of PMMA for the LCCC dimension and PBA for the GPC dimension. The resulting two-dimensional chromatogram showed a major copolymer peak (roughly estimated at >70%) which, from the LCCC data, contained a total PMMA molecular weight (Mn) of about 110,000. Using the Mn value of 9600 for the PMMA macromonomer, an average number of grafts per polymer chain was estimated at about 11.5. From the second dimension the overall molecular weight of this peak was estimated to be 580,000. The two-dimensional chromatogram showed two other series of copolymer peaks, but no PBA homopolymer was detected. The overall composition of the major copolymer peak calculated from the two-dimensional HPLC data was about 85wt% BA and 15wt% MMA. This composition varies from the expected composition of 72wt% BA and 28wt% MMA (calculated from an NMR analysis of the composition, taking into account that only about 70% of the macromonomer was converted to copolymer), but is reasonable considering the complexity of the copolymer system and the analysis of it.

Example 11: Evaluation Of Shear Stability Of Graft Copolymer Compositions

Shear stability tests were carried out on several graft copolymer compositions made in the previous examples. Shear stability was tested by placing a drop of the graft copolymer composition on the index finger and rubbing the composition between the thumb and index finger. A copolymer composition passed if it could be rubbed until it dried by water evaporation without the formation of coagulum, and failed if it flocculated after a few rubs and became ropy. All of the copolymer compositions tested were stable colloidally under static conditions. The results are reported in Table 9 below.

Table 9: Finger Rub Test Results for Graft Copolymer Compositions

Example	Stabilized acid	Finger Rub Test
3.4	pMAA-MM	Pass
3.5	pMAA-MM	Pass
3.6	pMAA-MM	Pass
3.7	pMAA-MM	Pass
3.8	pMAA-MM	Pass
3.9	MAA	Fail
3.10	MAA	Fail
3.11	MAA	Fail
3.12	MAA	Fail
4.1	pMAA-MM	Pass
4.2	pMAA-MM	Pass
4.3	pMAA-MM	Pass
4.4	pMAA-MM	Pass
8.1	pMAA-MM	Pass

The data in Table 9 shows that graft copolymer compositions prepared with an acid containing macromonomer had surprisingly good shear stability in comparison to graft copolymer prepared with an acid monomer. It was also discovered that good shear stability could be obtained, without the use of an acid containing macromonomer, such as by adding a surfactant such as Triton™ X-405, a nonionic surfactant supplied by Union Carbide, to the copolymer composition.

What is claimed is:

1. A method of making a graft copolymer comprising:

(a) forming a macromonomer aqueous emulsion comprising one or more water-insoluble particles of macromonomer, wherein the macromonomer comprises polymerized units of a first ethylenically unsaturated monomer, the macromonomer further having

(i) a degree of polymerization of from 10 to 1000,

(ii) at least one terminal ethylenically unsaturated group,

(iii) less than 5 weight percent polymerized acid-containing monomer, and

(iv) less than one mole percent of polymerized mercaptan-olefin compounds;

(b) forming a monomer composition comprising at least one second ethylenically unsaturated monomer; and

(c) combining at least a portion of the macromonomer aqueous emulsion and at least a portion of the monomer composition to form a polymerization reaction mixture and polymerizing the macromonomer with the second ethylenically unsaturated monomer in the presence of an initiator to produce a copolymer composition comprising graft copolymer particles.

2. The method of Claim 1 wherein the step of forming the macromonomer aqueous emulsion comprises polymerizing in an aqueous emulsion the at least first ethylenically unsaturated monomer in the presence of a transition metal chelate chain transfer agent and a free radical initiator to form the macromonomer particles.

3. The method of Claim 2 wherein the first ethylenically unsaturated monomer is polymerized in the presence of a macromolecular organic compound having a hydrophobic cavity.

4. The method of Claim 1 wherein the monomer composition comprises an aqueous emulsion comprising the at least one second ethylenically unsaturated monomer.

5. The method of Claim 1 wherein the second ethylenically unsaturated monomer diffuses into the macromonomer particles and swells the macromonomer particles.

6. The method of Claim 1 wherein the macromonomer comprises as polymerized units less than 1 weight percent of acid containing monomer.

7. The method of Claim 1 wherein the first ethylenically unsaturated monomer is an α–methyl vinyl monomer, a non α-methyl vinyl monomer terminated with a α-methyl vinyl monomer, or combinations thereof.

8. The method of Claim 7 wherein the first ethylenically unsaturated monomer is methyl methacrylate, ethyl methacrylate, 2-ethylhexyl methacrylate, isobornyl methacrylate, butyl methacrylate, lauryl methacrylate, stearyl methacrylate, styrene terminated by α-methyl styrene, or combinations thereof.

9. The method of Claim 1 wherein the second ethylenically unsaturated monomer is selected from the group consisting of acrylate esters; methacrylate esters; styrene; substituted styrenes; olefinically unsaturated nitriles; olefinically unsaturated halides; vinyl esters of organic acids; N-vinyl compounds; acrylamide; methacrylamide; substituted acrylamides; substituted methacrylamides; hydroxyalkylmethacrylates; hydroxyalkylacrylates; vinyl ethers; dienes and combinations thereof.

10. The method of Claim 9 wherein the second ethylenically unsaturated monomer is selected from the group consisting of C_1 to C_{18} alkyl acrylate, styrene, butadiene, and combinations thereof.

11. The method of Claim 1 wherein the macromonomer and the second ethylenically unsaturated monomer are polymerized in the presence of an acid containing monomer, acid containing macromonomer, or combinations thereof.

12. The method of Claim 11 wherein the macromonomer and the second ethylenically unsaturated monomer are polymerized in the presence of an acid containing macromonomer, the acid containing macromonomer comprising as polymerized units from 50 weight percent to 100 weight percent of an acid containing monomer, based on the total weight of the acid containing macromonomer.

13. The method of Claim 1 wherein the macromonomer and ethylenically unsaturated monomer are polymerized in the presence of a macromolecular organic compound having a hydrophobic cavity.

14. The method of Claim 1 wherein all the macromonomer aqueous emulsion and all the monomer composition are combined prior to beginning the polymerization.

15. The method of Claim 1 wherein the macromonomer and the second ethylenically unsaturated monomer are combined by gradually feeding at least a portion of the monomer composition into the macromonomer aqueous emulsion in the presence of the initiator.

16. A graft copolymer produced by the process of claim 1.

17. A copolymer composition comprising water insoluble graft copolymer particles, wherein the graft copolymer particles comprise:

(a) from 2 weight percent to 90 weight percent of macromonomer, based on the total weight of the copolymer, wherein the macromonomer is water insoluble and comprises from 10 to 1000 polymerized units of at least one first ethylenically unsaturated monomer, less than 1 mole percent of polymerized mercapto-olefin compounds, and less than 5 weight percent polymerized acid-containing monomer; and

(b) from 10 weight percent to 98 weight percent of polymerized units of at least one second ethylenically unsaturated monomer, based on the total weight of the copolymer.

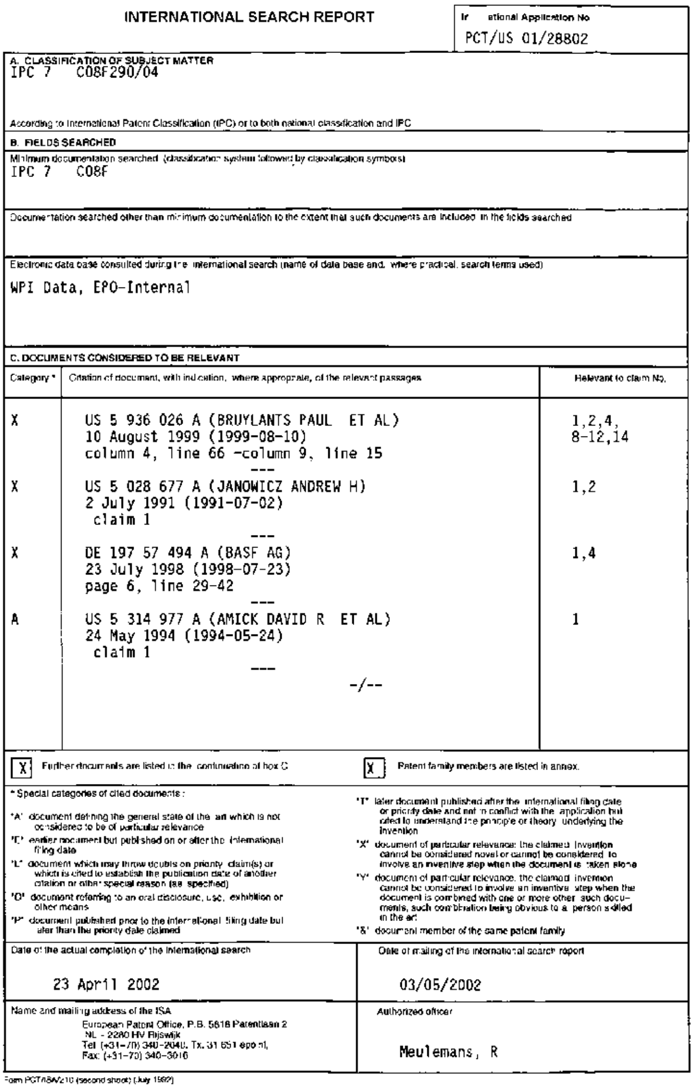
18. The copolymer composition of Claim 17 wherein the macromonomer comprises as polymerized units less than 1 weight percent acid containing monomer, based on the total weight of the macromonomer.

19. The copolymer composition of Claim 18 wherein the copolymer composition further comprises from 0.2 weight percent to 10 weight percent of an acid containing macromonomer, or acid containing monomer based on the total weight of the copolymer.

20. The copolymer composition of Claim 19 wherein the graft copolymer comprises a backbone and one or more side chains, wherein the side chains are pendant from the backbone and comprise the water insoluble macromonomer, and wherein the backbone comprises the polymerized units of the second ethylenically unsaturated monomer.

21. The copolymer composition of Claim 20 wherein the acid containing macromonomer is attached to the surface of the copolymer particles.

【国際調査報告】



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/28802

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F290/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 936 026 A (BRUYLANTS PAUL ET AL) 10 August 1999 (1999-08-10) column 4, line 66 -column 9, line 15 ---	1,2,4, 8-12,14
X	US 5 028 677 A (JANOWICZ ANDREW H) 2 July 1991 (1991-07-02) claim 1 ---	1,2
X	DE 197 57 494 A (BASF AG) 23 July 1998 (1998-07-23) page 6, line 29-42 ---	1,4
A	US 5 314 977 A (AMICK DAVID R ET AL) 24 May 1994 (1994-05-24) claim 1 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 23 April 2002	Date of mailing of the international search report 03/05/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Meulemans, R

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CD09