PATENT SPECIFICATION (11) 1 564 653

1 564 653

(21) Application No. 30324/77 (22) Filed 19 Jul. 1977 (19)
(31) Convention Application No's. 706974 (32) Filed 19 Jul. 1976
776167 10 Mar. 1977 in
(33) United States of America (US)
(44) Complete Specification Published 10 Apr. 1980
(51) INT. CL.^{3} C08F 8/00
(52) Index at Acceptance
C3J CE CR DB
C3P JC

THE PATENT OFFICE LONDON

(54) PROCESS FOR PREPARING SUBSTANTIALLY LINEAR WATER-SOLUBLE INTERPOLYMERIC INTERFACIALLY SPREADING POLYELECTROLYTES

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

It is known from U.S. Patent 3,917,574, issued November 4, 1975 to Gibbs et al., to make substantially linear water-soluble interpolymeric interfacially spreading polyelectrolytes of the type contemplated herein in a continuous monomer addition solution polymerization process wherein at least one ionic hydrophilic monomer and at least one nonionic hydrophobic monomer in a polar mutual solvent are added to a polymerization reactor at a rate no greater than the rate of polymerization and in a ratio which is substantially equal to that desired in the resulting polymer phase.

It is also known from U.S. Patent 3,965,032, issued June 22, 1976 to Gibbs et al, to make such substantially linear interpolymeric interfacially spreading polyelectrolytes by polymerization of a functional nonionic monomeric mixture in a nonaqueous solvent, followed by isolation of the polymer and subsequent conversion to an ionic derivative.

It is often the case when copolymerizing ionic and nonionic monomers that the monomers are not present in the same phase during polymerization and more than one polymerization reaction is occurring. The reaction mixture forms two phases with the ionic monomers preferentially distributed in one phase and the nonionic monomers in the other. Polymerization can take place simultaneously in both phases, forming a complex mixture of highly charged water-soluble polymer and slightly charged essentially nonionic polymer. Further, only a limited number of solvents are available which can compatibilize nonionic and ionic species and such solvents are usually expensive and difficult to separate from the polymer.

In addition, monomer removal is a problem in purifying these mixtures. For ecological and health reasons, even low levels of monomers are not permissible. Since solution reactions rarely go to high conversion, the unreacted monomer must be separated from the polymer. The simplest way is to strip off the monomers and solvent, then redissolve the polymer in water for subsequent use. But ionic monomers are nonvolatile. Therefore, they must be removed by fractional precipitation extraction or dialysis. And, since in most cases any polymeric surfactant synthesized will be soluble in the same solvents as the monomer, dialysis is the only practical approach.

Added to the above problems are the fact that ionic monomers are often difficult to prepare, purify and store and very often undergo small amounts of homopolymerization wherein the homopolymer cannot be removed from the monomer and ends up as a contaminant in the final product.

The present invention provides a process comprising the steps of (1) the homogeneous polymerization in an aqueous emulsion of a mixture of ethylenically unsaturated nonionic monomers wherein at least one of the monomers contains a reactive group to form an interpolymer containing nonionic functional groups, then (2) adding a coreactant compound to the aqueous emulsion in an amount sufficient to convert the interpolymer to a water-soluble polyelectrolyte the polyelectrolyte having a charge which is the same as the charge of the emulsion of (1) above, the process being effected in a manner so as to produce a substantially linear water-soluble interpolymeric interfacially spreading polyelectrolyte as hereinafter defined.

By "a substantially linear water-soluble interpolymeric interfacially spreading polyelectrolyte" we mean a polyelectrolyte composed of a mixture of nonionic hydrophobic units and ionic hydrophilic units wherein the nonionic hydrophobic units are copolymerized ethylenically unsaturated monomers which when in the form of an amorphous homopolymer is less than 0.1 percent soluble in water and wherein the monomer has no substituent extending more than 10 Angstrom units from the point of ethylenic unsaturation the units being randomly distributed in the backbone of the polyelectrolyte and wherein the ionic hydrophilic units are copolymerized ethylenically unsaturated monomers which when in the form of amorphous homopolymers are soluble in water and wherein the ionic hydrophilic units remain substantially ionized over a pH range of 0 to 14; and the polyelectrolyte when incorporated into a dispersion is adsorbed at the disperse phase of the dispersion in a substantially flat configuration and where the area occupied by each ionic hydrophilic unit of the polyelectrolyte at the disperse phase surface is from 60 to 100 square Angstrom units per ionic hydrophilic unit, and wherein the polyelectrolyte has an adsorption constant equal to or greater than 1 at the point where the disperse phase is saturated with the polyelectrolyte wherein the adsorption constant is determined as the amount of polyelectrolyte in the disperse phase divided by the amount of polyelectrolyte in the continuous phase.

It is a further embodiment of the present invention that a stabilizing amount of a polyelectrolyte, of the type as described herein, is used as the surfactant in the preparation of the aqueous emulsion of step (1).

Utilization of the process of the present invention provides an aqueous solution of a polyelectrolyte which is free of undesirable contaminants and which is ready for use. The material is particularly adapted for use as a surfactant in the preparation of emulsions or dispersions of polymeric materials, such as styrenebutadiene latexes.

The preferred interpolymeric interfacially spreading polyelectrolytes (ISPE) as prescribed herein are copolymers of essentially random structure, narrow composition distribution and low molecular weight, i.e., having a number average molecular weight of less than 100,000 and are water soluble or at least spontaneously dispersible in water to form colloidal solutions.

The number of different monomers combined in step (1) to form the reactive interpolymer is not critical to the process provided all are nonionic and at least one contains a reactive functional group. In practice, the number of monomers is normally limited to 4 or 5 with no more than two containing reactive functional groups since there is little advantage in polymer properties to be gained by using more complex mixtures. But this is not a limitation to the process since any number of monomers can be combined. In most cases, a single reactive functional monomer suffices to make an ISPE since its primary purpose is to provide a site on the interpolymer for forming an ionic substituent. But in some cases, a combination is desirable as, for example, when small amounts of a very reactive functional group promotes the more rapid conversion of the other in step (2).

The combination of functional monomers must be selected to avoid interfering reactions, e.g. a combination of such monomers should not be selected wherein one monomer yields an anionic site and another monomer a cationic site on the resultant ISPE. Furthermore, a nucleophilic monomer should not be combined with an alkylating monomer.

The polymerization is carried out with a mixture of nonionic monomers thus avoiding the incompatibility problem existing in a mixture containing an ionic component. When all components are compatible and copolymerize to form a water-insoluble polymer, the conditions of classical emulsion polymerization are realized. Polymerization occurs in or on the polymer particles but not in the aqueous phase. Since the polymer particles are the principal loci of polymerization, there are no competing simultaneous polymerization reactions leading to mixtures of products. Instead, random interpolymers of narrow composition distribution can be formed.

If the reactivity ratios are favorable, the emulsion copolymerization can be carried out batch-wise to high conversion. In cases where the reactivity ratios are not favorable, composition drift would result at high conversion. To avoid this and obtain narrow composition distribution, the monomers can be metered into the reaction at the rate at which they are converted to polymer.

The essential ingredients in an emulsion polymerization reaction are monomers which form water-insoluble polymers, emulsifiers and initiators. The choice of ingredients and their proportions in the recipe determine the characteristics of the reaction and the product.

It is important in the present process to carry out the polymerization at the highest possible rates to minimize contact of the reactive functional monomers with the hot aqueous environment. This can be accomplished by combining low organic/aqueous phase ratio, high surfactant level, high initiator level and high temperature. These conditions lead to a fluid latex and very high conversions with short run times. The polymer formed is of low molecular weight and narrow composition distribution. Polymers of low molecular weight, e.g., 1000 to 40,000 and preferably $<10,000$ are especially useful because of their faster kinetics of adsorption. In many applications, such as in emulsion and suspension polymerization, this is very important.

The surfactants are critical to the process and may be either anionic or cationic depending on the type of ISPE desired. Cationic emulsion polymerization process is preferred for which combinations of a cationic ISPE with a conventional cationic surfactant and sometimes (optionally) nonionic surfactants, may be employed. The preferred combination is a relatively high level of ISPE surfactant, i.e., up to 12 parts or more based on monomer with from 0 to 3% of a conventional surfactant. Both species can be selected to have the same cationic structure as desired in the product ISPE. If this is done, the ISPE can be utiized in whatever amount desired because after reaction, it becomes indistinguishable from the product. The conventional surfactants include the classes of salts of aliphatic amines, especially the fatty amines, quaternary ammonium salts and hydrates, fatty amides derived from disubstituted diamines, fatty chain derivatives of pyridinium compounds, ethylene oxide condensation products of fatty amines, sulfonium compounds, isothiouronium compounds and phosphonium compounds.

Free radical forming initiators suitable for the preparation of cationic ISPE's include those which form either nonionic or cationic end groups on the polymer chains. The nonionic types such as hydroperoxides and azo compounds are preferred, especially hydrogen peroxide, t-butylhydroperoxide (TBHP) and azobisisobutyronitrile. They are employed at high levels, e.g., from 0.5-5 weight percent and can be added in one shot or introduced continuously into the reaction depending on the reactivity of the initiator. Redox systems which can function in a cationic emulsion polymerization, such as TBHP and hydroxylamine, may also be utilized.

Molecular weight is a complex function of many variables but in this process, it can be controlled by choice of temperature, initiator level and chain transfer agent. Polymerization can be carried out using temperatures of from 25-100°C but temperatures of from 70-90°C are preferred for most monomers. This results in run times of less than 12 and usually less than 5 hours with conversions exceeding 95%. The selection of chain transfer agent is also important. Most conventional chain transfer agents can be used, with alkyl polyhalides and mercaptans being preferred. Combinations of H_2O_2 with CBr_4 or mercapto ethanol are especially preferred.

An advantage of the present process is that particle size control is not necessary save only that the latex remain fluid enough to stir. It is also preferred to operate at relatively low solids, e.g., less than 30% solids and preferably from 20-25 percent solids. Small particle size, e.g., <2000Å is preferred since this allows for faster conversion in step 2, however, any particle size or particle size distribution is acceptable. Even small amounts of coagulum can be tolerated since in step 2, all species are ultimately converted to water-soluble products.

The process of this invention unexpectedly leads to narrow molecular weight distribution at low molecular weights. In fact, the distributions are virtually identical to those obtained in a solution process using the same monomers. By choice of initiator, chain transfer agent, and polymerization conditions, the number average molecular weight can be varied from 10^3 to 10^5 with

$$\frac{\overline{M}_w}{\overline{M}_n} \text{ in the range of 1.5 to 3.}$$

In step 2, the aqueous emulsion of step 1 is converted to an aqueous solution of polyelectrolyte. Any reaction between an added low molecular weight component and the functional groups on the polymer chain that takes place in aqueous media to yield a pH independent site on the polymer chain, can be employed. Exemplary are the class of nucleophilic displacement reactions between an nonionic nucleophile and nonionic alkylating agent to yield an organic cation as illustrated below:

$$RA + Z \rightarrow RZ^+A^-$$

where Z is a nucleophile, RA is the alkylating agent and A is a leaving group. RZ^+ is the derived onium cation and A^- its anion formed from the leaving group. Either reactant can be a substituent on the polymer chain and its counterpart coreactant is selected so as to yield a cationic polymeric product. It is, therefore, possible to make the same cationic product from these two different routes.

Nonionic monomers which form interpolymers with nucleophilic sites include the general classes of tertiary amines, phosphines and sulfides containing at least one polymerizable double bond as a substituent. Examples include vinyl pyridines, vinylbenzyl dialkyl amines, dialkyl amino alkyl acrylates and methacrylates and alkyl thio alkyl acrylates and methacrylates.

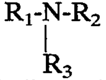
Mixtures of interpolymer latexes with the desired alkylating agent are allowed to react at from ambient temperature to 100°C, or higher if under pressure, to convert the nucleophilic sites to attached onium ions. As the reaction proceeds, the polymer particles become increasingly hydrophilic and eventually dissolve to form an aqueous solution of the ISPE. After reaction, the reaction product can be used as is or given other treatments such as stripping to remove unreacted alkylating agents.

The alkylating agents are selected to be highly reactive and volatile and must be at least slightly soluble, e.g., >0.001% in order to define through the aqueous phase to the latex particles. Preferred alkylating agents include alkyl bromides of 1-4 carbons, allyl and methallyl chlorides, benzyl chlorides, and dimethyl sulfate.

Preferentially, the alkylating site may be placed on the polymer chain by using an active halogen containing comonomer of the classes: vinyl aralkyl halides, haloalkyl butadienes, bromoalkyl acrylate and methacrylates and vinyl bromide. Preferred are vinylbenzyl chloride, chloromethylbutadiene and the bromoalkyl esters. Latexes containing these species in copolymerized form are reacted with carbon-containing nucleophiles which are stable in and can diffuse through aqueous media having a hetero atom as the center of nucleophilicity wherein each covalent bond of said hetero atom is to a carbon atom.

The nucleophilic compounds which are used advantageously in the practice of this invention are represented by the following classes of compounds, sometimes called Lewis bases:

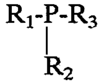
(a) monobasic aromatic nitrogen compounds;
(b) tetra (lower alkyl)thioureas;
(c) $R_1\text{-}S\text{-}R_2$ wherein R_1 and R_2 individually are lower alkyl, hydroxy lower alkyl or wherein R_1 and R_2 are combined as one alkylene radical having 3 to 5 carbon atoms;
(d)



$$R_1\text{-}\underset{\underset{R_3}{|}}{N}\text{-}R_2$$

wherein R_2 and R_3 individually are lower alkyl or hydroxy lower alkyl, or are combined as one alkylene radical having 3 to 5 carbon atoms and R_1 is lower alkyl, aralkyl or aryl except when R_2 and R_3 together are an alkylene radical then R_1 is lower alkyl or hydroxy lower alkyl; and

(e)

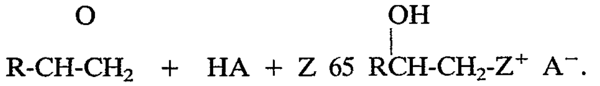


$$R_1\text{-}\underset{\underset{R_2}{|}}{P}\text{-}R_3$$

wherein R_1, R_2 and R_3 individually are lower alkyl, hydroxy lower alkyl or aryl.

In this specification the term lower alkyl means an alkyl having from 1 to 4 carbon atoms. Use of the nucleophilic component as the reactant is the preferred route because the monomer containing alkylating sites are less likely to interfere with emulsion polymerization and the coreactant nucleophiles are more water soluble and blend more readily into the latex. They are also easier to remove in a post reaction cleanup and are less toxic than coreactant alkylating agents.

Another general class of reactions suitable for the present process are the reactions of epoxides with nucleophiles and acids as shown below:



$$R\text{-}\overset{O}{CH\text{-}CH_2} + HA + Z\ 65\ R\overset{\overset{OH}{|}}{C}H\text{-}CH_2\text{-}Z^+\ A^-.$$

As described earlier, either the epoxide or the nucleophile may be attached to the polymer chain. Epoxide groups can be incorporated into the copolymer by copolymerization of an unsaturated epoxide such as glycidyl acrylate or methacrylate. Alternatively, the nucleophilic polymers described earlier can be reacted with a lower epoxide such as ethylene oxide, propylene oxide, glycidyl ethers and the like. Suitable acids for either case include HCl, H_2SO_4, and lower carboxylic acids, and are selected on the basis of the anion desired.

In the preparation of anionic ISPE's anionic emulsion polymerization is required. For such process, anionic ISPE's can be used with conventional anionic soaps known in the art and initiators which yield nonionic or anionic end groups. Any reaction can be used in step 2 which converts a functional copolymer in aqueous emulsion to a water-soluble anionic polyelectrolyte. For example, an anionic latex of a vinyl benzyl chloride copolymer can be formed and then post reacted with sulfite ion to yield a vinyl benzyl sulfonate anionic polyelectrolyte.

The following examples, wherein all parts and percentages are by weight, illustrate the present invention:

Example 1

A series of functional monomers were copolymerized in emulsion. The reaction ingredients and conditions are set forth on the following Table I. The continuous addition polymerization reaction of step 1 was conducted by metering the designated monomers along with an aqueous stream containing cationic polymeric surfactant, H_2O_2 and $FeCl_3 \cdot 6H_2O$ into a polymerization reactor over a one-hour period, followed by heating the admixture for an additional one hour at the designated temperature. The remaining reactions were conducted using a batch polymerization technique. In each instance a water-soluble, essentially contaminant-free ISPE of indicated composition was obtained using the ingredients and conditions as specifically set forth in step 2 of Table I.

TABLE I

	Experiment No.			
	1	2	3	*4*
Step 1				
Emulsion Polymerization: Water (deionized)	(Enough to make 25% max. solids)			
Polymeric Surfactant[1]	5.0	10.0	10.0	5.0
Cationic Soap[2]	-	1.0	1.0	-
H_2O_2	2.25	2.25	2.25	2.25
$FeCl_3 \cdot 6H_2O$	0.005	0.005	0.005	0.005
tMethyl Methacrylate				
48.0				
36.6				
66.0				
60.0				
Glycidyl Methacrylate	52.0	-	-	-
Bromoethyl Methacrylate	-	63.4	-	-
Chloromethyl Butadiene	-	-	34.0	-
4-Vinyl Pyridine	-	-	-	40.0
1-Dodecanethiol	-	0.25	0.25	-
Carbon Tetrabromide	-	-	-	1.0
Polymerization Method	Continuous Addition	Batch	Batch	Batch
Time (hrs)/Temp.(°C)	2/80	2/80	2/80	1/80

TABLE I (CONT)

Step 2

Polyelectrolyte Preparation: Wt. of latex = 25 g copolymer	105	111	111	110
Wt. of Water	115	111	111	110
Wt. of Dimethylsulfide (2.5/1) Stoichiometry	14.2	-	12.9	-
Wt. of Acetic Acid (1/1)	5.5	-	-	-
Wt. of 25% Trimethyl Amine (1.1/1)	-	21.4	-	-
Wt. of Methyl Bromide	-	-	-	9.0
Time (hrs)/Temp. (°C)	16/50	16/50	16/50	72/25
Charge density(3)	-	0.286	0.285	0.408
Activity; Material Balance(4)	0.138	0.134	0.146	0.164
Activity; Titration Analysis(4)	-	0.107	0.127	0.149

(1) Cationic ISPE, as per USP 3,965,032 composed of copolymer of 3 moles of methyl methacrylate and 2 moles of vinyl benzyl dimethyl sulfonium chloride.

(2) Dodecylbenzyl dimethyl sulfonium chloride.

(3) Meq. of onium ion/gm. solution.

(4) Grams polyelectrolyte per gram solution.

Example 2

A series of emulsion polymerization reactions were carried out by batch polymerization as per Runs 2 through 4 of Example 1, using a mixture of 60 mole percent methylmethacrylate, 40 mole percent vinyl benzyl chloride, varying amount of the polymerization initiator H_2O_2, varying amounts and types of chain transfer agents, about 7 weight percent of a preformed cationic ISPE (as per USP 3,965,032) composed of 3 moles of methyl methacrylate and 2 moles of vinyl benzyl dimethyl sulfonium chloride, and about 0.5 weight percent of the conventional soap dodecylbenzyl dimethyl sulfonium chloride. The following Table II sets forth the compositions used as well as the molecular weight of the products formed.

TABLE II

Run No.	*MMA*	*VBC*	*Mole % Based on Monomers* H_2O_2	*Mole % Based on Monomers* CBr_4	*Mole % Based on Monomers* *DT*	$\overline{M}w \times (10^3)$	$\overline{M}n \times (10^3)$	$\overline{M}w/\overline{M}n$
5	60	40	8	--	--	69.8	26.7	2.61
6	60	40	6.68	--	0.15	43	18.2	2.36
7	60	40	6.68	--	0.6	35.3	14.8	2.39
8	60	40	1.62	0.81	--	25.5	9.9	2.55
9	60	40	3.15	1.58	--	14.3	5.6	2.56
10	60	40	6	3	--	8	3.6	2.23

MMA - Methylmethacrylate
VBC - Vinylbenzyl chloride
H_2O_2 - Hydrogen peroxide
CBr_4 - Carbon tetrabromide
DT - 1-Dodecanethiol

Example 3

Multicomponent interpolymers were prepared in a batch process as in Example 2 using same ISPE as surfactant.

TABLE III

Date Reference 120-C-0058	*(4A) 3 Components*		*(9A)* (1) *2 Reactive Monomers*	
Emulsion Polymerization: (Batch)				
DI Water	(Enough to make 25% max. solids)			
Polymeric surfactant (2)	12.0		12.0	
h_2O_2	2.70		2.43	
$FeCl_3 \cdot 6H_2O$	0.0060		0.0054	
Acrylonitrile	20.0		11.9	
Methyl Methacrylate	-		22.3	
Styrene	30.0		-	
Glycidyl Methacrylate	-		31.7	
Vinylbenzyl Chloride	50.0		34.1	
$HSCH_2CH_2OH$	3.88		3.49	
Time (hrs.)/Temp.(°C)	1/75		1/75	
Polyelectrolyte Preparation:	*(4B)*	*(4C)*	*(9B)*	*(9C)*
Wt. Latex	224	224	220	220
Wt. DI Water	112	112	110	110
Wt. N,N-Dimethylethanolamine	14.6	---	19.8	---
Wt. Dimethylsulfide	---	10.0	---	13.8
Wt. Acetic Acid	---	---	6.7	6.7
Time (hrs.)/Temp.(°C)	0.5/70	1.5/50	0.5/70	1/50
Activity (1.0 = 100%)				
Material Balance	0.201	0.191	0.210	0.196
Gravimetric Analysis	0.220	0.186	0.255	0.226
Titration Analysis	0.180	0.171	0.196	0.182

(1) Equal mole concentration of each monomer.
(2) Cationic ISPE, as per USP 3,965,032 composed of copolymer containing 3 moles methylmethacrylate/2 moles vinylbenzyl chloride.

Each of the above reaction products were easily converted to water-soluble, essentially contaminant free, ISPE's by reaction as set forth in step 2 of Table I, Example 1.

Further, the products of the emulsion reaction, as set forth in Table II above, were found to have essentially equivalent molecular weight values as materials produced by a solution polymerization technique. More particularly, such solution polymerization comprised preparing a mixture containing methyl ethyl ketone and a monomer mixture comprising 60 mole percent methyl methacrylate and 40 mole percent vinyl benzyl chloride, along with 1.7 mole percent (based on monomer) of the polymerization initiator azobisbutyronitrile and from 0.36 to 3.64 mole percent (based on monomer) of carbon tetrabromide as a chain transfer agent. The mixture was then metered, over a period of one hour, into a reactor containing additional methyl ethyl ketone. The final mixture was then refluxed for a period of five hours.

It was unexpected that materials having sufficiently low molecular weight to be useful as surfactants could be prepared by an emulsion polymerization process. Further, it was unexpected that such a process would provide a means of obtaining products having a narrow molecular weight distribution, such as is normally obtained only by using solution polymerization techniques. More particularly, molecular weights obtained by emulsion polymerization are affected by the same variables as in any free radical process. For example, increases in initiator concentration and temperature as well as the use of chain transfer agents normally decrease the molecular weight of the reaction product. However, such result is often accompanied by a broadening of the molecular weight distribution due to the generation of a fraction of low molecular weight material resulting from primary termination reactions. In contrast to these expectations, the process of the present invention provides polymers having molecular weights as low as can be obtained by solution polymerization and with comparable molecular weight distribution.

WHAT WE CLAIM IS:-

1. A process comprising the steps of (1) the homogeneous polymerization in an aqueous emulsion of a mixture of ethylenically unsaturated nonionic monomers wherein at least one of the monomers contains a reactive group to form an interpolymer containing nonionic functional groups, then (2) adding a coreactant compound to the aqueous emulsion in an amount sufficient to convert the interpolymer to a water-soluble polyelectrolyte the polyelectrolyte having a charge which is the same as the charge of the emulsion of (1) above, the process being effected in a manner so as to produce a substantially linear water-soluble interpolymeric interfacially spreading polyelectrolyte as hereinbefore defined.

2. A process as claimed in claim 1 in which the interpolymeric interfacially spreading polyelectrolyte is a water-soluble cationic compound.

3. A process as claimed in claim 2 in which a stabilizing amount of the cationic interfacially spreading polyelectrolyte is used as a surfactant in the preparation of the aqueous emulsion.

4. A process as claimed in claim 1 in which the functional groups are alkylated sites or epoxide groups and the coreactant compound is a nucleophilic compound, or a necleophilic compound together with an acid, respectively.

5. A process as claimed in claim 1 in which the functional groups are nucleophilic sites and the coreactant is an alkylating agent, or an epoxide together with an acid.

6. A process as claimed in claim 4 in which the alkylating sites are derived from a comonomer selected from a vinyl aralkyl halide, a haloalkyl butadiene, a bromoalkyl acrylate, a bromoalkyl methacrylate, and vinyl bromide.

7. A process as claimed in claim 4 or claim 6 in which the epoxide groups are derived from glycidyl arcylate or glycidyl methacrylate.

8. A process as claimed in any one of claims 4, 6 and 7 in which the nucleophilic compound is selected from

(a) monobasic aromatic nitrogen compounds;
(b) tetra (C_{1-4} alkyl)thioureas;
(c) R_1-S-R_2 wherein R_1 and R_2 individually are C_{1-4} alkyl, hydroxy C_{1-4} alkyl or wherein R_1 and R_2 are combined as one alkylene radical having 3 to 5 carbon atoms;
(d)

$$\begin{array}{c} R_1\text{-}N\text{-}R_2 \\ | \\ R_3 \end{array}$$

wherein R_2 and R_3 individually are C_{1-4} alkyl or hydroxy C_{1-4} alkyl, or are combined as one alkylene radical having 3 to 5 carbon atoms and R_1 is C_{1-4} alkyl, aralkyl or aryl except when

R_2 and R_3 together are an alkylene radical then R_1 is C_{1-4} alkyl or hydroxy C_{1-4} alkyl; and

(e) 

$$R_1\text{-}\underset{\displaystyle R_2}{\underset{|}{P}}\text{-}R_3$$

wherein R_1, R_2 and R_3 individually are C_{1-4} alkyl, hydroxy C_{1-4} alkyl or aryl.

9. A process as claimed in claim 5 in which the nucleophilic sites are derived from a comonomer selected from a vinyl pyridine, a vinylbenzyl dialkyl amine, a dialkyl amino alkyl acrylate, a dialkyl amino alkyl methacrylate, an alkyl thio alkyl acrylate, and an alkyl thio alkyl methacrylate.

10. A process as claimed in claim 5 or claim 9 in which the alkylating agent is selected from a $C\text{-}_{1-4}$ alkyl bromide, allyl chloride, methallyl chloride, benzyl chloride, and dimethyl sulfate.

11. A process as claimed in any one of claims 5, 9 and 10 in which the epoxide is selected from ethylene oxide, propylene oxide and a glycidyl ether.

12. A process as claimed in claim 4 or claim 5 in which the acid is HCl, H_2SO_4 or a lower carboxylic acid.

13. A process as claimed in claim 2 or claim 3 in which the polyelectrolyte is the reaction product of methyl methacrylate, vinylbenzyl chloride and dimethyl sulfide.

14. A process as claimed in claim 2 or claim 3 in which the polyelectrolyte is the reaction product of methyl methacrylate, glycidyl methacrylate, dimethyl sulfide and acetic acid.

15. A process as claimed in claim 2 or claim 3 in which the polyelectrolyte is the reaction product of methyl methacrylate, bromoethyl methacrylate and trimethyl amine.

16. A process as claimed in claim 2 or claim 3 in which the polyelectrolyte is the reaction product of methyl methacrylate, chloromethyl butadiene and dimethyl sulfide.

17. A process as claimed in claim 2 or claim 3 in which the polyelectrolyte is the reaction product of methyl methacrylate, 4-vinyl pyridine and methyl bromide.

18. A process as claimed in claim 2 or claim 3 in which the polyelectrolyte is the reaction product of styrene, acrylonitrile, vinyl benzyl chloride and N,N-dimethylethanolamine.

19. A process for preparing a substantially linear water-soluble interpolymeric interfacially spreading polyelectrolyte substantially as hereinbefore described in any one of the Examples.

20. A substantially linear water-soluble interpolymeric interfacially spreading polyelectrolyte which has been prepared by a process as claimed in any one of claims 1 to 19.

21. A polyelectrolyte as claimed in claim 20 having a number average molecular weight of less than 100,000.

22. A process for the preparation of emulsions or dispersions of polymeric materials involving the use of a polyelectrolyte as claimed in claim 20 or claim 21 as a surfactant.

23. A process as claimed in claim 22 for the preparation of styrene-butadiene latexes.

24. The product of the process as claimed in claim 22 or claim 23.

BOULT, WADE & TENNANT,
Chartered Patent Agents,
34 Cursitor Street, London,
EC4A 1PQ.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.