

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 October 2003 (30.10.2003)

PCT

(10) International Publication Number
WO 03/089481 A1

(51) International Patent Classification⁷: **C08F 6/04**,
C08J 3/09

(81) Designated States (*national*): AU, BR, CA, CN, ID, IN,
JP, KR, MX, NZ, PH, PL, SG, UA.

(21) International Application Number: PCT/US03/11262

(22) International Filing Date: 10 April 2003 (10.04.2003)

(25) Filing Language: English

(26) Publication Language: English

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

(30) Priority Data:
10/126,287 19 April 2002 (19.04.2002) US
10/373,409 24 February 2003 (24.02.2003) US

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

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Published:

- with international search report

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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 03/089481 A1

(54) Title: PROCESS FOR PURIFICATION OF ALKOXYSTYRENE POLYMERS

(57) Abstract: Polymers derived from 4-alkoxystyrene are purified by fractionalization plus heating and cooling of the polymers in alcoholic solvents.

PROCESS FOR PURIFICATION OF ALKOXYSTYRENE POLYMERS

BACKGROUND OF THE INVENTION

Copolymers and terpolymers, when isolated from reaction solution are a mixture of
5 compounds of varying composition and molecular weight. Typically they contain small
quantities of starting material and by-products which are undesirable in the final polymer. The
polymer mixture is precipitated from the solvent or solvent mixture by adding the mixture to a
second solvent, as for example water, hexane, heptane, octane, petroleum ether, or a mixture
thereof. The polymer is then dried under a nitrogen atmosphere. The subject of this invention
10 pertains to a method of purifying the polymer.

Davidson, in U. S. Patent 5,945,251, discloses a method of purifying polyhydroxystyrene
polymers by adding an amine, a hydrophilic solvent, a hydrophobic solvent, and water to the
polymer; separating the aqueous phase; then removing the hydrophilic solvent and the
hydrophobic solvent to form the purified polymer.

15 Zempini, et al. in U. S. 5,789,522 and U. S. 5,939,511, extracts impurities from a
phenolic resin by dissolving the resin in a photoresist solvent and extracting the water-soluble
impurities therefrom.

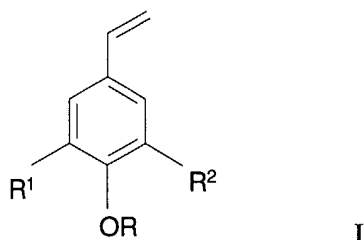
SUMMARY OF THE DISCLOSURE

20 The present invention provides a novel process for improving the glass transition
temperatures and reducing the polydispersity values of polymer intermediates that have been
polymerized by precipitation from methanol. The polymers that are susceptible to treatment
with the method of this invention are polymers of 4-alkoxystyrene. The 4-alkoxystyrene
derived polymers are then transesterified to 4-hydroxyphenyl-containing polymers useful in
25 paints, resins, thickening agents, and in photoresist compositions. The present invention process
is an improvement over the prior art and is quite efficient. Specifically the invention provides a
method of removing unreacted monomers, low molecular weight polymers, and the like from the
crude polymer mixture before the transesterification step. Many analytical methods can be
utilized to quantify the improvement in the purity of polymers. Average molecular weight,
30 nuclear magnetic resonance, chromatography, and glass transition temperature are all effective in
certain instances with certain molecules and characteristic side chains.

As previously described in the prior art, the crude polymer after polymerization is separated from the alcohol by filtration, centrifugation, decantation, or the like. According to the method of this invention, the polymer is subject to fractionalization whereby it is suspended in methanol and the solid is separated from the methanol. This procedure is repeated as long as
 5 necessary to remove by-products and low molecular weight materials that are more soluble in the methanol than the desired polymer. In this manner, the undesirable monomeric impurities and oligomers are soluble in the solvent (such as methanol) depending upon temperature and thus are removed during each fractionation step.

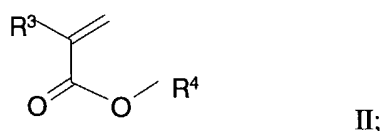
DETAILED DESCRIPTION OF THE INVENTION

This invention provides a process for the improvement in the composition of polymers derived from the monomer I,



wherein R is either $-C(O)R^5$ or $-R^5$; as a homopolymer or a copolymer typically with one or
 15 more of the following monomers:

an acrylate monomer having the formula II,



and/or with one or more ethylenically unsaturated copolymerizable monomers (EUCM) selected from the group consisting of styrene, 4-methylstyrene, styrene alkoxide wherein the alkyl portion is
 20 $C_1 - C_5$ straight or branch chain, tert.-butylstyrene, cyclohexyl acrylate, tert.-butyl acrylate, tert.-butyl methacrylate, maleic anhydride, dialkyl maleate, dialkyl fumarate and vinyl chloride.
 wherein:

- i) R^1 and R^2 are the same or different and independently selected from the group consisting of:
 hydrogen;
 25 fluorine, chlorine or bromine;

alkyl or fluoroalkyl group having the formula $C_nH_xF_y$ where n is an integer from 1 to 4, x and y are integers from 0 to $2n+1$, and the sum of x and y is $2n+1$; and phenyl or tolyl;

ii) R^3 is selected from the group consisting of:

5 hydrogen; and

methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or tert.-butyl;

iii) R^4 is methyl, ethyl, n-propyl, iso-propyl, n-butyl, i-butyl, tert.-butyl, t-amyl, benzyl,

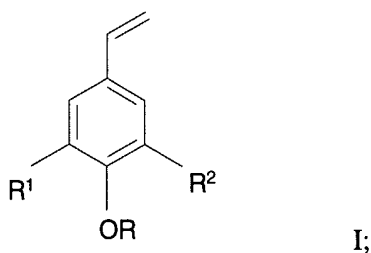
cyclohexyl, 9-anthracenyl, 2-hydroxyethyl, cinnamyl, adamantyl, methyl or ethyl or

hydroxyl adamantyl, isobornyl, 2-ethoxyethyl, n-heptyl, n-hexyl, 2-hydroxypropyl,

10 2-ethylbutyl, 2-methoxypropyl, 2-(2-methoxyethoxyl), oxotetrahydrofuran, hydroxy-trimethylpropyl, oxo-oxatricyclo non yl, 2-naphthyl, 2-phenylethyl, phenyl, and the like; and

iv) R^5 is C_1 - C_4 alkyl,

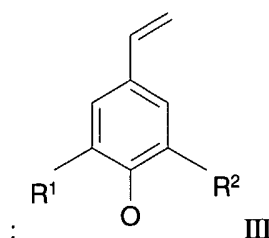
typically manufactured by subjecting a monomer of formula I,



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or a monomer of the formula I and/or monomer II, and/or one or more of said copolymerizable monomers (EUCM) to suitable polymerization conditions in an alcoholic solvent and in the presence of a free radical initiator at suitable temperature for a sufficient period of time to produce a crude polymer of corresponding composition. After purification by the method of

20 this invention, the purified polymer is transesterified to a polymer containing the monomer of formula III:



by (1) subjecting said polymer to transesterification conditions in said alcoholic solvent in the presence of catalytic amounts of a base catalyst at suitable temperature such that the

transesterified by-product ester formed is continuously removed from the reaction mixture to form the homopolymer of I or the copolymer of I, and/or II, and/or said copolymerizable monomer, (EUCM) or (2) subjecting the polymer to acidic hydrolysis with a strong acid. The polymer is then optionally passed through an ion-exchange bed to remove said base or acid catalyst.

It is also within the scope of the present invention to prepare a homopolymer of Formula I from the monomer of Formula III. As another embodiment, polyhydroxystyrene (PHS) can be prepared from acetoxystyrene monomer (ASM).

The scope of the present invention thus covers (a) a homopolymer of Formula I derived from Formula III monomer; (b) a copolymer derived from Formula II and Formula III monomers; (c) a copolymer derived from Formula III monomers and the EUCM; and (d) a terpolymer derived from monomers of Formula II, Formula III, and EUCM. It is also within the scope of the present invention to use other monomers such as norbornene monomers, fluorine monomers and the like to form a crude polymer product to be treated by the novel processes of the present invention.

In conjunction with Formula II (an acrylate monomer) set forth herein, some preferred acrylate monomers are (1) MAA-methyl adamantyl, (2) MAMA-methyl adamantyl methacrylate, (3) EAA-ethyl adamantyl acrylate, (4) EAMA-ethyl adamantyl methacrylate, (5) ETCDA-ethyl tricyclodecanyl acrylate, (6) ETCDMA-ethyl tricyclodecanyl methacrylate, (7) PAMA-propyl adamantyl methacrylate, (8) MBAMA-methoxybutyl adamantyl methacrylate, (9) MBAA-methoxybutyl adamantyl acrylate, (10) isobornylacrylate, (11) isobornylmethacrylate, (12) cyclohexylacrylate, and (13) cyclohexylmethacrylate. Other preferred acrylate monomers which can be used are (14) 2-methyl-2-adamantyl methacrylate; (15) 2-ethyl-2-adamantyl methacrylate; (16) 3-hydroxy-1-adamantyl methacrylate; (17) 3-hydroxy-1-adamantyl acrylate; (18) 2-methyl-2-adamantyl acrylate; (19) 2-ethyl-2-adamantyl acrylate; (20) 2-hydroxy-1, 1, 2-trimethylpropyl acrylate; (21) 5-oxo-4-oxatricyclo-non-2-yl acrylate; (22) 2-hydroxy-1, 1, 2-trimethylpropyl 2-methacrylate; (23) 2-methyl-2-adamantyl 2-methacrylate; (24) 2-ethyl-2-adamantyl 2-methacrylate; (25) 5-oxotetrahydrofuran-3-yl acrylate; (26) 3-hydroxy-1-adamantyl 2-methylacrylate; (27) 5-oxotetrahydrofuran-3-yl 2-methylacrylate; (28) 5-oxo-4-oxatricyclo-non-2-yl 2-methylacrylate.

In one embodiment of the present invention, co-polymers having polyhydroxystyrene (PHS) and one or more of the above acrylate monomers are some of the materials that can be purified by the novel processes of the present invention. It is to be understood the purification processes set forth herein can be used to purify other monomers classes which have been polymerized. These

monomer classes include, without limitation, vinyl acetate, acrylics, styrenes, styrenes-acrylics, olefins such as ethylene and propylene, acrylonitrile, maleic anhydride, and mixtures thereof. The polymerization of these monomers can be carried out via cationic, non ionic and/or free radical. These are other embodiments of the present invention. However, the description set forth herein is generally directed to the styrenic, styrenic/acrylate, styrenic/acrylate/norbornyl type monomers.

The polymerization, purification, and/or transesterification steps are carried out on an anhydrous basis (i.e. < about 5,000 ppm water). The alcoholic solvent for the polymerization is an alcohol having 1 to 4 carbon atoms and is selected from the group consisting of methanol, ethanol, propanol, isopropanol, t-butanol, and combinations thereof. The amount of solvent used is not critical and can be any amount which accomplishes the desired end result.

The free radical initiator for the polymerization may be any initiator that achieves the desired end result. The initiator may be selected from the group consisting of 2,2'-azobis(2,4-dimethylpentanenitrile), 2,2'-azobis(2-methylpropanenitrile), 2,2'-azobis(2-methylbutanenitrile), 1,1'-azobis(cyclohexanecarbonitrile), t-butyl peroxy-2-ethylhexanoate, t-butyl peroxy-pivalate, t-amyl peroxy-pivalate, diisooctanoyl peroxide, decanoyl peroxide, succinic acid peroxide, di(n-propyl) peroxydicarbonate, di(sec-butyl) peroxydicarbonate, di(2-ethylhexyl) peroxydicarbonate, t-butylperoxyneodecanoate, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane, t-amylperoxyneodecanoate, dimethyl 2,2'-azobisisobutyrate, and combinations thereof.

The initiator is typically selected from the group consisting of 2,2'-azobis(2,4-dimethylpentanenitrile), 2,2'-azobis(2-methylpropanenitrile), 2,2'-azobis(2-methylbutanenitrile), 1,1'-azobis(cyclohexanecarbonitrile), t-butyl peroxy-2-ethylhexanoate, t-butyl peroxy-pivalate, t-amyl peroxy-pivalate, and combinations thereof.

The polymerization conditions are not critical and can be any temperature and pressure that will produce the desired end result. In general, the temperatures are from about 30°C to about 100°C, preferably from about 40°C to about 100°C, and most preferably from about 45°C to about 90°C. The pressure may be atmospheric, sub-atmospheric or super-atmospheric. The polymerization time is not critical, but generally will take place over a period of at least one minute in order to produce a polymer of corresponding composition.

After the polymerization step and prior to the transesterification step, the crude polymer is subjected to a purification procedure wherein the same type alcoholic solvent (first solvent) is used to purify the crude polymer via a multi-step fractionation process. Additional first solvent is added to the crude polymer mixture, and the resultant slurry is stirred vigorously and/or heated

to boiling (about 66°C) for several minutes, and then chilled to as low as 25°C and allowed to stand. This permits the slurry to produce a phase separation, and then the liquid is removed by centrifugation, filtration, decantation or by similar means. The process is repeated at least one more time until no further purification is identified, as for example, until a small sample of the decanted solvent, upon evaporation to dryness shows substantially no residue. This fractionation process is generally carried out 2 to 10 times, i.e. heating, cooling, separating, and the solvent replacement.

One of the important measures of the degree of impurity of the crude polymer produced from the polymerization of the monomers is the polydispersity value. In general, it is desirable to have a low value, for example, less than about 3; the lower value is indicative that the polymerization reaction was more uniform in chain length. The uniqueness of this purification step is that the desired polymer formed is to some degree not soluble in the solvent and that the undesired, low molecular weight average polymers and undesired monomers are soluble in the solvent. Thus the novel purification/fractionalization step, provides the removal of these undesirable materials. In general, the polydispersity of the crude polymer is measured before, during and after this purification/fractionalization step, with the objective of reducing this value by at least about 10% of what the value of the original crude polymer was before the purification treatment. Preferably it is desirable to yield a product whose polydispersity is below about 2.0. It is to be understood that polydispersity means the ratio of weight average molecular weight (Mw) over the number average molecular weight (Mn) as determined by Gel Permeation Chromatography (GPC).

In the transesterification step, the purified polymer from the polymerization step is subjected to said transesterification conditions in an alcoholic solvent in the presence of catalytic amounts of a base catalyst. (It is to be understood that after the purification step set forth above, there still remains some alcoholic solvent mixed with the desired polymer, but additional solvent should be added in order to keep the polymer in a fluid state. The transesterification could be conducted without the addition of this additional solvent, but the reaction would be more difficult and possibly take longer.) The base catalyst is such that it will not substantially react with said alkyl acrylate monomer II, or with said co-polymerizable monomers (EUCM). The base catalyst is either an alkalic metal hydroxide or an alkalic metal alkoxide. The base catalyst is selected from the group consisting of lithium hydroxide, lithium methoxide, lithium ethoxide, lithium isopropoxide, sodium hydroxide, sodium methoxide, sodium ethoxide, sodium isopropoxide, potassium hydroxide, potassium methoxide, potassium ethoxide, potassium

isopropoxide, cesium hydroxide, cesium methoxide, cesium ethoxide, cesium isopropoxide, and combinations thereof.

If a hydrolysis is utilized to effect removal of the phenol blocking group, the acid should be a member of the strong acids, as for example hydrochloric acid, hydrobromic acid, sulfuric acid, or the like.

Thus and according to the method of this invention, after polymerization of the acyloxy-derived polymer, and prior to the transesterification the crude polymer is subjected to this novel fractionation process which provides a substantially purified polymer which then can be further treated.

In another embodiment of the present invention, there is provided a solvent swap after the transesterification step (which uses a catalyst) and the catalyst removal step. In this solvent swap step, the alcoholic solvent (containing the purified polymer) is then exchanged with an aprotic/organic solvent which is a photoresist compatible solvent, and the alcoholic solvent is removed by distillation. The term "photoresist compatible solvent" is one that is commonly used in the photoresist art as demonstrated in US 5,945,251 (column 4, lines 17-27), US 5,789,522 (column 13, lines 7-18) and US 5,939,511, all of which mention PGMEA and which is set forth in the following Examples 1 and 2. All of these patents are incorporated herein by reference in toto. This photoresist compatible solvent can be a member selected from the group glycol ethers, glycol ether acetates and aliphatic esters having no hydroxyl or keto group. Examples of the solvent include glycol ether acetates such as ethylene glycol monoethyl ether acetate and propylene glycol monomethyl ether acetate (PGMEA).

This invention is further illustrated by the following examples that are provided for illustration purposes and in no way limits the scope of the present invention.

Examples (General)

In the Examples that follow, the following abbreviations are used:

ASM – p-Acetoxystyrene monomer

t-BPP – tert.-butyl peroxy-pivalate

THF – Tetrahydrofuran

GPC – Gel permeation chromatography

GC – Gas chromatography

FTIR – Fourier transform infrared spectroscopy

NMR – Nuclear magnetic resonance spectroscopy, usually of either proton, ^1H ;

and/or carbon 13, ^{13}C nuclei.

DSC – Differential scanning calorimetry

UV-Vis – Ultraviolet-Visible Spectroscopy

5 General Analytical Techniques Used for the Characterization: A variety of analytical techniques were used to characterize the co- and terpolymers of the present invention that included the following:

NMR: ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer with 5 mm probes at 400 and 100 MHz, respectively.

10 GPC: GPC was performed on a Waters gel permeation chromatograph equipped with refractive index detection.

GC: GC analysis was performed on a Hewlett Packard Model 5890 series II gas chromatograph equipped with a DB-1 column.

FTIR: FTIR was recorded on a Mattson Genesis Series FTIR.

15 DSC: A Perkin Elmer 7700 DSC was used to determine the T_g (glass transition temperature) of the co- and terpolymers of this invention. The heating rate was maintained at $10^\circ\text{C}/\text{minute}$, generally, over a temperature range of 50°C to 400°C . The flow rate of nitrogen or air is maintained at $20\text{ mL}/\text{min}$.

20 UV-Vis of samples were taken using a Hewlett Packard Vectra 486/33VL UV-Vis spectrophotometer.

Example 1

Poly(4-hydroxystyrene) in propyleneglycolmonomethyl ether acetate

To a four neck 12 liter flask, fitted with a mechanical stirrer, condenser, nitrogen inlet
25 and thermowell, 4-acetoxystyrene (2752.3 g, 16.97 moles), and methanol (3075.0 g) were added. The flask was purged with nitrogen and then heated to reflux (66°C) over a period of one hour. Then, 2,2'-azobis(2,4-dimethylvaleronitrile) (146.0 g, 0.59 moles) was added to the hot reactor as a slurry in methanol (250 g). The reactor was heated at reflux for 2 hours and then an additional charge of 2,2'-azobis(2,4-dimethylvaleronitrile) (24.3 g, 0.1 moles) was done. The
30 reactor was heated for an additional 6 hours and then was cooled to room temperature.

The solids were extracted by successive replacements of the solvent as follows. The reactor was heated to 60°C with stirring. The heat was removed and the reactor was allowed to cool without stirring to 44.3°C . The top layer (899 g) of solvent was removed by suction and

was replaced with methanol (1495 g). The reactor was again heated to 60 °C and cooled to 41.9 °C without stirring. The top layer (1700 g) was again removed by suction and was replaced with methanol (1705 g). The reactor was again heated to 60 °C and cooled to 46.2 °C without stirring. The top layer (1633 g) was again removed by suction and was replaced with methanol (1765 g). The reactor was again heated to 60 °C and cooled to 45.0 °C without stirring. The top layer (1905 g) was again removed by suction and was replaced with methanol (1955 g). The reactor was again heated to 60 °C and cooled to 46.0 °C without stirring. The top layer (2145 g) was again removed by suction and was replaced with methanol (2215 g). The reactor was again heated to 60 °C and cooled to 46.0 °C without stirring. The top layer (2241 g) was again removed by suction and was replaced with methanol (1700 g). All of the solids during each extraction were analyzed for molecular weight by GPC, table I. The reactor was then cooled to room temperature.

The purified poly(4-acetoxystyrene) was converted to poly(4-hydroxystyrene) as follows. The reactor was fitted with a Dean Stark trap and condenser. A solution of 25.0 weight percent of Sodium methoxide in methanol (64.24g, 0.30 moles) was added to the reactor. The reactor was then heated to reflux (64 °C). The overhead distillate was removed and replaced with methanol with equal weight. The reactor was heated at reflux for 7.5 hours. The reactor was then cooled to room temperature. This solution was then passed through a column of Amberlyst A15 (2" x 16") at 40 mL/min at room temperature to remove metal contamination.

The solvent was exchanged from methanol to propyleneglycolmonomethyl ether acetate (PGMEA) as follows. The solution was added to a 4 neck, 12 liter flask fitted with a distillation head and receiver, thermowell, mechanical stirrer, and nitrogen inlet. The reactor was heated to 25 °C to 48 °C under vacuum (120 torr to 10 torr) to remove methanol. To the reactor, a total of 4975 g PGMEA was added as the methanol was removed. The amount of solids present was determined by density and the solution was adjusted to 35.0 weight percent with PGMEA. An overall yield of 1634 g of polymer (81.7% theoretical yield) was obtained.

Example 2

Poly(4-hydroxystyrene) in propyleneglycolmonomethyl ether acetate

To a four neck 12 liter flask, fitted with a mechanical stirrer, condenser, nitrogen inlet and thermowell, 4-acetoxystyrene (2752.3 g, 16.97 moles), and methanol (3081.0 g) were added. The flask was purged with nitrogen and then heated to reflux (66 °C) over a period of one hour. Then, 2,2'-azobis(2,4-dimethylvaleronitrile) (146.1 g, 0.59 moles) was added to the hot reactor

as a slurry in methanol (250 g). The reactor was heated at reflux for 2 hours and then an additional charge of 2,2'-azobis(2,4-dimethylvaleronitrile) (24.4 g, 0.01 moles) was done. The reactor was heated for an additional 6 hours and then was cooled to room temperature.

The solids were extracted by successive replacements of the solvent as follows. The reactor was heated to 60 °C with stirring. The heat was removed and the reactor was allowed to cool without stirring to 45.0 °C. The top layer (1129 g) of solvent was removed by suction and was replaced with methanol (1817 g). The reactor was again heated to 60 °C and cooled to 47.0 °C without stirring. The top layer (1627 g) was again removed by suction and was replaced with methanol (1624 g). The reactor was again heated to 60 °C and cooled to 44.0 °C without stirring. The top layer (1668 g) was again removed by suction and was replaced with methanol (1613 g). The reactor was again heated to 60 °C and cooled to 47.0 °C without stirring. The top layer (1514 g) was again removed by suction and was replaced with methanol (1745 g). The reactor was again heated to 60 °C and cooled to 45.0 °C without stirring. The top layer (1822 g) was again removed by suction and was replaced with methanol (2288 g). The reactor was again heated to 60 °C and cooled to 43.0 °C without stirring. The top layer (22471 g) was again removed by suction and was replaced with methanol (1607 g). All of the solids during each extraction were analyzed for molecular weight by GPC, table 1. The reactor was then cooled to room temperature.

The purified poly(4-acetoxystyrene) was converted to poly(4-hydroxystyrene) as follows. The reactor was fitted with a Dean Stark trap and condenser. A solution of 25.0 weight percent of Sodium methoxide in methanol (64.24 g, 0.30 moles) was added to the reactor. The reactor was then heated to reflux (64 °C). The overhead distillate was removed and replaced with methanol with equal weight. The reactor was heated at reflux for 7.5 hours. The reactor was then cooled to room temperature. This solution was then passed through a column of Amberlyst A15 (2" x 16") at 40 mL/min at room temperature to remove metal contamination.

The solvent was exchanged from methanol to propyleneglycolmonomethyl ether acetate (PGMEA) as follows. The solution was added to a 4 neck, 12 liter flask fitted with a distillation head and receiver, thermowell, mechanical stirrer, and nitrogen inlet. The reactor was heated to 25 °C to 48 °C under vacuum (120 torr to 10 torr) to remove methanol. To the reactor, a total of 4000 g PGMEA was added as the methanol was removed. The amount of solids present was determined by density and the solution was adjusted to 35.0 weight percent with PGMEA. An overall yield of 1708 g of polymer (85.4% theoretical yield) was obtained.

Table 1. Molecular weight analysis of poly(4-acetoxystyrene) purification by extraction.

Sample	Example 1			Example 2		
	Weight average Molecular Weight	Number average Molecular Weight	Polydispersity	Weight average Molecular Weight	Number average Molecular Weight	Polydispersity
Original solid	9,556	5,083	1.88	8,866	4,501	1.97
1 st extraction	9,845	5,594	1.76	9,830	5,093	1.93
2 nd extraction	10,009	5,888	1.70	10,049	5,742	1.75
3 rd extraction	10,371	6,285	1.65	10,112	5,879	1.72
4 th extraction	9,921	6,162	1.61	10,327	5,969	1.73
5 th extraction	10,362	6,476	1.60	9,394	5,559	1.69

5

Example 3**Poly (hydroxystyrene-co-ethoxyethoxystyrene)**

To a 3L 4 neck round bottom flask containing 1.30 kg, 34.5 wt% polyhydroxystyrene solution in PGMEA, camphoresulphonic acid, 400mg was added under nitrogen atmosphere and the mixture was stirred at 23 °C for 2 hours for homogeneity. The solution was then cooled to 5 °C and 127 g, ethylvinylether was added drop wise with stirring under nitrogen at the reaction temperature between 5 °C to 10 °C (2 hours). After the addition, the mixture was stirred for additional 6 hours at 5 °C. Amberlyst A-21, 33 g which was pretreated with PGMEA was added to the reaction mixture and stirred for 2 hours at 25 °C. The resin was removed by filtration and 1.43 kg, 39.3% poly (hydroxystyrene-co-ethoxyethoxystyrene) copolymer solution was obtained. The characterization of the copolymer and the ratio determination were done by NMR. Hydroxystyrene/ethoxyethoxy-styrene ratio was determined to be 60/40, molecular weight was determined by GPC (polystyrene standard) to be Mw=10,819 with the polydispersity 1.77.

20

Example 4**Poly (hydroxystyrene-co-t-butoxycarbonyloxystyrene)**

To a 2L round bottom flasks containing 1.03 kg, 35.1 wt% polyhydroxystyrene solution in PGMEA, p-dimethylaminopyridine, 0.72 g in 11 g PGMEA was added under nitrogen and the mixture was stirred at 23 °C for one hour. Di-t-butyl dicarbonate, 124.4 g was added to the solution at 23 °C and stirred under nitrogen for 6 hours at 23 °C. Vacuum was applied to the solution at 20 mmHg with stirring for 1 hour at 23 °C for removal of carbon dioxide formed as a by-product in the solution. Dowex Mac-3, 30 g which was pretreated with PGMEA was added to

the reaction mixture and stirred for 2 hours at 23 °C. The resin was removed by filtration and 1.14 kg, 36.6 wt% poly (hydroxystyrene-co-t-butoxycarbonyloxystyrene) copolymer solution was obtained. The characterization of the copolymer and the ratio determination were done by NMR. Hydroxystyrene/t-butoxycarbonyloxystyrene ratio was determined to be 82/18, molecular weight was determined by GPC to be Mw=11,711 with polydispersity 1.67.

Example 5

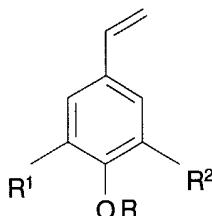
The following example illustrates the use of the method of this invention on the purification of a copolymer of 4-acetoxystyrene/tert.-butyl acrylate. 3282.8 g 4-acetoxystyrene, and 254 g tert.-butyl acrylate is polymerized in 3140 g methanol using 204.3 g tert.-butyl peroxyvalate as a catalyst. A sample of the polymer is isolated for analytical purposes. After polymerization was complete, 1390 g of methanol was removed at 58 °C. and replaced with 1392 g of fresh methanol. The slurry was heated to reflux and cooled to 48 °C. Another 1595 g of methanol was removed and replaced with 1590 g of fresh methanol. Again the slurry was heated to reflux and cooled. The methanol was removed and replaced with 1800 g of fresh methanol and the mixture was then transesterified with 39.8 g sodium methoxide. The polydispersity value of the purified polymer is 12% lower than the value of the crude polymer.

While specific reaction conditions, reactants, and equipment are described above to enable one skilled in the art to practice the invention, one skilled in the art will be able to make modifications and adjustments which are obvious extensions of the present inventions. Such obvious extensions of or equivalents to the present invention are intended to be within the scope of the present invention, as demonstrated by the claims which follow.

CLAIMS

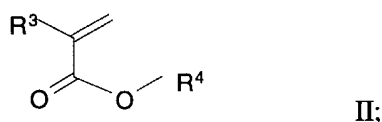
What is claimed is:

1. A method of purifying crude polymers derived from acyloxystyrene or alkoxy styrene of the group consisting of



wherein R is either $-C(O)R^5$ or $-R^5$; as a homopolymer or a copolymer with one or more of the following monomers:

an acrylate monomer having the formula II,



and/or with one or more ethylenically unsaturated copolymerizable monomers taken from the group consisting of styrene, 4-methylstyrene, styrene alkoxide wherein the alkyl portion is $C_1 - C_5$ straight or branch chain, tert.-butylstyrene, cyclohexyl acrylate, tert.-butyl acrylate, tert.-butyl methacrylate, maleic anhydride, dialkyl maleate, dialkyl fumarate and vinyl chloride, wherein:

- i) R^1 and R^2 are the same or different and independently selected from the group consisting of:
 - hydrogen,
 - fluorine, chlorine, bromine,
 - alkyl and fluoroalkyl group having the formula $C_nH_xF_y$ where n is an integer from 1 to 4, x and y are integers from 0 to $2n+1$, and the sum of x and y is $2n+1$,
 - phenyl, and tolyl;
- ii) R^3 is selected from the group consisting of:
 - hydrogen,
 - methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, and tert.-butyl;
- iii) R^4 is methyl, ethyl, n-propyl, iso-propyl, n-butyl, i-butyl, tert.-butyl, t-amyl, benzyl, cyclohexyl, 9-anthaceny, 2-hydroxyethyl, cinnamyl, adamantyl, methyl or ethyl or hydroxyl adamantyl, isobornyl, 2-ethoxyethyl, n-heptyl, n-hexyl, 2-hydroxypropyl, 2-ethylbutyl, 2-methoxypropyl, 2-(2-methoxyethoxyl), oxotetrahydrofuran,

hydroxy trimethylpropyl, oxo-oxatricyclo non yl, 2-naphthyl, 2-phenylethyl, phenyl.
and mixtures thereof; and

iv) R⁵ is C₁-C₄ alkyl

consisting essentially of subjecting said crude polymer, after polymerization thereof, to a fractionalization procedure wherein said crude polymer in an alcoholic solvent is (a) suspended therein and additional solvent is added, (b) heated and/or stirred for a sufficient period of time to permit dissolution of the undesirable monomeric impurities and oligomers in said crude polymer, (c) cooling the resultant mixture, (d) separating the alcoholic solvent from said polymer and (e) repeating said steps (a) – (d) until the polydispersity value of the purified polymer is about 10% less than that polydispersity value of the crude polymer.

2. The process as set forth in claim 1 wherein the solvent is selected from the group consisting of methanol, ethanol, propanol, isopropanol, t-butanol and mixtures thereof.

3. The process as set forth in claim 1 wherein the acyloxystyrene is acetoxystyrene monomer and is the only monomer used.

4. The process as set forth in claim 3 wherein the acetoxystyrene polymer in purified form has a polydispersity value of less than 2.0.

5. The process as set forth in claim 4 wherein the solvent is methanol.

6. The process as set forth in claim 1 wherein after said polymerization and fractionalization, there is an additional step of transesterification of the purified polymer which is conducted by adding additional alcoholic solvent and in the presence of catalytic amounts of a catalyst.

7. The process as set forth in claim 6 wherein after the transesterification step, there is an additional step of removing the catalyst from the reaction mixture of the transesterified product in said alcoholic solvent by passing said mixture through an ion-exchange bed in order to remove said catalyst therefrom.

8. The process as set forth in claim 7 wherein the entire process is conducted on an anhydrous basis.

9. The process as set forth in claim 8 wherein in step (e) the fractionalization is conducted from about 2 to about 10 times.

10. The process as set forth in claim **9** wherein after the catalyst removal step, there is an additional step wherein said alcoholic solvent is removed and replaced by a photoresist compatible solvent.

11. The process as set forth in claim **10** wherein the photoresist compatible solvent is selected from the group consisting of glycol ethers, glycol ether acetates, aliphatic esters having no hydroxyl or keto group, and mixtures thereof.

12. The process as set forth in claim **11** wherein the photoresist compatible solvent is either propylene glycol monomethyl ether acetate or ethyl lactate.

13. A method of purifying crude polymers consisting essentially of subjecting said crude polymer, after polymerization thereof, to a fractionalization procedure wherein said crude polymer in an alcoholic solvent is (a) suspended therein and additional solvent is added thereto, (b) heated and/or stirred for a sufficient period of time to permit dissolution of the undesirable monomeric and oligomers in said crude polymer, (c) cooling the resultant mixture, (d) separating the alcoholic solvent from said polymer and (e) repeating said steps (a)-(d) until the polydispersity value of the purified polymer is about 10% less than that polydispersity value of the crude polymer.

14. The process as set forth in claim **13** wherein the solvent is selected from the group consisting of methanol, ethanol, propanol, isopropanol, t-butanol and mixtures thereof.

15. The process as set forth in claim **14** wherein there is an additional step wherein said alcoholic solvent is removed and replaced by a photoresist compatible solvent.

16. The process as set forth in claim **13** wherein the crude polymer is derived from a monomer or combination of monomers selected from the group consisting of vinyl acetate, acrylics, styrenes, styrenes-acrylics, olefins, acrylonitrile, maleic anhydride, and mixtures thereof.

17. The process as set forth in claim **13** wherein after the purification step the alcoholic solvent containing said purified polymer is removed and replaced by a photoresist compatible solvent which is selected from the group consisting of glycol ethers, glycol ether acetates, aliphatic esters having no hydroxyl or keto group, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/11262

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08F6/04 C08J3/09

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 C08J

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02 00736 A (TRIQUEST LP) 3 January 2002 (2002-01-03) claim; example page 1, line 28 - page 2, line 16 page 5, line 18 - page 6, line 12	1-17
X	US 5 625 007 A (SHEEHAN MICHAEL T ET AL) 29 April 1997 (1997-04-29) claims; example 57 column 3, line 14 - line 67 column 7, line 1 - line 30 column 10, line 36 - line 41	1-17
X	WO 01 40321 A (TRIQUEST LP) 7 June 2001 (2001-06-07) abstract; claims; examples	1,6-13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

30 July 2003

Date of mailing of the international search report

06/08/2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/11262

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 99 57163 A (TRIQUEST LP) 11 November 1999 (1999-11-11) abstract; claims -----	1

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