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(54) Title: PURIFICATION MEANS

(57) Abstract: Polymers containing 4-alkoxystyrene are purified by multiple slurrying of the polymer in methanol.

TITLE

PURIFICATION MEANS

BACKGROUND OF THE INVENTION

Copolymers and terpolymers, when isolated from reaction solution are a mixture of 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 non-solvent, as for example water, hexane, heptane, octane, petroleum ether, or a mixture thereof. The polymer is then dried in air or a nitrogen atmosphere. The subject of this invention 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.

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

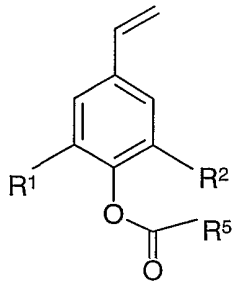
The present invention provides a novel process for improving the glass transition temperatures of polymer intermediates that have been polymerized by precipitation from methanol. The polymers that are susceptible to treatment with the method of this invention are polymers of 4-alkoxystyrene. The 4-alkoxystyrene

polymers are then hydrolyzed or transesterified to 4-hydroxystyrene–containing polymers useful in paints, resins, thickening agents, and in photoresist compositions. The 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. Many analytical methods can be utilized to quantify the improvement in the purity of polymers. Average molecular weight, nuclear magnetic resonance, chromatography, and glass transition temperature are all effective in certain instances with certain molecules and characteristic side chains.

As previously described, 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 reslurried in methanol and the solid is separated from the methanol. This procedure is repeated as long as necessary to remove by-products and low molecular weight materials that are more soluble in the methanol than the desired polymer.

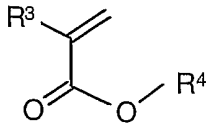
DETAILED DESCRIPTION OF THE INVENTION

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



I;

as a homopolymer and/or typically with one or more of the following monomers: an acrylate monomer having the formula II,



II;

and/or with one or more ethylenically unsaturated copolymerizable monomers i. e.; styrene, 4-methylstyrene, tert.-butylstyrene, cyclohexyl acrylate, tert.-butyl acrylate, tert.-butyl methacrylate, maleic anhydride, dialkyl maleate, dialkyl fumarate and vinyl chloride, and the like.

wherein:

i) R^1 and R^2 may be the same or different and independently selected from the group consisting of:

hydrogen;

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 may be selected from the group consisting of:

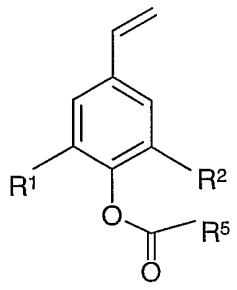
hydrogen; and

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

iii) R^4 may be methyl, ethyl, n-propyl, iso-propyl or tert.-butyl; and

iv) R^5 may be methyl or ethyl and alkyl is having 1 to 4 carbon atoms,

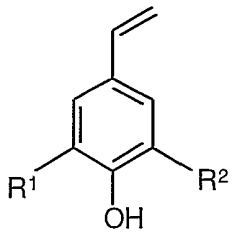
typically manufactured by subjecting a monomer of formula I,



I;

or a monomer of the formula I and/or monomer II, and/or one or more of said copolymerizable monomers 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 polymer of corresponding composition . After purification by the method of this invention the purified polymer is hydrolyzed or transesterified to a polymer containing the monomer of formula III:



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, II, and said copolymerizable monomer, 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;

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 peroxypivalate, t-amyl peroxypivalate, diisononanoyl 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, 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 peroxypivalate, t-amyl peroxypivalate, 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.

In step (1), in a transesterification, the crude polymer from step (a) is subjected to said transesterification conditions in an alcoholic solvent in the presence of catalytic amounts of a base catalyst. The base catalyst is such that it will not substantially react with said alkyl acrylate monomer II, or with said co-polymerizable monomers. 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.

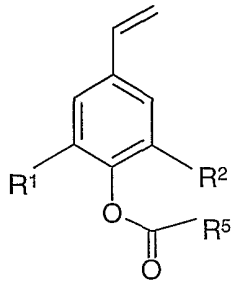
According to the method of this invention, after complete polymerization of the alkoxystyrene-containing polymer, and prior to the hydrolysis or transesterification the crude polymer is slurried in methanol. The slurry is then stirred vigorously or is heated to boiling for several minutes and then chilled or allowed to stand until cool. The purified polymer is removed by centrifugation, filtration, decantation, or by similar means, and the process is repeated until no further purification is identified, as for example, until a small sample of the decanted methanol upon evaporation to dryness shows no residue.

Example

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 peroxypivalate 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.

What is claimed is:

1. A method of purifying crude polymers containing alkoxystyrene of the group consisting of



I;

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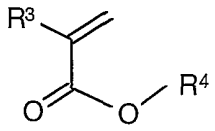

II;

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hydrogen;

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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 may be selected from the group consisting of:

hydrogen; and

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

iii) R^4 may be methyl, ethyl, n-propyl, iso-propyl or tert.-butyl; and

iv) R^5 may be methyl or ethyl, and wherein alkyl is having 1 to 4 carbon atoms consisting of slurrying the polymer is methanol, heating or stirring the slurry, and removing the methanol to provide a purified product.