Synthesis and Application of Water-Soluble Hyperbranched Poly(ester)s from Maleic Anhydride and Glycerol

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ABSTRACT: A water-soluble hyperbranched polyester with a considerable number of hydroxyl terminal groups was synthesized by reacting maleic anhydride and glycerol in the absence of a solvent. The synthesized intermediate product was converted to the hyperbranched polyester by condensation polymerization, and the water by-product produced during the esterification reaction may be removed by vacuum distillation. In the synthesis process, the crosslinking reaction occurs readily if maleic anhydride is in excess. The result shows that the product synthesized by this one-step method is insoluble in water at room temperature, whereas the product of a quasi one-step method, in which pentaerythritol was added as a core molecule, has good water solubility when pentaerythritol and the raw material have a molar ratio of 1 : 100 or 1 : 150. The resulting hyperbranched polyester was purified by column chromatography and characterized by infrared spectrometry. The synthetic hyperbranched polyester was used at 0.5% as a crosslinking agent for acrylic ester to inform acrylic ester latex film; the water absorption of the film was decreased significantly, the viscosity was increased, and some mechanical properties were improved. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3376–3381, 2009

Key words: hyperbranched polyester; water solubility; synthesis; crosslinking agent; acrylic ester latex

INTRODUCTION

Hyperbranched polymers have attracted a great deal of attention in the macromolecule field due to their peculiar structures, unique properties, and potential applications.[1] The simple preparation method and so many outstanding properties, such as highly branched degree, highly reactive characteristic, and ball-shaped molecules structure, make hyperbranched polymers have good solubility and low viscosity. These advantages are causing people to pay more attention to further studies in different fields.

The solubility of hyperbranched polymers is determined to a large extent by the terminal structures. A large amount of terminal polar groups make the hyperbranched polymer have good solubility in some polar solvents, such as *N*,*N*-dimethylformamide, ethanol, pyridine, etc. Most of the hyperbranched polyesters that have been synthesized are water insoluble.[2–8] The hyperbranched polymers that are water-soluble are due to the amount of terminal hydrophilic groups, such as carboxyl, hydroxyl, amido, ether group, etc.; for example, the highly polar terminal groups of carboxylic acid can make the hyperbranched polyphenyl water-soluble. The number of the hydrophilic groups can be adjusted by controlling the reaction conditions. Increasing the degree of branching of the product through core molecule is also an effective method.[9–12] Hyperbranched polyesters have been used as crosslinking agents for polyurethane[13,14] and also to improve the properties for coatings. Wang et al. synthesized a kind of water-soluble hyperbranched polyester and used it as comonomer for preparing acrylic latex; the hardness and stability of the latex film was increased.[15]

It has not been reported that hyperbranched polyester is used as a crosslinking agent for acrylic ester latex. In this work, a kind of water-soluble hyperbranched polyester was synthesized from commercially available monomers and was used as a crosslinking agent of acrylic ester latex; the mechanical properties of latex film were improved.

EXPERIMENTAL

Materials

Maleic anhydride and glycerol were purchased from Shenyang Xinxi Reagent Co. (Shenyang, China).

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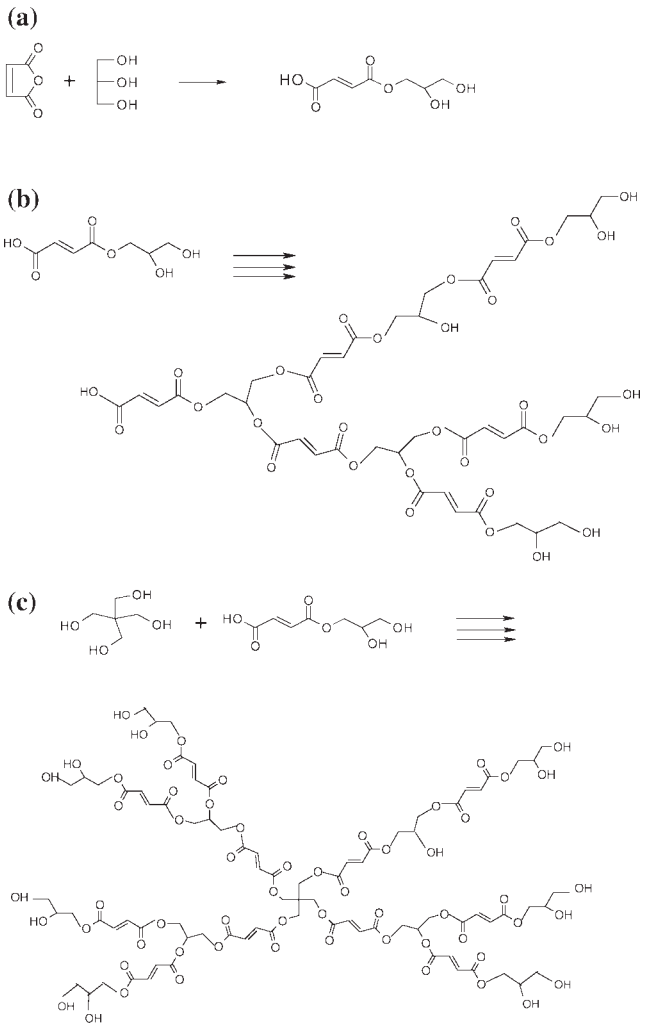

Figure 1 Schematic of the synthesis of (a) the intermediate and (b and c) the hyperbranched polyester.

Pentaerythritol, methyl acrylate, and butyl acrylate were purchased from Shanghai First Reagent Co. (Shanghai, China). All chemicals were used as received.

The acrylic ester latex was prepared by the preemulsification semicontinuous seeded emulsion polymerization method, with methyl acrylate, butyl acrylate, and 2% acrylic acid monomers, and a mixed emulsifier of sodium dodecylsulphate and the nonionic detergent OP-10 (Nikko Chemicals, Tokyo, Japan).

Synthesis of the water-soluble hyperbranched polyester

In the first step, maleic anhydride and glycerol were placed into a three-necked glass reactor flask fitted with a gas inlet pipe for N_2. The mixture of materials was melted at 65°C (above the 60°C melting point of maleic anhydride) under N_2 with constant stirring for 1 h, so that the maleic anhydride was dissolved completely in the glycerol and the solution was completely clear. The reaction is shown schematically in Figure 1(a).

In the second step, the temperature was kept at 100°C for 2 h, 120°C for 2 h, and 140°C for 4 h, while the pressure was reduced to 100 mbar (1 bar = 10^5 Pa). The water formed during the reaction was removed by distillation to increase the esterification conversion yield. This method was termed "one-step method." The structural diagram of the product is shown in Figure 1(b).

As an alternative to the one-step method, hyperbranched polyester was synthesized by a quasi one-step method. Pentaerythritol dissolved in 5 mL of water was added to the intermediate, and the mixture was stirred until the system appeared homogeneous. The hyperbranched polyester was synthesized through esterification and vacuum distillation as described above. The ideal molecular formula of the hyperbranched polyester is shown in Figure 1(c).

Measurements

The hyperbranched polyester was purified by column chromatography using aluminum oxide and silica gel as the fixed phase, and ethanol as the mobile phase.

The infrared (IR) measurements were made with a Bruker-Tensor 27 Fourier transform IR spectrometer.

The molecular mass and its distribution of the hyperbranched polyester were obtained on the HP 1100 gel-permeation chromatograph [G6000 PW (XL) column] with water as the solvent and poly(ethylene oxide) as the standard sample.

Surface morphology of acrylic ester latex film was analyzed by using scanning electron microscopy (JEOL JSM-6360LA; Japan) operating at accelerating voltages of 15 kV.

The intrinsic viscosity of hyperbranched polyester solution was determined by using an Euler viscometer at 25°C. The dynamic viscosity was measured with NDJ-99 rotation-viscometer, and the temperature was increased gradually from 20 to 75°C.

The solubility of the synthetic hyperbranched polyester in solvents, such as water, acetone, ethanol, tetrahydrofuran, methylbenzene, chloroform, *N*,*N*-dimethyl formamide, etc., was investigated.

TABLE I
The Appearance of the Polyester at Different Feed Ratios

Sample	Molar ratio[a]	Yield (%)	Appearance of the product
1	1 : 1	88.0	Light color and transparent
2	2 : 3	89.2	Light color and transparent
3	3 : 2	–	Gelation

[a] Maleic anhydride/glycerol.

TABLE II
The Influence of the Amount of Pentaerythritol on the Solubility of the Product

Sample	Molar ratio of pentaerythritol to raw material	Yield (%)	$M_n \times 10^3$	$M_w \times 10^3$	PDI	Appearance of the product	Water solubility at 25°C g/L
4	0 : 1	88.0	14.3	30.0	2.1	—	0.0
5	1 : 50	88.5	12.8	70.4	5.5	High-viscosity, films are formed on the surface	0.0
6	1 : 100	84.5	11.0	118.8	10.8	Low-viscosity, light color and transparent	120.7
7	1 : 150	85.7	8.7	138.3	15.9	Low-viscosity, light color and transparent	120.0
8	1 : 175	79.6	4.1	82.0	20.0	Low-viscosity, light color and transparent	5.2
9	1 : 200	78.6	3.2	85.4	26.7	Low-viscosity, light color and transparent	3.8

RESULTS AND DISCUSSION

The synthetic reaction influence factors

A homogeneous, transparent, and stable product could be obtained by vacuum distillation to remove the water continuously. If the product still contained water at the end of the reaction, an ester hydrolytic degradation reaction occurred after a period of time, and, after about 2–3 days, the product was in a white turbid state.

The effect of reactant feed ratio on product behavior was studied. Table I shows that crosslinking reaction occurred readily when maleic anhydride was in excess. This is because the excess maleic anhydride was likely to react with the many terminal hydroxyl groups of the hyperbranched polyester. However, the crosslinking reaction did not occur when glycerol was in excess, because the temperature required is >260°C for the hydroxyl intermolecular dehydration reaction, and the system is unable to satisfy the request. The product appeared white, turbid, and unstable when glycerol was excessive.

The solubility of the product

The water solubility of the synthetic hyperbranched polyester obtained by the one-step method (Table I) was poor; yet, a quasi one-step method was adopted, using pentaerythritol as a core molecule to enhance the degree of branching of the product and to increase the amount of terminal hydroxyl groups. The effect of different feed ratios of pentaerythritol to raw material on the solubility of the product is shown in Table II. The molar ratio of maleic anhydride to glycerol was 1 : 1, and pentaerythritol dissolved in 5 mL of water was added. Samples in Table II form a creamy white emulsion in water at room temperature if an extra sample (1.0 g) more than the solubility was added in 1 L water. When the temperature was increased to 50°C, the product dissolved completely in water; but, as the temperature was decreased, the white turbidity appeared again. In water at room temperature, the product is in a coiled state and is insoluble, owing to the long ester bond chains, easily coiled, a number of polar groups are enclosed by nonpolar molecular chains. The molecular chains stretch out gradually when heated, exposing the polar hydroxyl groups to the solvent, making the product soluble in water. Only when the molar ratio of pentaerythritol to raw material was 1 : 100 or 1 : 150 did the product has better water solubility at room temperature, which can be explained as follows.

With the amount of pentaerythritol increased, the degree of branching and the amount of terminal hydroxyl groups of the product increased, so that the water solubility increased. But with the molar ratio of pentaerythritol to raw material increased further, the molecular mass of the product decreased, and the amount of terminal hydroxyl groups of the product and the water solubility decreased also.

The solubility of the hyperbranched polyester in organic solvents was also studied. Sample 1 in Table I (synthesized by the one-step method) and Sample 6 in Table II (synthesized by the quasi one-step method) were chosen to test the solubility of the

TABLE III
The Solubility of the Hyperbranched Polyester

	Solubility at 25°C in different kind of solvent (g/L)							
Sample	Acetone	Alcohol	Tetrahydrofuran	Methylbenzene	Chloroform	*N*,*N*-Dimethyl formamide	*N*,*N*-Dimethyl acetamide	Ethyl acetate
1	10.6	83.7	0.0	0.0	0.0	151.3	126.0	12.8
6	11.4	147.5	0.0	0.0	0.0	172.0	133.9	13.2

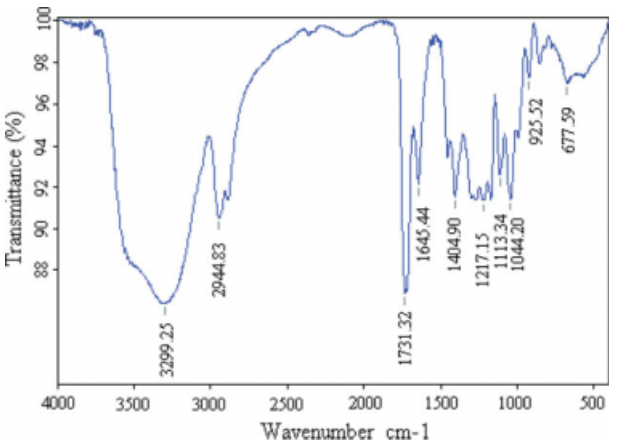

Figure 2 The IR spectrum of the synthetic hyperbranched polyester. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hyperbranched polyester in some common organic solvents; the results are shown in Table III. The product contains a large number of polar groups; it can dissolve readily in polar organic solvents; and it has better solubility in solvents such as *N*,*N*-dimethyl formamide and *N*,*N*-dimethyl acetamide, which have a stronger polarity than that of water, allowing a stronger interaction with the polar groups of the product. The product is soluble in some nonpolar solvents, such as acetone and ethyl acetate, which may be due to interaction between the ester bonds and the nonpolar groups of the solvent.

IR spectrum of the hyperbranched polyester

The IR spectrum of the purified sample (Sample 6 in Table II) in Figure 2 shows a peak for the hydroxyl groups at 3299 cm^{-1} and peaks for the carbonyl groups at 1731, 1217, and 1113 cm^{-1}. The peak at 1044 cm^{-1} is attributed to the C—O groups; the peak at 1645 cm^{-1} is attributed to the C=C groups; and the peaks at 926 and 677 cm^{-1} are ascribed to the

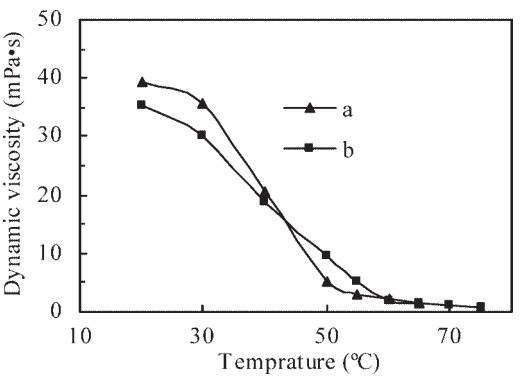

Figure 3 The viscosity–temperature curve of the hyperbranched polyester.

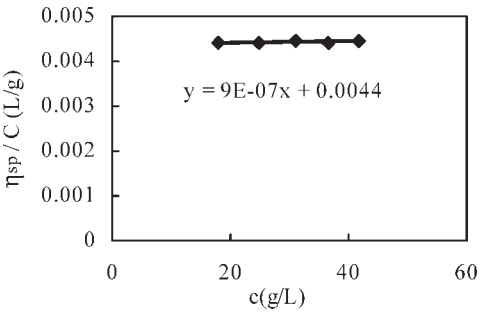

Figure 4 Relationship between η_{sp}/c and the polymer concentration (c) at 25°C in water.

trans C—H and the *cis* C—H groups, respectively. The IR spectrum of the product is in agreement with the target hyperbranched polyester. Figure 2 shows that the absorption peaks of the product are broadened, which may be due to the hydrogen bond formed between the many terminal hydroxyl groups of the product. On the other hand, the stretching vibration peak is broadened also if there are C=O and C=C bonds are in the conjugated form.

Viscosity behavior of the product

The viscosity–temperature relationship of the product, with the feed ratio of raw material to pentaerythritol of 100 : 1 (curve a) or 150 : 1 (curve b), was determined; the results are shown in Figure 3.

The viscosity decreased rapidly with increasing temperature up to 60°C and was nearly constant above that temperature. This could be because coiled chain with ester bonds has not been stretched out in the lower temperature range and the product represented a high level of viscosity. As the temperature increased gradually, the coiled chain with ester bonds stretched piece by piece, and the viscosity is decreased rapidly. As temperature increased beyond 60°C, the coiled chain was stretched nearly completely, hence the viscosity was constant.

The viscosity of linear macromolecules varies greatly with molecular mass, and the viscosity of hyperbranched polyester macromolecules does not change very much due to their ball-shaped molecular structure. After all, the molecular

TABLE IV
The Effects of Content of the Hyperbranched Polyester on the Viscosity and Water Absorption of Acrylic Ester Latex Film

Run	c (%)	v at 25°C (mP S)	Water absorption (%)
1	0	79	40.0
2	0.5	120	12.5
3	1.0	103	36.7
4	1.5	89	52.1
5	2.0	68	52.7

TABLE V
The Effect of the Added Crosslinking Agent on the Mechanical Properties of Acrylic Ester Latex Film

No.	Crosslinking agent at 0.5%	Tensile strength (MPa)	Fracture strength (kN/m)	Strength retention after immersion in water (%)	Extension (%)
1	No	0.67	3.05	65	580
2	Yes	1.73	16.58	89	610

hydromechanics radius of hyperbranched polymers does not change by much with an increased molecular mass. The intrinsic viscosity of Sample 6 in Table II was determined. Figure 4 illustrates the relationship between reduced viscosity (η_{sp}/c) and polymer concentration (c). The solution viscosity of hyperbranched polymers is well known to be very low, due to the lack of intermolecular entanglement. Figure 4 shows that the η_{sp}/c-c curve is nearly parallel with the horizontal ordinate; therefore, we can obtain the following equation approximately:

$$\eta_{sp}/c[\eta] \quad (1)$$

The value of η_{sp}/c was independent of c; that is, the viscosity of the polymer was not increased along with the solution concentration increased, indicating little interaction between the polymer molecules.

The use of a hyperbranched polyester as a crosslinking agent for acrylic ester latex

Hyperbranched polymers can be used as crosslinking agents due to their large number of active end groups. The effects of varying the content of hyperbranched polyester (Sample 6 in Table III) on the viscosity and water absorption of acrylic ester latex film are shown in Table IV. On one hand, when the content of hyperbranched polyester was less than 0.5%, it acted as a crosslinking agent. When the content was greater than 0.5%, however, the viscosity of the system decreased due to the spherical molecular structure of the hyperbranched polyester. On the other hand, when the content of hyperbranched polyester was less than 0.5%, the hydroxyl groups in the hyperbranched polyester molecules reacted readily with the —COOH and —COOR groups in the latex, which improved the waterproofness and decreased the water absorption. However, when the content of hyperbranched polyester was increased further, the unreacted hydrophilic hydroxyl groups increased the water absorption of the latex film.

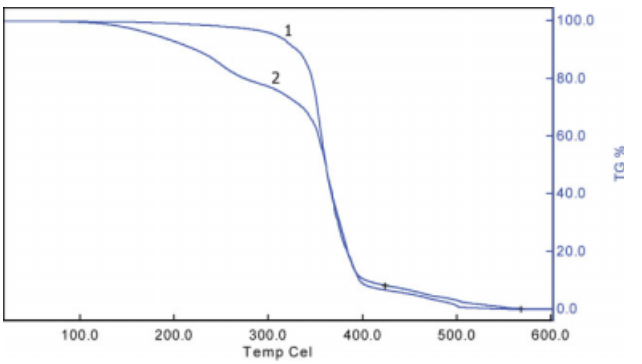

Figure 5 Thermogravimetry of the latex film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The mechanical properties of acrylic ester latex (Runs 1 and 2 in Table IV) are shown in Table V, where it can be seen that the tensile strength, fracture strength, and the strength retention after immersion of the latex film in water are all increased when the amount of crosslinking agent achieved 0.5%; however, the extension does not change very much. These results indicate that the mechanical properties of the polymer latex film are increased due to the chemical crosslinking.

The thermogravimetry curves of the acrylic ester latex film by itself (curve 2) and with 0.5% crosslinking agent (curve 1) are shown in Figure 5, where it

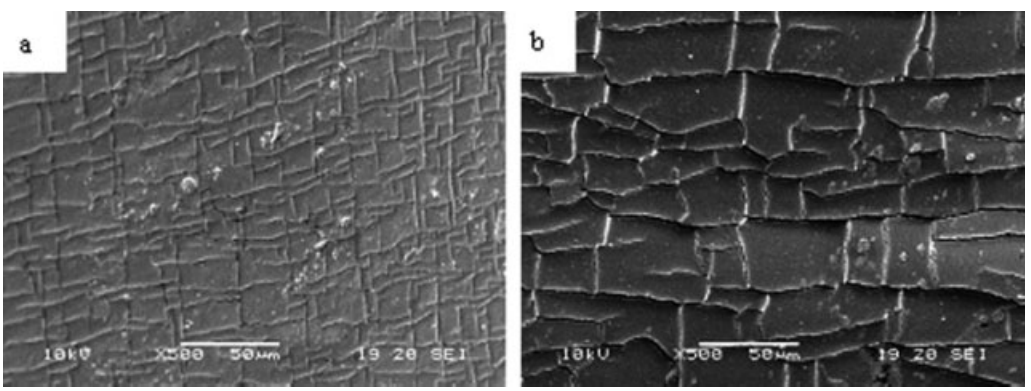

Figure 6 SEM photographs for surfaces of (a) acrylic ester latex film crosslinked with 0.5% hyperbranched polyester reacted at 90°C; (b) acrylic ester latex film alone.

can be seen that the thermal stability of the film is increased by the addition of the crosslinking agent.

Figure 6 shows SEM micrographs of the acrylic ester latex film with 0.5% crosslinking agent [Fig. 6(a)] and acrylic ester latex by itself [Fig. 6(b)]. It can be seen clearly that the cracks of adding crosslinking agent [Fig. 6(a)] are much narrower than those of no adding [Fig. 6(b)], indicating a fine and close texture due to the hyperbranched polyester crosslinking agent.

CONCLUSION

The hyperbranched polyester was synthesized with maleic anhydride, glycerol, and pentaerythritol, either by the one-step method or quasi one-step method. The solubility of the product in water and in organic solvent was studied, and the use of the product as crosslinking agent of the acrylic ester latex was also investigated.

First, the intermediate was synthesized by reacting maleic anhydride and glycerol, without solvent; the molar ratio of maleic anhydride and glycerol of 1 : 1 was chosen to avoid the occurrence of crosslinking. The water by-product was removed by vacuum distillation. In the one-step method, the synthesized intermediate was converted to the hyperbranched polyester by condensation polymerization. It was shown that the product was insoluble in water at room temperature and had good solubility in water when temperature was above 50°C and stronger polarity in solvent. In the quasi one-step method, to enhance the degree of branching of the product and the amount of terminal hydroxyl groups, pentaerythritol was added to the synthesized intermediate as a core molecule so that the product would have good water solubility at room temperature when the molar ratio of pentaerythritol to raw material was 1 : 100 and 1 : 150. Viscosity varying behavior of the water-soluble hyperbranched polyester was analyzed; the viscosity decreased rapidly with increasing temperature up to 60°C and was hereof constant above that temperature. The value of η_{sp}/c was independent of c.

The use of the synthesized, water-soluble, hyperbranched polyester as a crosslinking agent for acrylic ester latex was studied. When the amount of the hyperbranched polyester was 0.5%, the viscosity of the latex increased, and the water absorption of acrylic ester latex film decreased, the mechanical properties of the latex film were increased due to the chemical crosslinking.

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