Synthesis and Characterization of a Hyperbranched Polyol with Long Flexible Chains and Its Application in Cationic UV Curing

XIAOYIN HONG, QIDAO CHEN, YUEMEI ZHANG, GUANGRONG LIU

Department of Chemistry, Tsinghua University, Beijing, 100084, People's Republic of China

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ABSTRACT: A hyperbranched polyol with long flexible chains on the molecule surface was synthesized and characterized. The effect of the hyperbranched polyol as flexibilizer and chain-transfer agent on cationic UV curing was investigated. It was found the hyperbranched polyol could markedly improve the mechanical properties of cured film. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1353–1356, 2000

Key words: hyperbranched polyol; flexible chains; cationic UV curing; chain-transfer agent; flexibilizer

INTRODUCTION

Since the discovery of dendrimers and hyperbranched polymers in the early 1980s by Tomalia[1] and Newkome,[2] the research of dendrimers and hyperbranched polymers has become an attractive field. Dendrimers and hyperbranched polymers are globular macromolecules, having a highly branched structure, in which many generations of repeating monomers ABx ($x \geq 2$) converge to a core. They have unique three-dimensional symmetrical structure, shape, branching pattern, and a low amount of intermolecular or intramolecular entanglements. Subsequently, dendrimers and hyperbranched polymers have much lower viscosity and higher solubility than the linear counterparts, which makes them interesting for coating applications. Additionally, there is a large number of end groups on the molecule surface of dendrimers and hyperbranched polymers. Therefore, dendrimers and hyperbranched polymers possess high activity, and it is possible to modify for different purposes.[3]

Dendrimers and hyperbranched polymers have also been introduced into the field of UV curing to improve the activity of the formulations and the properties of cured film. For instance, M. Johansson synthesized a series of acrylate functional hyperbranched polyester resins, which were all free radically UV cured with little or no oxygen inhibition found.[4] W. F. Shi investigated the photopolymerization of dendritic methacrylated polyesters, including the synthesis, properties, characteristics, and kinetics.[5] But there are few reports about the application of dendrimers and hyperbranched polymers in cationic UV curing. In our present work, a hyperbranched polyol with long flexible chains on the molecule surface was synthesized and characterized. The effect of the hyperbranched polyol as flexibilizer and chain-transfer agent on cationic UV curing was investigated.

EXPERIMENTAL

Spectra

^{1}H-NMR spectra were recorded on a Bruker 250 MHz with $CDCl_3$ as solvent and the chemical

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Correspondence to: X. Hong (hongxy@mail.tsinghua.edu.cn).

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shifts were reported in ppm downfield relative to internal tetramethylsilane. IR spectra were measured on SHINADZU IR-408 infrared spectrometer.

Materials

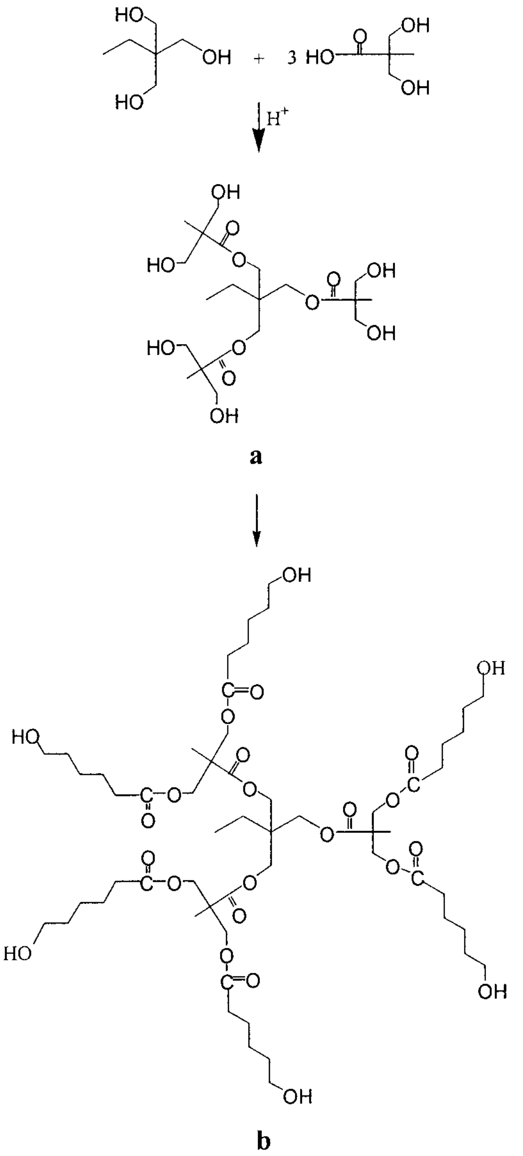
2,2-Bis(hydroxymethyl) propionic acid (bis-MPA) and ϵ-caprolactone were purchased from Aldrich. 3,4-Epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (Cy179) and 1-hydroxylcyclohexyl phenyl acetone (Irgacure 184) was supplied by Ciba-Geigy. SR015 leveling agent F of Sartomer Co. was adopted to improve the flowability. Bisphenol A epoxy resin E51 was obtained from the Institute of Chemistry, Chinese Academy of Science. Dibutyltin dilaurate was supplied by the Third Chemical Factory of Beijing. All the above materials were used as received. 2-ethyl-2- (hydroxymethyl)-1,3-propanediol (TMP) was dried to constant weight before use. All solvents were distilled before use. Diphenyl iodonium hexafluorophosphate was synthesized according to the literature.[6]

Synthesis

The synthesis route of the hyperbranched polyol with long flexible chains is shown in Scheme 1. TMP (0.05mol, 6.71 g), bis-MPA (0.15mol, 20.12 g), and p-toluenesulfonic acid (0.07 g) were carefully mixed in a three-necked flask equipped with a mechanical stirrer, a drying tube, and a nitrogen inlet. The flask was placed in an oil bath previously heated to 140°C. The mixture was left to react with a flow of nitrogen to remove the water, which was formed during the esterification reaction. Five hours later, the nitrogen flow was removed and the flask was connected to a vacuum line (15 mm Hg) to continue the reaction for 2 h. After the removal of vacuum line, toluene (20 mL) was added to the mixture to remove the residual water by distillation. After drying of the obtained white and viscous mixture at 15 mm Hg, ϵ-caprolactone (0.30 mol, 34.2 g) and dibutyltin dilaurate (0.012 wt %) were added to the mixture, and reacted at 180°C for 1 h. A pale yellow viscous liquid was obtained. The hydroxyl value was 293, close to the theoretical value of 288.3. The ^{1}H-NMR spectrum was in accordance with the proposed structure.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) measurement was performed on the synthesized hyperbranched polyol (b) to determine its molecular weight. A Waters 515 pump and a Waters 2410 DRI detector were used. Tetrahydrofuran was used as eluant; the flow rate was 1 mL/min.



Scheme 1 Idealized reaction scheme for the synthesis of the hyperbranched polyol with long flexible chains.

Cationic UV Curing

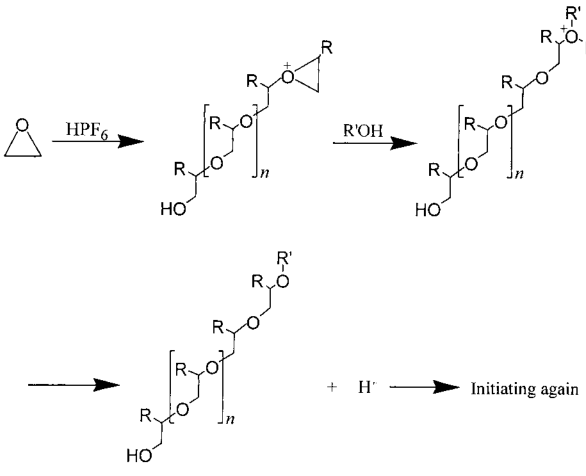
Cy179, bisphenol A epoxy resin E51, hyperbranched polyol, diphenyl iodonium hexafluorophosphate, Irgacure 184, and SR015 leveling agent F were mixed at the ratio of 60 : 40 : 10 : 3 : 3 : 0.5. Films of the mixture were drawn on glass plates or burnished tin plates with specified thickness and then cured with a 1000W medium pressure mercury arc lamp.

Film Properties

The mechanical properties of cured film were determined by bend test (ISO 1519-1973E standard), falling weight test (ISO / TR 6272-1979E standard) and relative hardness:

Relative hardness = pendulum hardness of film/that of glass plate

The solvent resistance of cured film was determined by MEK double rubs.



Scheme 2 Chain-transfer reaction of polyol.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Hyperbranched Polyol with Long Flexible Chains

As reported by A. Hult, a relatively low esterification temperature, 140°C, was chosen to suppress the side reactions such as etherification and *trans*-esterification.[7] During the synthesis of hydroxyl functional hyperbranched polyester (a, Scheme 1), the content of acid was measured by titration with KOH alcoholic solution to monitor the conversion of bis-MPA to the corresponding ester. At the end of the reaction, the content of acid dropped from the original 75 to below 2 wt %, indicating that the bis-MPA was consumed almost completely. This was confirmed by IR spectra, which showed no band of remaining carboxylic acid (1696 cm^{-1}, carbonyl), but only ester (1732 cm^{-1}, carbonyl).

As shown in Scheme 1, the ideal hydroxyl functional hyperbranched polyester (a) has 6 hydroxyl end groups and a theoretical molecular weight of 476 g/mol. Thus the hydroxyl functional hyperbranched polyester (a) has a theoretical hydroxyl value of 697.5. The actual hydroxyl value determined by titration is 690.4 and it can be calculated that the obtained hyperbranched polyester has a molecular weight of 476 g/mol. All these values are very close to the theoretical values.

Though most of the water formed during the reaction was removed by nitrogen gas and evaporation under vacuum condition, it was very important to remove the residual water, because it would terminate the cationic polymerization of epoxy resins. Toluene was used as entrainer to bring out the residual water and anhydrous $CuSO_4$ was used to test whether there was still residual water. No change of color from white to blue was observed, indicating that the residual water was removed.

The synthesis of the hyperbranched polyol (b) was achieved by a ring-opening reaction of hydroxyl functional hyperbranched polyester (a) with η-caprolactone catalyzed by dibutyltin dilaurate. ^{1}H-NMR showed the signal of —CH_2CH_2OH (δ = 3.6ppm, t) of the hyperbranched polyol (b) and the characteristic signals of $\equiv$C—CH_2OH (δ = 3.50, 3.68ppm) of hydroxyl functional hyperbranched polyester (a) disappeared, indicating the ring-opening reaction had taken place (Scheme 1).

The molecular weight of the hyperbranched polyol (M_w = 2437, M_n = 1927) was determined by GPC. As no appropriate hyperbranched polymer standards are available for calibration, the result was relative to linear polystyrene standards and was therefore not an absolute value. However, it could be seen the polydispersity was very narrow ($H = M_w/M_n = 1.26$).

The inherent viscosity, $\ln\eta_r/c$, of the hyperbranched polyol, determined by Ubbelohde viscometer at 25°C, was 4.50 mL/g. The hyperbranched polyol (b) is soluble in acetone, toluene, and ethanol, and insoluble in diethyl ether, petroleum ether, and carbon tetrachloride.

Effect of the Hyperbranched Polyol (b) on Cationic UV Curing

It is well known that hydroxyl can be reacted with a growing cationic chain of epoxy resins by chain-

Table I Effect of Hyperbranched Polyol (b) on the Properties of Cured Film

Formulation	A	B
Cy179	60	60
Bisphenol A epoxy resin E51	40	40
Hyperbranched polyol (b)	/	10
Photoinitiator[a]	3	3
Irgacure 184	3	3
SR015 leveling agent F	0.5	0.5
Properties		
Bend test (ϕ, mm)	8	<2
Following weight test (kg · m)	0.2	>0.5
Pendulum hardness	0.82	0.75
MEK double rubs	91[b] >250[c]	87[b] >250[c]
Curing time (s)	13	14

[a] Diphenyliodonium hexafluorophosphate.

transfer mechanism. Meanwhile, an ether linkage is formed and a proton is released, which can again initiate the cationic polymerization (Scheme 2). Owing to the multiplicity of the epoxy group, the crosslinking network can be formed.[8] It is consistent with the result in Table I that no obvious change of curing speed has been observed.

As shown in Table I, the hyperbranched polyol (b) could improve the mechanical properties of cured film in an obviously way. The result of bend test, 8 mm, represents the diameter of the first mandrel at which the coating cracked and/or became detached from the burnished tin plate. The larger the diameter, the worse the toughness of cured film. Therefore, the improvement of the toughness of cured film by hyperbranched polyol is obvious. Even at the smallest diameter of 2 mm, failure did not occur. The hyperbranched polyol (b) also has a positive effect on the falling weight test. The product of the falling weight with the minimum drop height, at which the film cracked or stripped from the substrate, increased from 0.20 kg · m to more than 0.50 kg · m after the addition of the hyperbranched polyol (b) to the cationic UV curing system. The improvement of mechanical properties is probably contributed to the long flexible chains on the molecule surface and the special structure of the hyperbranched polyol (b), with a relatively hard core of hyperbranched polyester and a soft outer layer. Other properties, such as solvent resistance and hardness, have no obvious change, indicating that the hyperbranched polyol (b) does not act as a simple flexibilizer, but has taken part in the reaction and been introduced into the polymer networks. Further research is being continued in our laboratory.

CONCLUSIONS

A hyperbranched polyol with long flexible chains (b) on the molecule surface was synthesized and chemically characterized. The properties of cationic UV cured films before and after the addition of the hyperbranched polyol (b) were compared and an obvious improvement of mechanical properties was observed.

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