Photopolymerization of Hyperbranched Aliphatic Acrylated Poly(amide ester). I. Synthesis and Properties

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ABSTRACT: The hyperbranched aliphatic poly(amide ester) (HAPAE) was synthesized based on 4-N,N-di(2-hydroxy ethyl)-4-ketobutyric acid prepared by the reaction of succinic anhydride with diethanol amine, as an AB_2 monomer (repeating unit), and with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, as a core molecule, using acid catalysis. The second generation of the product was characterized by measuring dynamic viscosity, which decreased sharply with the increase in frequency. The product exhibits relative thermal stability as analyzed by thermogravimetry in a nitrogen atmosphere. The glass transition temperature, determined by differential scanning calorimetry, is -27 °C. The molar mass was measured by vapor pressure osmometry. The polydispersity, measured by size exclusion chromatography, is 2.16. Dynamic mechanical thermal analyses were performed to characterize the thermal properties of the ultraviolet-cured films of the acrylate-modified HAPAE. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1630–1636, 2001

INTRODUCTION

Nonlinear polymers, such as dendritic macromolecules, have received increasing attention during recent years because of the potential properties of their highly branched and functionalized, three-dimensional globular structure compared with that of the traditional linear polymers.[1,2] Dendrimers, which have perfect and well-defined branching structures, are usually prepared step by step, using either divergent or convergent methods.[3–5] However, these complex synthetic procedures that involve isolating and purifying the products at every step limit large-scale preparation.

The one-step synthesis (i.e., one-pot process) makes the hyperbranched polymer more readily available and more easily prepared on a large scale. This attractive feature has led to the development of novel synthetic routes for the preparation of hyperbranched polymers.[6–8]

In recent years, there have been many studies dealing with aromatic structures (e.g., aromatic ether, aromatic ester, aromatic ketone, and aromatic amine) as linkages in the dendritic polymer structure.[9–12] With regard to aliphatic structure, 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) has been used frequently as an AB_2 monomer because of its low viscosity.[13–16] But there are still other monomers for use in synthesizing new hyperbranched polymers.

In this paper, we present the synthetic routes, using acid catalysis, of 4-N,N-di(2-hydroxy ethyl)-4-ketobutyric acid (DKBA) by the reaction between succinic anhydride and diethanol amine and of a new hyperbranched aliphatic poly(amide ester) (HAPAE) based on DKBA as an AB_2

monomer and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol as a core molecule. The synthetic procedure involves no purification steps, which facilitates large-scale production.

EXPERIMENTAL

Materials

Succinic anhydride was supplied by Aldrich, Germany. Diethanol amine and all other chemicals for synthesis were purchased from the Third Reagent Company of Shanghai, China. The multifunctional comonomer added to the formulation was trimethylolpropane triacrylate (TMPTA, supplied by Sartomer Company). 1-Hydroxy-cyclohexyl-phenyl ketone (Irgacure-184, Ciba Geigy) was used as a photoinitiator. All the materials in this study were used as received without further purification.

Measurements

Infrared (IR) spectra of the HAPAE ending with hydroxyl/acrylate were recorded on a MAGNA-IR 750 Fourier-transform infrared (FTIR) spectrometer smeared on a NaCl prism to form a thin film. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JNM-FX90Q (Joe Company, Japan) using $CDCl_3$ as a solvent. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer differential scanning calorimeter that was calibrated according to the standard procedures, using a heating rate of 20 K/min. The glass transition temperature (T_g) was determined as the inflexion point of the curve showing heat capacity as a function of temperature. Thermogravimetric analysis (TGA) was carried out with a Shimazhu TGA-50 using a heating rate of 10 K/min in nitrogen atmosphere. Vapor phase osmometry (VPO) measurements were performed on a QX-08 apparatus at 35 °C, using acetone as a solvent. Size exclusion chromatography (SEC) was performed on a Waters 244 SEC-LC chromatograph, with connected 10^2, 500, 10^3, and 10^4 Å microstyragel columns in series and a Waters model R401 differential refractometer as a detector. The flow rate was kept at 1.0 mL/min and tetrahydrofuran (THF) was used as an eluent at 12 °C. THF was purified by a standard method for chromatography. Dynamic mechanical properties were measured by shear rheometry (Dynamic Analyzer RDAII). A viscous sample was examined at 25 °C using two parallel plates of 12.5-mm radius with a 1.00-μm gap over a wide range of frequencies.

The storage modulus (E'), the loss modulus (E''), and Tan (δ) were measured versus temperature by the dynamic mechanical thermal analyzer (DMTA; Rheome Tric SCI Apparatus Ltd., NJ, USA) with a double cantilever geometry at a frequency of 1 Hz and a heating rate of 2 °C/min. The softening point (T_s) was defined as the extrapolated onset of the drop of E''. And the glass transition temperature (T_g) was defined as the peak of the Tan (δ) curve. The ratio T_s/T_g indicates the width of the Tan (δ) peak. The residual unsaturation (RU) was measured by infrared (IR) spectroscopy. The unsaturation peak at 810 cm^{-1} was monitored and the ester peak at 1728 cm^{-1} was used as an internal reference.

Synthesis

4-N,N-Di(2-hydroxy ethyl)-4-ketobutyric Acid (DKBA)

Succinic anhydride (0.2 mol, 20.0g), diethanol amine (0.2 mol, 21.0g), and methanol (30 mL) were mixed in an ice-cooled reaction three-necked flask equipped with a nitrogen inlet and a mechanical stirrer. The mixture was heated to 50 °C after succinic anhydride was dissolved completely. The reaction continued under nitrogen atmosphere until the FTIR bands at 1776 and 1850 cm^{-1} for anhydride in the solution disappeared, and then the nitrogen stream was turned off and the flask was connected to a vacuum line to remove methanol. The FTIR spectra of the product showed absorption bands at 3600–3200 cm^{-1} (hydroxyl), 1730 cm^{-1} (carbonyl of carboxylic acid), and 1646 cm^{-1} (carbonyl of amide). The acid number of 282 mg KOH/g was obtained by a titration. The conversion reached was typically 97%.

Second Generation of Hyperbranched Aliphatic Poly(amide ester) (HAPAE-2)

p-Toluene sulfuric acid (51.5 mg) was carefully mixed in a three-necked flask with DKBA (50.0 mmol, 10.3 g) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP) (5.56 mmol, 0.746 g) in the stoichiometric ratio 9:1. The flask was equipped with a nitrogen inlet, a drying tube, and a stirrer, and was heated to 130 °C in an oil bath for 2 h. Then the nitrogen stream was turned off and the flask was connected to a vacuum line (10 mbar,
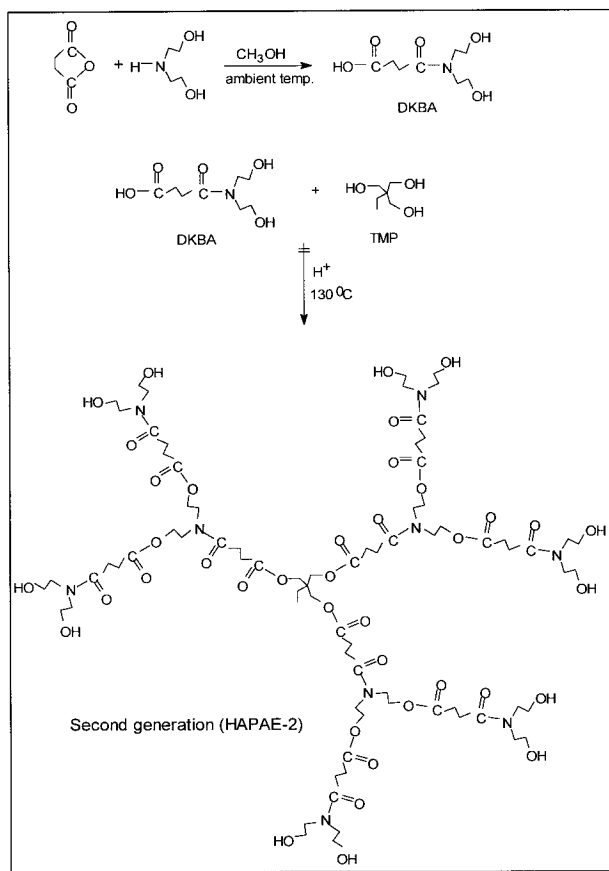
Figure 1 Reaction scheme for the synthesis of monomer (DKBA) and the second generation of hyperbranched aliphatic poly(amide-ester) (HAPAE-2).

cooling trap) for 1 h for complete removal of all water. FTIR (NaCl) spectra showed peaks at 3380 cm^{-1} (hydroxyl), 1730 cm^{-1} (carbonyl of ester), and 1646 cm^{-1} (carbonyl of amide). The acid number of the product is 8 mg KOH/g as determined by a titration. The idealized formulae of the HAPAE-2, with 12 theoretical hydroxyl groups, is shown in Figure 1. The resulting polymer ending with hydroxyl groups is a glassy, slightly yellow solid at room temperature, and soluble in dimethylformamide (DMF) and hot methanol.

Hyperbranched Aliphatic Acrylated Poly(amide ester) (HAPAE-2-A)

HAPAE-2 (14.2 g, 93.7 mmol OH) and *N,N*-dimethylaminopyridine (DMAP; 0.30 g, 2.5 mmol) were dissolved in a reaction vessel with dichloromethane (30 mL) and triethylamine (TEA; 12 mL). Acryloyl chloride (8.4 mL, 103 mmol) mixed with dichloromethane (50 mL) was slowly added to the vessel that was held at 0 °C by placement in

an ice bath. The mixture was then left stirring at ambient temperature for 12 h. The solution was extracted with HCl (2 M) and $NaHCO_3$ (10%) solutions twice, then dried over $MgSO_4$, filtered, and finally evaporated, yielding a slight yellow viscous resin.

Ultraviolet (UV) Curing of HAPAE-2-A

The mixture of HAPAE-2-A and Irgacure-184 (3 wt %), without or with TMPTA added, was prepared on a glass plate with a special frame as a support. Then the sample was exposed to the UV lamp (1 kW, 80 W/cm; made by Lantiao Company, Beijing, People's Republic of China), and irradiation was carried out for 100 s, which was considered to be sufficient cure. Test specimens (30 × 8 × 1mm) were cut out of the plate.

RESULTS AND DISCUSSION

Preparation of Hyperbranched Acrylated Poly(amide ester)

The AB_2 type monomer, DKBA, was prepared according to a simple amidation procedure between anhydride and amine. To avoid anhydride reacting with alcohol, a reaction temperature <60 °C was used, and methanol was used as a solvent. The acid number of DKBA obtained was 282 mg KOH/g compared with the theoretical acid number of 273 mg KOH/g. Therefore, amidation degree of ~97% was obtained. Consequently, the DKBA can be used as a monomer for preparing hyperbranched poly(amide ester) without any purification.
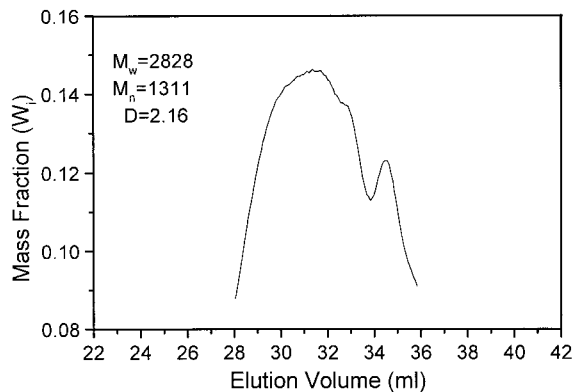

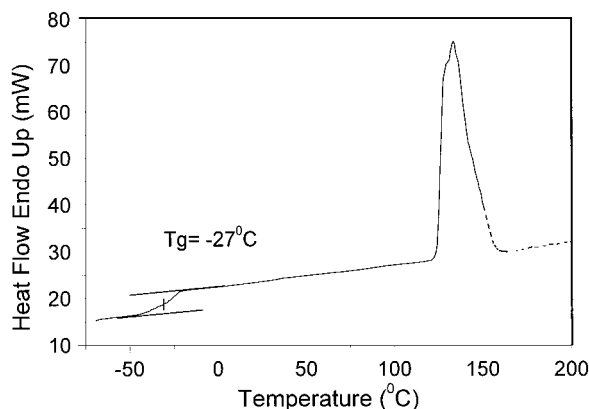**Figure 2** Molecular weight distribution of HAPAE-2 by SEC.

Figure 3   DSC thermogram of HAPAE-2 at a heating rate of 20 K/min.

Figure 5   Idealized molecular structure of HAPAE-2-A.

The hyperbranched poly(amide ester) was synthesized from DKBA and TMP according to common acid-catalyzed esterification procedure. The esterification was carried out in bulk and driven toward high conversion by continuously removing water as it formed. Removal is essential to obtain high molar mass and was done with nitrogen as the carrier gas at an early stage of the polymerization and under reduced pressure when the condensation has reached completion. A relatively low esterification temperature, 130 °C, was chosen to suppress unwanted side reactions, such as, etherifications and *trans*-esterification.

The architecture of hyperbranched substances involves some characterization problems, mainly because many methods are based on calibration with linear polymer of known molar mass and polydispersity index. Hyperbranched materials exhibit relationships between molar mass and hydrodynamic radius, R_h, or radius of gyration, S, different from those of their linear counterparts of
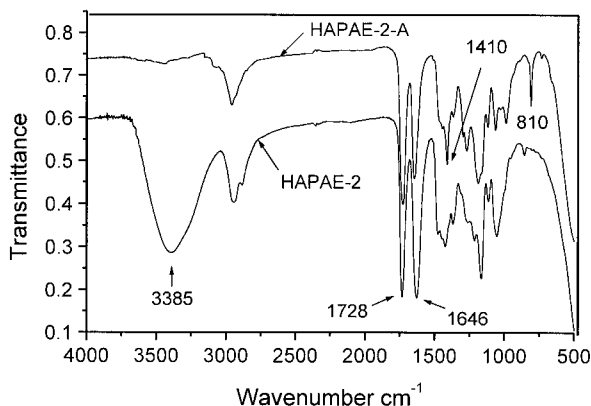
the same molar mass. Because R_h is smaller for a branched polymer than for its linear counterpart of the same molar mass, it is expected that molar mass as determined by SEC, calibrated with linear polystyrene standards, will be lower. As can be seen from Figure 2, HAPAE-2 have a rather wide and bimodal distribution of molecular weight, relating to the elution volumes of 31.5 and 34.5 mL, which is the same as obtained from the hyperbranched aromatic/aliphatic polyesters.[17] This result implies that there are products in the HAPAE-2 system; one is the three hydroxyl groups of TMP that have reacted completely, and the other is two hydroxyl groups of TMP that have reacted. In addition, the peak of 31.5 mL is
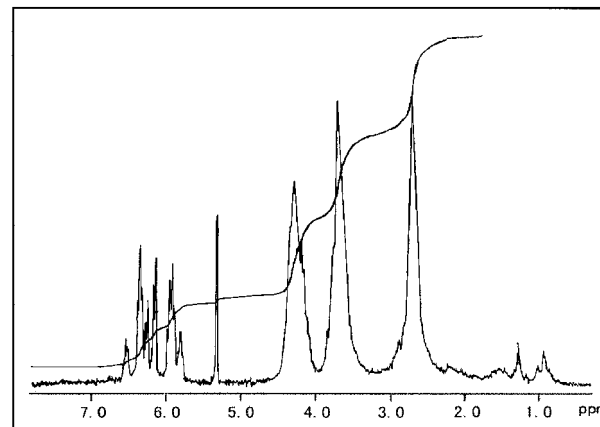

Figure 4   FTIR spectra of HAPAE-2 and HAPAE-2-A.

Figure 6   ¹H NMR spectrum of HAPAE-2-A.

Table I   Correspondence between H Number in HAPAE-A and Peak Area by ^{1}H NMR

Parameter	Shift of H, ppm				
	6.6–5.8	5.3	4.3–4.2	3.7–3.6	2.7–2.6
Corresponding H	$CH_2\!\!=\!\!CH\!-$	$-OH$	$-CH_2-O-$	$-N\!\!\big\langle\!\!\begin{array}{c}CH_2-\\CH_2-\end{array}$	$\begin{array}{cc}O & O\\ \| & \|\\ -C-CH_2-CH_2-C-\end{array}$
Ratio of Peak Area	32	2	41	41	42

much bigger than that of 34.5 mL, indicating that the product with which TMP reacted completely is the main product. The polydispersity measured by SEC analysis is 2.16. The molecular weight distribution is mainly attributed to incomplete reaction between DKBA and TMP, hyperbranched poly(amide ester) fragmentation during reaction.

As expected, the molecular weights determined by SEC were smaller than the theoretical molecular weights. The average molecular weight (M_n) obtained by VPO measurement is 1620 g/mol compared with the calculated value of 1819 g/mol. This result indicates a degree of reaction of ~90%; that is, the average functionality of 11 was obtained with this synthesis system. The glass transition temperature (T_g) and melting temperature (T_m) measured by DSC were −27 and 130 °C, respectively, as shown in Figure 3.
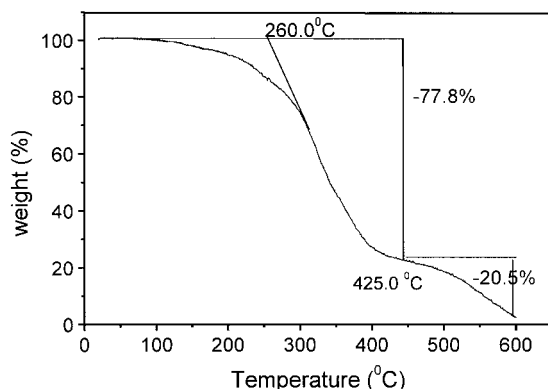
The hyperbranched poly(amide ester) has hydroxyl groups that easily react with acryloyl chloride. Dichloromethane was used as a solvent because the phase separation worked well and its boiling point, where evaporation is easy, is only

40 °C. The completion of the reaction was followed by the disappearance of the hydroxyl peak (3700–3000 cm^{-1}) in the FTIR spectrum of the reaction mixture, as shown in Figure 4. The double bonds introduced are the chain ends of the molecule and will, therefore, be located at the surface of the oligomeric spheres, which is highly favorable for UV cure. The idealized molecular structure of HAPAE-2-A is outlined in Figure 5.

The product (HAPAE-2-A) was analyzed by ^{1}H NMR and the results are shown in Figure 6. The ratios of H number in HAPAE-2-A, which exactly corresponded to that of the peak area, are shown in Table I. We can calculate the yield of HAPAE-2-A to be ~85% by the ratio of H number in the double bond and hydroxyl group.

Rheological Behavior

It is well known that the hyperbranched polymer exhibits relative low intrinsic viscosity because of the unique compact molecular structure compared with a linear polymer of similar molar mass.[18] From Figure 7 it can be seen that HAPAE-2 has a high modulus viscosity because of
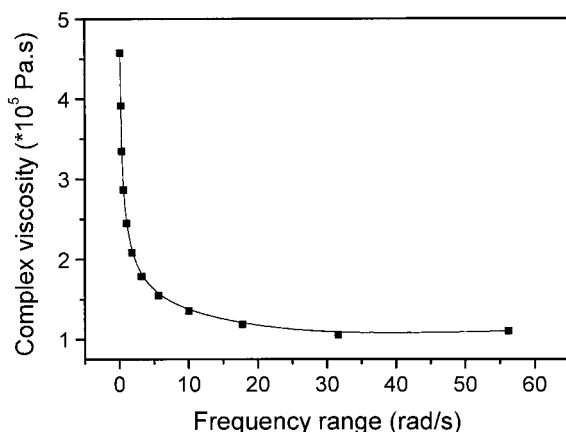
Figure 7   Complex viscosity of HAPAE-2 at varying frequencies.

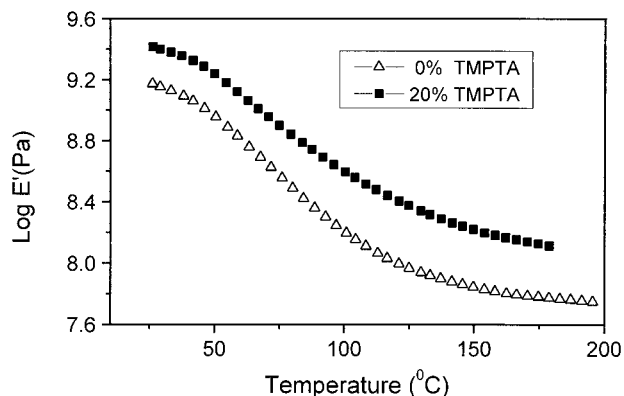**Figure 8**   TGA thermogram of HAPAE-2 at a heating rate of 10 K/min.

Figure 9 E' versus temperature for UV-cured HA-PAE-2-A films.

Figure 10 Tan (δ) versus temperature for UV-cured HAPAE-2-A films.

the dense hydroxyl groups in this system, resulting in intermolecular hydrogen bonding [hyperbranched poly(amide ester) aggregation]. However, the dynamic viscosity of HAPAE-2 decreased drastically (~70%) when the frequency was increased to 20 rad/s. This result can be explained as follows: the shear force becomes large enough to overcome the intermolecular hydrogen bonding interaction quickly, which results in decreasing viscosity of this system.

Thermal Properties

TGA analysis has shown that the hyperbranched poly(amide ester) has good thermal stability, ~11% weight lost until 260 °C, as shown in Figure 8. The amide bond began to break at 260 °C. When the amide bonds break completely, the HAPAE-2 weight loss occupies ~77.8%, which is close to the theoretical value of weight percent of the outer position (81.0%). After reaching 425 °C, the inner portion decomposed, and ~1.7% remained up to 600 °C.

DMTA is a quick and direct method for the determination of softening temperature (T_s) and glass transition temperature (T_g). The dynamic mechanical properties of UV-cured HAPAE-2-A films without and with TMPTA added are shown
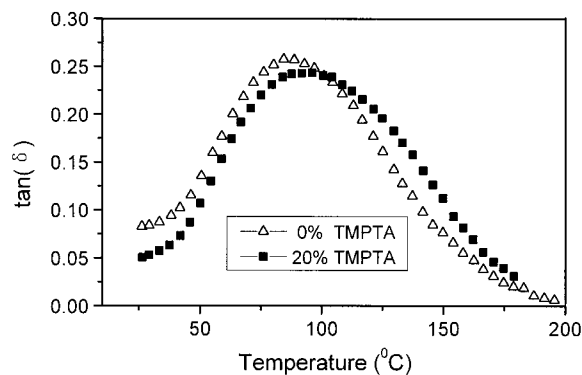
in Figures 9 and 10 and listed in Table II. The T_g of the cured HAPAE-2-A film without TMPTA added was lower than that with 20 wt% TMPTA added. This result is interpreted as due to higher RU of 26% for HAPAE-2-A resin compared with 16% for the resin containing 20% TMPTA, which results from the higher viscosity of the resin without TMPTA added. However, the value of T_s/T_g for the cured HAPAE-2-A film without TMPTA added is higher than that with TMPTA added. It can be suggested that the network homogeneity of the former is better than the latter, which may also account for the more homogeneous network structure of the former.

CONCLUSION

A new hyperbranched aliphatic polymer, based on succinic anhydride and diethanol amine as the raw materials of an AB_2 monomer (repeating unit) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol as a core molecule, has been synthesized and characterized. A reaction degree of ~90% was found; that is, an average functionality of 11 was obtained with this synthesis system. The product exhibits relative good thermal stability. UV curing of this resin without or with comonomer added was readily achieved. A more homogeneous

Table II Mechanical Testing Data for HAPAE-A Resins

Sample No.	HAPAE-2-A (%)	TMPTA (%)	T_s (°C)	T_g (°C)	T_s/T_g	RU (%)
1	100	0	45	89	0.878	26
2	80	20	44	93	0.866	16

network structure may be obtained with the UV-cured film without TMPTA added, as indicated by DMTA measurements.

ACKNOWLEDGEMENT

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