

Synthesis and Characterization of Castor-Oil-Modified Hyperbranched Polyurethanes

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ABSTRACT: A series of castor-oil-modified hyperbranched polyurethanes were synthesized via an $A_2 + B_3$ approach based on castor oil, macroglycol poly(ϵ -caprolactone)diol or poly(ethylene glycol) (PEG), and diphenyl methane diisocyanate, with or without a chain extender. The yield of the product was 95%, and the polymers were soluble in common organic polar solvents. The synthesized polymers were characterized with Fourier transform infrared spectroscopy, NMR, wide-angle X-ray diffraction, and gel permeation chromatography measurements. The degree of branching of the polymers was calculated from their respective $^1\text{H-NMR}$ spectra

with the help of model compounds and found to be varied from 0.7 to 0.8. The hard-segment content, the nature of the macroglycol, and the composition of the polymers had prominent effects on the thermal degradation and crystallization of the hyperbranched polymers. The crystallization of poly(ϵ -caprolactone) and PEG as soft segments occurred well in the hyperbranched polymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 736–743, 2009

Key words: hyperbranched; polyurethanes; synthesis; thermal properties

INTRODUCTION

The study of the structure–property relationships in polyurethanes has gained tremendous importance because of their various applications^{1,2} as thermoplastic elastomers, foams, fibers, adhesives, coating materials, and so forth. The properties of polyurethanes can be monitored by the judicious variation of chemical constituents as well as the composition of the soft and hard segments. A large number of reports are available in the literature on the effects of the structures of hard segments and soft segments on the physical, thermal, and chemical properties of these polymers.^{3–5}

Today, the high price of petroleum raw materials, scarcity of petroleum products, and stringent environmental rules and regulations are pressuring synthetic polymer scientists to use natural renewable resources as the feedstocks for the development of many industrially important polymers. These feedstocks, espe-

cially vegetables, are well accepted by synthetic polymer chemists for social, economic, and environmental reasons. Fortunately, many researchers are now using renewable natural resources as their feedstocks for the development of many polymers.^{6–15}

Castor oil is one of the most important renewable resources for the production of many industrial polymers and is obtained from the castor seed of the castor plant, *Ricinus communis*. The unusual composition and chemistry of castor oil make it quite valuable for many applications, including the preparation of polyurethane.¹⁶ Approximately 90% of fatty acids in castor oil are ricinoleic acid. Ricinoleic acid, a mono-unsaturated, 18-carbon fatty acid, has a hydroxyl-functional group at the twelfth carbon; this is a very uncommon property for a biological fatty acid and is the main driving point for the direct use of this oil as a hydroxyl-containing trifunctional monomer (A_3). The vegetable oil also has other advantages such as (1) renewability, (2) easy availability in a large quantity, (3) environmental friendliness, (4) biodegradability, and (5) overall low cost.

Nonlinear highly branched polymers such as dendrimers and hyperbranched polymers have received considerable attention in recent years because of their unique architectural features and unusual properties.^{17–19} These macromolecules exhibit many useful properties such as higher solubility and lower melt and solution viscosity in comparison with their linear analogs of the same molar mass because of the highly functionalized, three-dimensional, globular, unentangled structure.^{20–22}

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TABLE I
Compositions and DBs of the Hyperbranched Polyurethanes

Polyurethane code ^a	Castor oil (mol)	Macroglycol (mol)	BD (mol)	MDI (mol)	DB
PCL-23	0.003	0.002	—	0.005	0.84
PCL-36	0.003	0.002	0.005	0.0045	0.75
PEG-36	0.004	0.001	0.005	0.0045	0.69
PEG-30	0.004	0.001	0.0005	0.0045	0.72
PEG-22	0.004	0.001	—	0.005	0.75

^a The number after the hyphen indicates the hard-segment content in the polymers. The molecular weight of PEG was 10,000 in PEG-22 only.

As hyperbranched polymers can be prepared by single-step processes versus multistep processes for structurally perfect dendrimers, the former can be obtained on a large scale at a reasonable cost, and this makes them more interesting for commercial applications.^{21,23} These are generally synthesized from AB_x ($x \geq 2$) monomers, but because of the infrequent commercial availability of this type of monomer, research tends to be focused on the employment of A₂ and B₃ monomers. A few successful attempts have already been made at the synthesis of hyperbranched polyethers, polyamines, polyamides, polyimides, and so forth^{24–26} using this strategy. In this investigation, an attempt was made to use this strategy to obtain vegetable-oil-based polyurethanes.

We report here the synthesis, characterization, and properties of a few hyperbranched polyurethanes based on castor oil.

EXPERIMENTAL

Materials

Castor oil (Aldrich Chemical, Castle Hill, Australia), poly(ethylene glycol) (PEG; Duksan Chemical, Seoul, Korea; molecular weight = 10,000 or 4000 g/mol), and 1,4-butane diol (BD; Duksan Chemical, Seoul, Korea) were used after drying *in vacuo* at 60°C overnight. 4,4'-Methylene bis(phenylisocyanate) (MDI; Junsei Chemical, Tokyo, Japan) and poly(ϵ -caprolactone)diol (PCL; Solvay Co., Warrington, UK; molecular weight = 3000 g/mol) were used as received. *N,N*-Dimethylformamide (DMF; Junsei Chemical, Seoul, Korea) was freshly purified.

Synthesis of the hyperbranched polyurethanes

A nitrogen-flushed three-necked reactor fitted with a mechanical stirrer was charged with an appropriate amount of a macroglycol and MDI (Table I) in DMF (15% solid content) at about 23°C. Then, the temperature of the reaction mixture was increased to 70°C, and stirring was continued for 3 h at that temperature. Then, the reaction mixture was cooled to 5°C, and the required amount of the DMF solution of castor oil with or without BD was added dropwise into the reaction mixture. The temperature of the

mixture was then raised to 110°C by stagewise heating, and stirring continued until there was no peak for NCO in the Fourier transform infrared (FTIR) spectrum. Then, the viscous polymer was dried in a gravity convection oven at about 60°C for 24 h in a Teflon mold, and this was followed by drying *in vacuo* at 50°C for 1 day. The synthesis of the model compounds of castor oil with 1, 2, and 3 equiv of phenyl isocyanate was performed separately, exactly in the same way as described in the second stage of the hyperbranched polymer synthesis.

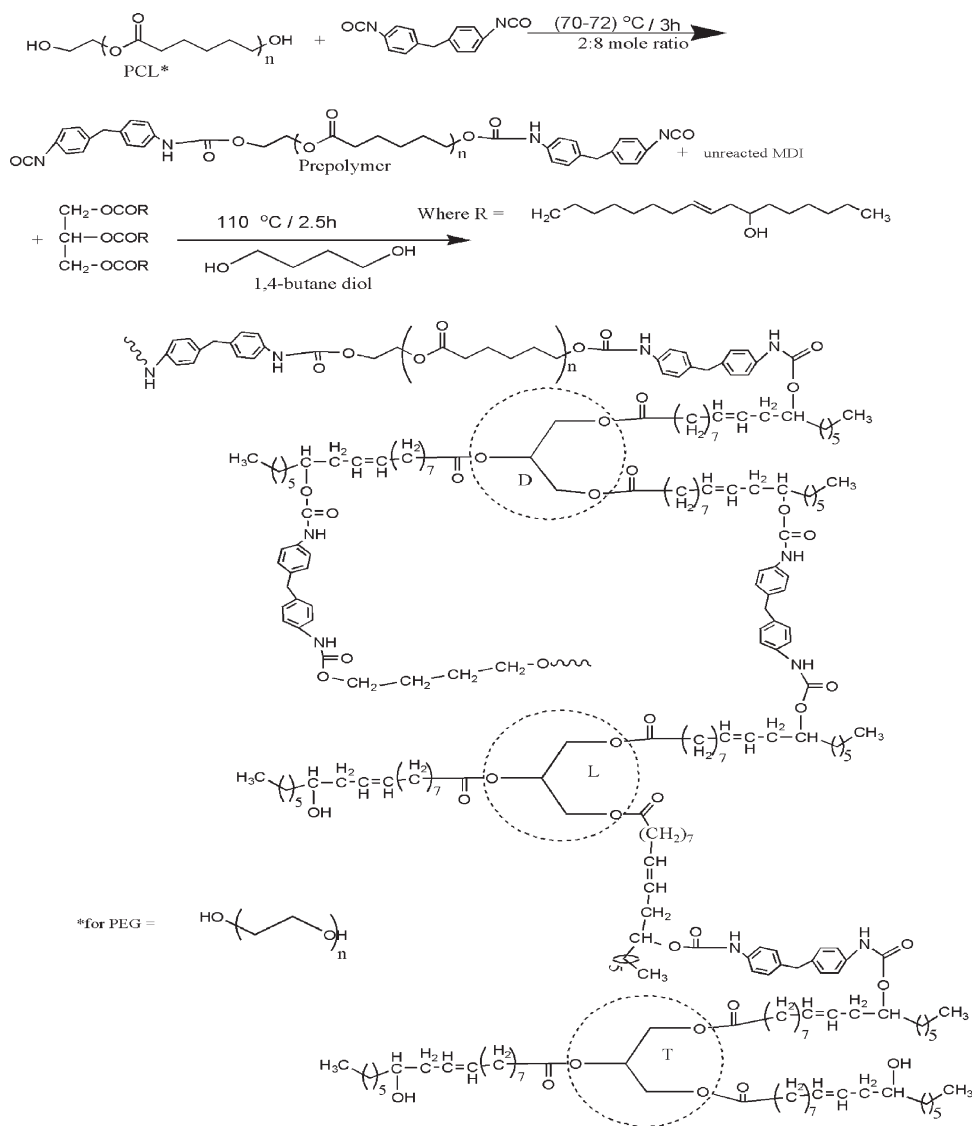
Measurements

The FTIR and ¹H-NMR spectra of the polymers were recorded with a Jasco FTIR 300E (Tokyo, Japan) with an attenuated total reflectance method and with a Bruker 400-MHz NMR spectrometer with tetramethylsilane as the internal standard and dimethyl sulfoxide-*d*₆ (DMSO) as the solvent, respectively. The thermal analysis of the polymers was performed with a TA Q50 system for thermogravimetric analysis (TGA) and a TA Instrument DSC 2010, New Castle, DE for differential scanning calorimetry (DSC) with a 30 mL/min nitrogen flow rate and a heating rate of 10°C/min. Wide-angle X-ray diffraction measurement was carried out with a Rigaku Rint 2100 series, Tokyo, Japan with Cu K α radiation at a scan rate of 5°/min. The molecular weights of the hyperbranched polymers were determined by gel permeation chromatography analysis (model 515, Water) with DMSO as the solvent.

RESULTS AND DISCUSSION

Synthesis of the hyperbranched polyurethanes

The hyperbranched polyurethanes were synthesized through the variation of hard segments for two different macroglycols with a two-step, one-pot prepolymerization via an A₂ + B₃ technique, as shown in Scheme 1. Five different hyperbranched polymers with different hard segments but the same NCO/OH ratio (1.0) were synthesized by changes in the compositions of the macroglycol (PCL or PEG), castor oil, BD, and MDI (Table I). The prepolymer was



Scheme 1 Synthesis of hyperbranched polyurethanes.

first prepared by the reaction of the macroglycol with excess diisocyanate at 70°C for 3 h without any catalyst, and that mixture (the isocyanate-terminated prepolymer and the unreacted diisocyanate) was used as an A₂ monomer for the synthesis of the hyperbranched polymer. The addition of the B₃ monomer, triglyceride of ricinoleic acids (castor oil), was then performed at a very low temperature (5°C) with the slow addition of a very dilute solution (10% in DMF), and the final stage of heating was performed at 110°C for 2.5 h. The addition of the B₃ monomer at a relatively elevated temperature caused gel formation. Even the use of the one-shot process led to a gel product. The high concentration of the reactants (>15%) also resulted in a gel product. Gelation was avoided with the high-dilution technique. However, the reaction of the final stage at room temperature or a temperature lower than

110°C did not produce the desired product. Thus, the reaction in the second stage was performed by a stagewise increase of the temperature up to 110°C to complete the reaction. The completion of the reaction was confirmed by the FTIR study and by the determination of the isocyanate value with the butyl amine titration method.

Characterization of the hyperbranched polyurethanes

The hyperbranched polyurethanes of both types (PCL- and PEG-based macroglycols) were found to be soluble in common organic polar solvents such as DMF, DMSO, *N,N*-dimethylacetamide, and tetrahydrofuran (THF), and they also could be softened and hardened by repeated heating above 120°C and cooling at room temperature. These results indicate that

TABLE II
Molecular Weights and Molecular Weight Distributions of the Hyperbranched Polyurethanes

Molecular weight (g/mol)	PCL-23 ($\times 10^{-4}$) ^a	PCL-36 ($\times 10^{-4}$) ^a	PEG-36 ($\times 10^{-4}$) ^a	PEG-30 ($\times 10^{-4}$) ^a
M_w	3.62	6.36	14.87	8.13
M_n	1.87	2.37	4.59	2.90
M_w/M_n	1.93	2.68	3.23	2.79

M_w = weight-average molecular weight; M_n = number-average molecular weight.

^a The number after the hyphen indicates the hard-segment content in the polymers (wt %).

the synthesized polymers are thermoplastic in nature. The molecular weight and molecular weight distribution of the polymers (Table II) indicate that these polyurethanes may have good properties and processing characteristics. The increases in the molecular weight with increasing hard-segment content may be due to an increase in the reactivity of the reactant and easy accessibility of the active site of the polymer chain to the small molecules.

The FTIR spectra (Figs. 1 and 2) of all the hyperbranched polymers with various hard segments were taken. The absorption band due to NCO groups disappeared as no intense and sharp band at about 2250–2270 cm^{-1} for the polymers was found, and this confirmed the completion of the reaction, which was further proved by the determination of the isocyanate value by the butyl amine method.

In polyurethanes, NH groups may form hydrogen bonding with urethane carbonyl C=O, ester carbonyl C=O (oil or PCL), or ether oxygen C—O—C (PEG).²⁷ In the FTIR spectra of the polymers (Figs. 1 and 2), the C=O absorption band appeared at 1733–1719 cm^{-1} and split into two in each case. Also in these FTIR spectra, the NH absorption bands appeared at 3321–3316 cm^{-1} for polymers without the chain extender BD, whereas for polymers with

BD, a broad absorption from 3330 to 3410 cm^{-1} appeared. This broad band case may be due to the combination of NH and OH frequencies and also due to the presence of hydrogen bonding.

It is well established that the position and intensity of these vibrations are extremely sensitive to the strength and specificity of the hydrogen bonds that form.²⁸ The phase separation in polyurethanes can be characterized by the measurement of the intensity and position of the hydrogen-bonded NH stretching vibrations.^{29,30} Usually, a significant amount of N—H...O=C (urethane) hydrogen bonding indicates extensive phase separation.³¹ Thus, the tendency of phase separation increases with the increase in the hard-segment content. The C=O stretching frequencies are very complex for such polyurethanes as they are influenced by C—N stretching and C—C—N deformation as well as N—H bending.³²

The structure of the polyurethanes was further confirmed by ¹H-NMR spectroscopy analysis (Table III). ¹H-NMR spectra of the polymers (Figs. 3 and 4) indicated the presence of urethane linkages, castor oil, and MDI moieties along with other characteristic groups such as terminal CH₂, chain CH₂, and double bonds, as shown in Table III. The important peaks and corresponding functional groups of the polymers are shown in Table III.

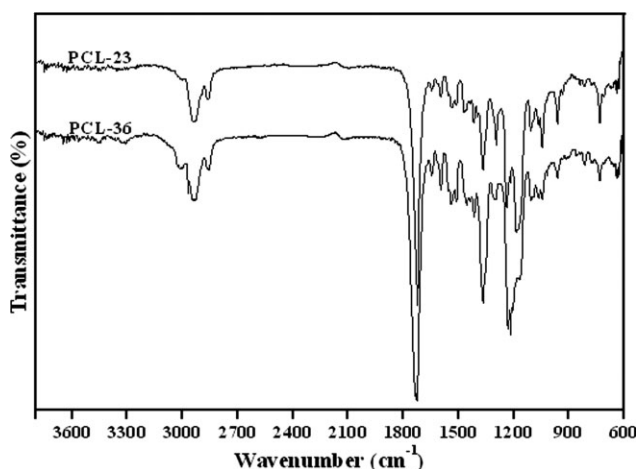


Figure 1 FTIR spectra of polyurethanes with PCL.

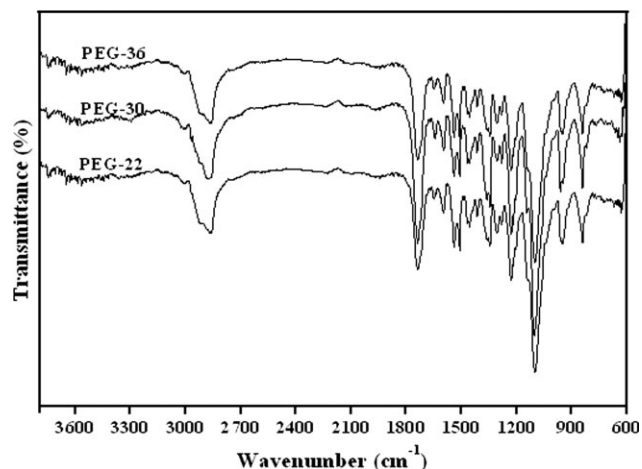


Figure 2 FTIR spectra of polyurethanes with PEG.

TABLE III
FTIR and ¹H-NMR Spectral Data for the Hyperbranched Polyurethane

Functional groups	Castor oil FTIR (cm ⁻¹)	Polymer	
		FTIR (cm ⁻¹)	¹ H-NMR/ ¹³ C-NMR (ppm)
—OH (free)	3378	3316–3332	δ = 4.03–4.54 and δ = 3.92–3.52 (CH attached with urethane and OH linkages, respectively, used for DB)
—C=O, carbonyl	1735 (ester)	1720–1727 (urethane)	δ = 1.46–1.35 (CH ₂ adjacent to urethane or —OH on methyl terminal side)
—C=C—	1651	1601–1623	δ = 1.9 (CH ₂ attached to C=C on the aliphatic side), δ = 2.1–2.3 [CH ₂ attached to C=C on the —OH or —O—C(=O) NH side or ester group], δ = 5.2–5.6 (H attached to C=C)
C—N	—	1070–1082	—
Aromatic	—	767–774	δ = 7.0–7.4
CH ₂ (chain)	2852–2921	2854–2924	δ = 1.22–1.86
CH ₂ (chain)	2852–2921	2854–2924	δ = 1.4–1.6 α to —OH or urethane
CH ₃ (terminal aliphatic)	—	1453–1461	δ = 0.84–0.89
CH ₂ (MDI)	—	—	δ = 3.42–3.47
—NH, urethane	—	3316–3332	δ = 8.3–8.5
—C—O (ester)	1178	1140–1167	δ = 2.1–2.3 [CH ₂ attached to C=C on the —OH or —O—C(=O) NH side]
CH ₂	—	2879–2935	δ = 3.63–4.25 (glycerol moiety), δ = 1.6 (CH ₂ next to terminal CH ₃)

Degree of branching (DB)

The structural perfection of hyperbranched polymers is usually characterized by the determination of their DB, which is determined with Fréchet's equation as follows:³³

$$DB = (D + T)/(D + T + L) \quad (1)$$

where *D*, *T*, and *L* refer to the number of dendritic, terminal, and linear units, respectively, in the structure of the polymer. Experimentally, DB is generally determined from NMR spectroscopy by a comparison of the integration of the peaks for the respective units in the hyperbranched polymer.³³ The structure

of the hyperbranched polymer is indeed a block construction of these three units. In this work, the dendritic, terminal, and linear units were very difficult to distinguish because of the complex structure of the B₃ monomer (triglyceride ricinoleic acids). Therefore, DB was determined here by a comparison of the reacted and unreacted B functional groups (hydroxyl group), and the same were compared with the model compounds. With the help of ¹H-NMR measurement, we found that the urethane [O—(C=O)—NH] linkages derived from the hydroxyl group of the ricinoleic acid moiety of the triglyceride of the B₃ monomers are sensitive to the number of B functional groups, and these can be

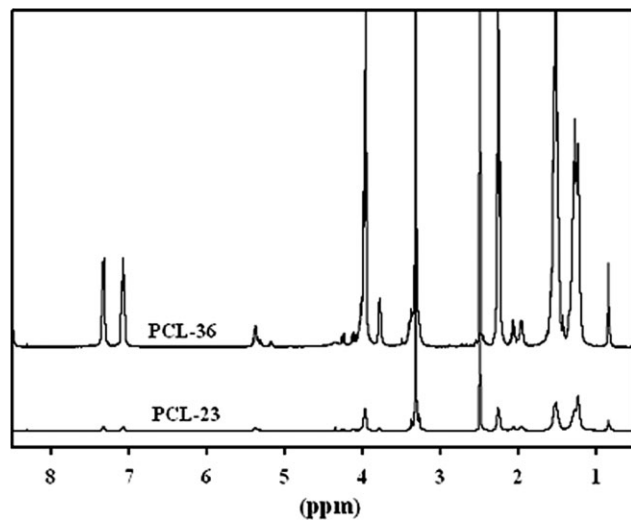


Figure 3 ¹H-NMR spectra of polyurethanes with PCL.

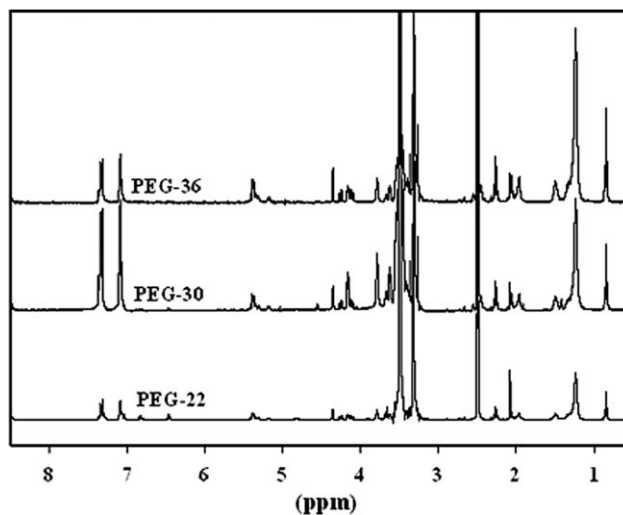


Figure 4 ¹H-NMR spectra of polyurethanes with PEG.

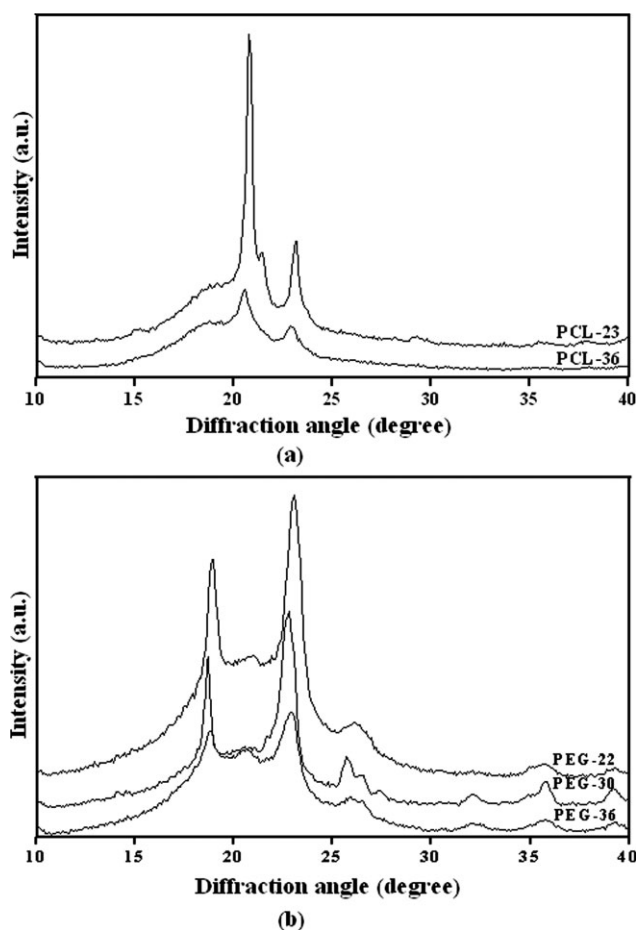


Figure 5 X-ray diffractograms of polyurethanes with (a) PCL and (b) PEG.

used to assign DB (Figs. 3 and 4). The relative amounts of the aforementioned units were calculated by the integration of the $^1\text{H-NMR}$ peaks of secondary C–H of substituted OH to urethane and unsubstituted OH. The peaks for the different units were assigned as discussed in the section on characterization. The values of DB for both polymers were calculated from the integration of $^1\text{H-NMR}$ peaks and are given in Table I. These values of DB indicate that these types of polymers exhibit a dendritic structure (DB was close to unity for the dendrimer and close to 0.5 for the hyperbranched polymer) rather than a more linear structure (DB was closer to zero).

Crystallization and thermal degradation

Figure 5 shows X-ray diffractograms for hyperbranched polyurethanes. It clearly indicates the presence of crystallinity in the hyperbranched polyurethane. There are two strong diffraction peaks at $2\theta = 21.2^\circ$ (4.19 Å) and $2\theta = 23.4^\circ$ (3.81 Å) due to (110) and (200) planes of PCL crystals³⁴ and at $2\theta =$

19° (2.36 Å) and $2\theta = 23.5^\circ$ (1.93 Å) due to (110) and (200) planes of PEG crystals.³⁵ This indicates that the crystallization of PCL in hyperbranched polymers can be well developed as in the linear polyurethanes.

Figures 6 and 7 show the DSC curves of hyperbranched polyurethanes with PCL and PEG macroglycols. The crystallization temperature (T_c), melting temperature (T_m), heat of crystallization (ΔH_c), and heat of fusion (ΔH_f) were obtained from the DSC measurements and are summarized in Table IV. The crystallinity of soft segments in hyperbranched polyurethanes was determined by the measurement of ΔH_c on cooling and with an enthalpy value of 136 J/g for 100% crystalline PCL³⁶ and 197 J/g for 100% crystalline PEG.³⁷ As shown in the figures and table, the crystallinity can be well developed and is significantly dependent on the hard-segment content. The crystallinity decreased with the weight percentage of

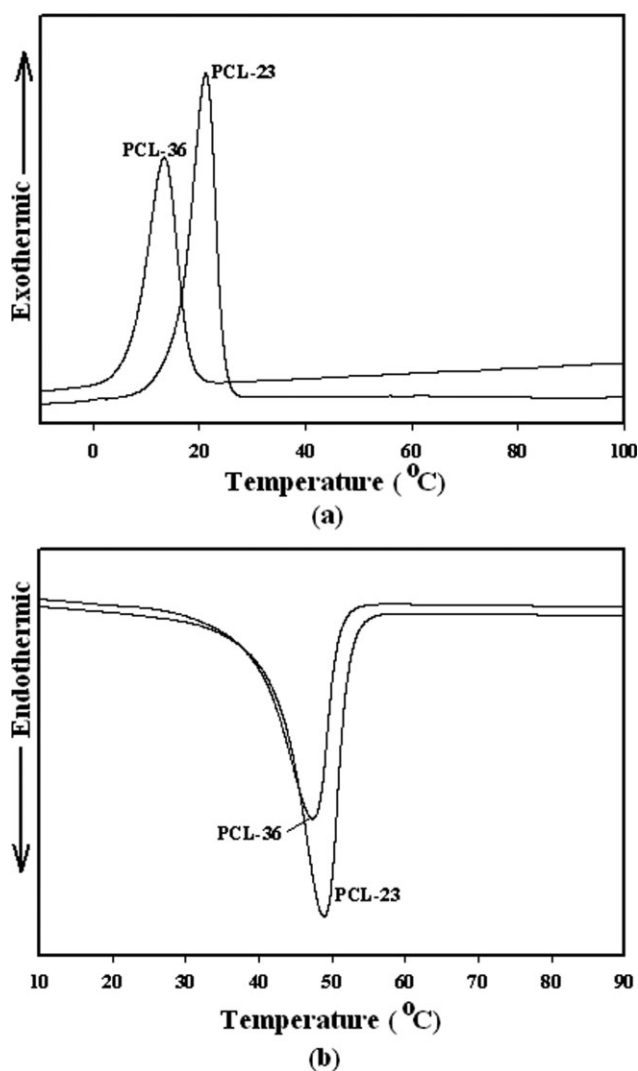


Figure 6 DSC curves for polyurethanes with PCL obtained on (a) cooling and (b) heating.

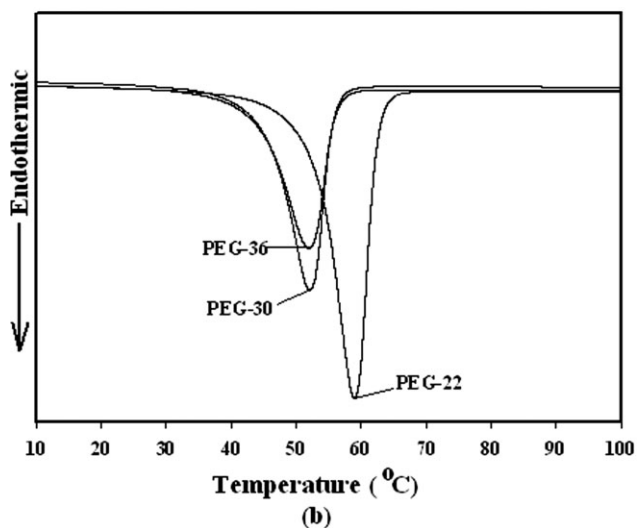
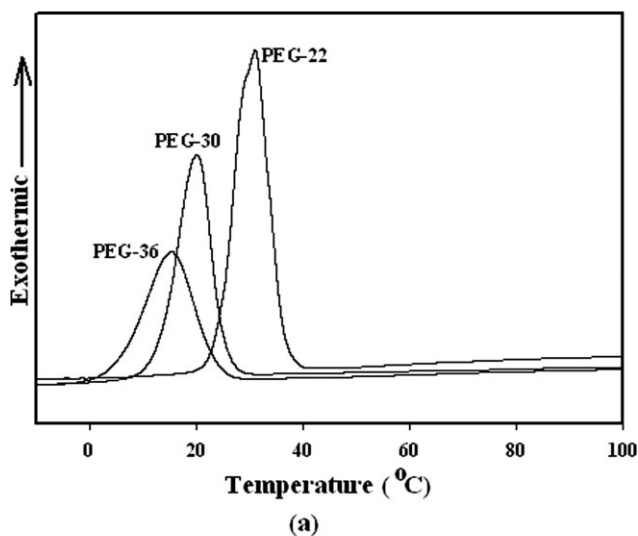


Figure 7 DSC curves for polyurethanes with PEG obtained on (a) cooling and (b) heating.

the hard segment increasing because of the decreased PCL and PEG soft-segment domains.

Figures 8 and 9 show TGA curves for the polyurethanes with PCL- and PEG-based polymers, respectively. The polymers decomposed in two steps due

TABLE IV
Thermal Properties of the Composites

Sample code ^a	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_f (J/g)	Crystallinity (%)
PCL-36	12.8	32.1	46.6	32.0	23.6
PCL-23	24.0	41.5	48.3	42.0	30.5
PEG-36	15.3	61.4	51.5	65.2	31.2
PEG-30	20.2	75.3	52.0	76.5	38.2
PEG-22	31.0	107	58.8	109	54.3

^a The number after the hyphen indicates the hard-segment content in the polymers (wt %).

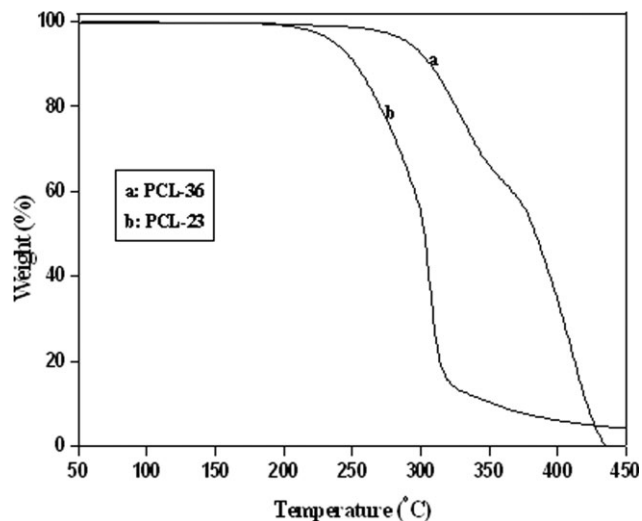


Figure 8 TGA thermograms of polyurethanes with PCL.

to the soft and hard segments in the polyurethane, and weight loss due to polymer decomposition was observed at about 250–350°C. During the reaction, if any allophanate and biuret linkages form, they reopen quite readily on heating at relatively high temperatures as they are most thermolabile. However, the urethane linkages decompose only at quite high temperatures, whereas the aromatic moiety of the diisocyanates decomposes at the highest temperature³⁸ in this case. This increase in the number of urethane linkages is also reflected in the thermal stability of the polymer, that is, the initial, 50%, and 90% decomposition temperatures and the weight residue at 500°C, as shown in Table V. With an increasing amount of the hard segment, the thermal stability increased in both cases.

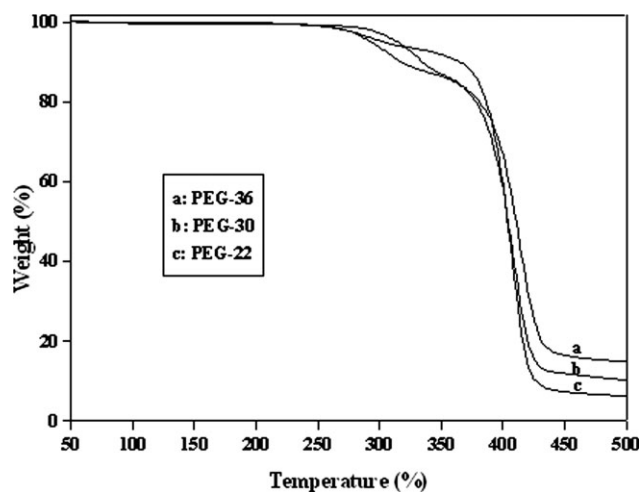


Figure 9 TGA thermograms of polyurethanes with PEG.

TABLE V
Initial Temperature (T_{initial}), 50% Decomposition Temperature ($T_{50\%}$), 90% Decomposition Temperature ($T_{90\%}$), and Char Residue at 550°C for the Cured Polyurethane Resins

Polyurethane code ^a	T_{initial}	$T_{50\%}$	$T_{90\%}$	Weight residue at 500°C (weight %)
PCL-23	218	305	350	3.3
PCL-36	270	385	420	0.0
PEG-36	274	410	>600	12.9
PEG-30	265	403	428	8.6
PEG-22	260	400	425	5.2

^a The number after the hyphen indicates the hard-segment content in the polymers (wt %).

CONCLUSIONS

Castor-oil-modified hyperbranched thermoplastic polyurethanes containing different hard segments and macroglycols without gel formation were synthesized successfully. The DB values of the polymers indicate that they are highly branched dendritic polyurethanes. The hard-segment content, the nature of the macroglycol, and the composition of the polymers have prominent effects on the thermal and crystallization properties. Because of the good crystallization behavior of the macroglycols, the synthesized materials could be useful for shape-memory applications. Further work is in progress and will be presented in due course.

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