

Hydroxyl-Terminated Poly(urethane acrylate) as a Soft Liner in Dental Applications: Synthesis and Characterization

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ABSTRACT: Hydroxyl-terminated poly(urethane acrylate)s were synthesized for use in biomedical applications. Acrylate end capping via an interesterification reaction was successfully achieved with methacryloyl chloride addition to the hydroxyl ends of the polyurethane at low temperatures. 2,4-Toluene diisocyanate, 1,6-hexane diisocyanate, and methylene diphenyl diisocyanate were used as diisocyanates for urethane synthesis, and they were end-capped with methyl methacrylate and hydroxyethyl methacrylate. The nature of the monomers that we used had an effect on the thermal and morphological properties that were interpreted in terms of the level of hydrogen bonding and the degree of phase separation. The synthe-

sized polymers were characterized by NMR, Fourier transform infrared/attenuated total reflectance spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and gel permeation chromatography. The number-average molecular weights of the poly(urethane acrylate)s were 2500–6000 g/mol. To use the polymer as a soft-liner material in denture applications, the residual isocyanate should not exist. In this study, we showed that a prepolymer without residual isocyanate could be synthesized. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 458–466, 2010

Key words: biocompatibility; dental polymers; esterification; polyurethanes; structure-property relations

INTRODUCTION

Polyurethanes are a unique class of polymers that have a wide range of applications.^{1,2} Because their properties can be readily tailored by the variation of their components, they have been used extensively as biomaterials. The applications include vascular prostheses, catheters, heart valves, and dental materials.^{3–14}

Urethane acrylates have been extensively investigated in the past as biomaterials useful in contact lenses,¹⁵ radiation,^{16,17} thermally sensitive materials,¹⁸ and dental materials.^{19–24} The matrix phases of dental composites, which are now widely used in restorative dentistry, are mostly di(meth)acrylate monomers. Although some urethane di(meth)acrylates have been commercialized for dental applications,²² they still hold promise to overcome the shortcomings of previously available resins.²⁴

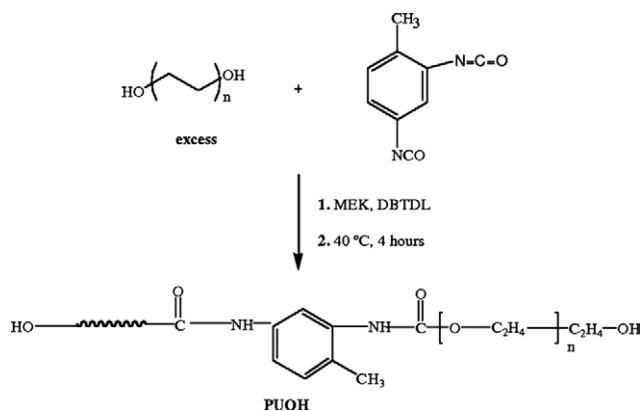
Soft-lining materials act as shock absorbers and reduce and distribute the stresses on the denture-

bearing tissues.^{25,26} If a patient cannot tolerate a hard denture because the tissues of the denture bear evidence of atrophy, the soft liner is placed between the denture prostheses and the tissue of patient. The most commonly used soft-liner materials are plasticized acrylic resins and silicones²⁷; other less common soft-liner materials include fluoroethylene copolymers, natural rubber, vinyl resins, hydrophilic acrylic polymers, and polyurethanes. They are synthesized in different forms and contain various additives. The soft-lining material should have properties such as biocompatibility, suitable mechanical strength, resistance to wetting, proper adherence, resistance to bacterial growth, nontoxicity, and the ability to be wetted by saliva.²⁸

Although polyurethanes are used in the fabrication of facial prostheses, their intensive use as a soft liners is avoided because of the possible risk of toxicity of the remaining isocyanates. However, isocyanates are very reactive and react readily with water. Therefore, a tailor-made soft liner from polyurethanes could solve the problem. The molecular weight of the prepolymer should be low, and the polymer should be end-capped with acrylate. There are many parameters, such as solubility, proper catalyst, temperature regulation, and heat dissipation, involved in the synthesis, and production of the proper material is not easy. The purpose of this

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Scheme 1 Synthesis of the PUOH prepolymer.

study was to synthesize and characterize hydroxyl-terminated poly(urethane acrylate) polymers that could be used as soft-lining materials for dentures. In this article, the synthesis mechanism and characterization of the product are reported. In later articles, the toxicity and antibacterial and rheological natures of the polymers will be given.

EXPERIMENTAL

Materials

2,4-Toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) were supplied by Aldrich (Milwaukee, WI) and were used as received. 1,6-Hexane diisocyanate (HDI) was purchased from Acros Organics (USA) with a purity better than 99.5%. Poly(ethylene glycol) [PEG; Sigma-Aldrich (St. Louis, MO); number-average molecular weight (M_n) = 200 g/mol] was dehydrated at 80°C *in vacuo* for 2 h to remove any absorbed moisture, and fresh PEG was used for each set of reactions. Methyl methacrylate (MMA) and hydroxyethyl methacrylate (HEMA) were purchased from Acros Organics. MMA was washed twice with aqueous 5% NaOH to remove hydroquinone (Aldrich) and twice with distilled water. It was dried with CaCl_2 and then with CaH_2 under nitrogen at a reduced pressure. The distillate was stored at low temperature and redistilled before use. HEMA was distilled under reduced pressure. Methyl ethyl ketone (MEK; >99%; Acros Organics), methanol (MeOH; Aldrich, 95%), dibutyl tin dilaurate (DBTDL; Aldrich), methacryloyl chloride (MAC; Fluka A.G., Buchs, Switzerland, 97%), and azobisisobutyronitrile (AIBN; Aldrich) were used without further purification.

Synthesis

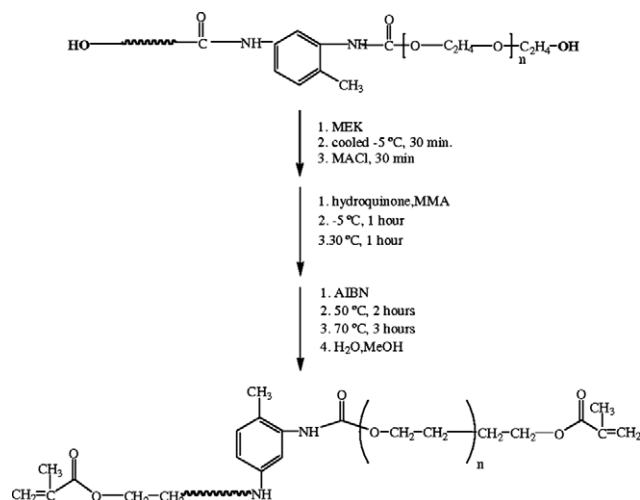
Synthesis of hydroxyl-terminated urethane (PUOH)

PUOH prepolymers were synthesized by the reaction between a diisocyanate; TDI, MDI, and HDI,

and an excess of PEG. The prepolymers were prepared in a three-necked, round-bottom, 250-mL Pyrex reaction flask equipped with an addition funnel, a reflux condenser, a thermometer, and a magnetic stirrer. The synthesis of the prepolymer from PEG ($M_n = 200$ g/mol) and TDI is given as an example in Scheme 1. Dried PEG (0.02 mol, 4 g) was poured into a flask containing MEK (50 mL). TDI (0.01 mol, 1.74 g) was mixed with MEK (50 mL), and the mixture was added through a dropping funnel under a nitrogen atmosphere. The solution was stirred continuously with a magnetic stirrer. When the addition of TDI was complete, the DBTDL (100 ppm) catalyst was added, and the reaction was continued for 4 h at 40°C. In addition to the di-*n*-butyl amine back-titration method, the NCO concentration was monitored by examination of the disappearance of the vibration band at 2270 cm^{-1} in the Fourier transform infrared (FTIR) spectrum.

Synthesis of hydroxyl-terminated poly(urethane acrylate)

PUOH prepolymers were end-capped with the acrylate monomers, MMA and HEMA, with the use of MAC (Scheme 2). The obtained PUOH prepolymer was diluted with MEK (100 mL) to decrease possible viscosity increase at low temperatures, and then, the mixture was cooled to -5°C by a dry-ice bath. The temperature was maintained at this level for 30 min, and with vigorous stirring, MAC (0.01 mol, 1 mL) was added dropwise under a nitrogen atmosphere. The mixture was then allowed to react for 30 min. Next, hydroquinone and MMA (0.02 mol, 2.00 g) were added, and the mixture was stirred for an hour at -5°C ; the bath was removed and the temperature was increased gradually to 30°C, and the reaction continued at this temperature for 1 h. After



Scheme 2 Acrylate end-capping reaction procedure for the hydroxyl-terminated polyurethane prepolymer.

TABLE I
Abbreviations of the Urethanes and Hydroxyl-Terminated Poly
(urethane acrylate) Polymers

Sample	Chemical composition	M_n (g/mol)	M_w (g/mol)	P_d
PUOH1	TDI/PEG	—	—	—
PUOH2	HDI/PEG	—	—	—
PUOH3	MDI/PEG	—	—	—
PUOHMMA1	TDI/PEG/MMA	4749	9820	2.068
PUOHMMA2	HDI/PEG/MMA	6234	13907	2.23
PUOHMMA3	MDI/PEG/MMA	5493	39486	7.19
PUOHHEMA1	TDI/PEG/HEMA	2590	2661	1.027

the addition of AIBN (1 wt % on the basis of acrylate, 0.02 g), the reaction temperature was first raised to 50°C for 2 h and then to 70°C for 3 h. The obtained polymer was filtered and washed with water and methanol several times and dried in a vacuum oven at 80°C for 1 day.

Measurements

FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer (Bruker Optics, Inc., Ettlingen, Germany) with an attenuated total reflectance (ATR) attachment (PIKE Technologies, Madison, WI), which had a MIRacle diamond crystal. All spectra were collected between 4000 and 600 cm^{-1} with 16 scans with a resolution of 4 cm^{-1} in transmission mode. The spectral data were acquired with OPUS 5.5 software (Bruker Optics, Inc.). ^1H - and ^{13}C -NMR spectra of the polymers were obtained by a Bruker 300-MHz NMR spectrometer (BioSpin, Ettlingen, Germany). Hexadeuterated dimethyl sulfoxide was used as the solvent. The proton signals were referenced to tetramethylsilane at 0 ppm as the internal standard. A Polymer Laboratories Ltd. (Church Stretton, UK) PL-GPC 220 gel permeation chromatograph was used to determine the molecular weight distribution of the polymers with the use of polystyrene standards. The samples were dissolved in dimethyl formamide (1% w/v solutions), which was used also as a carrier solvent at a rate of 1 mL/min. Differential scanning calorimetry (DSC) thermograms were recorded on a PerkinElmer Diamond differential scanning calorimeter (USA) provided with an intracooler device. Measurements in the temperature range from -70 to 150°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere were performed. Standard 40- μL aluminum pans with perforated lids, were used. Thermogravimetric analysis (TGA) of the obtained polymers was carried out on a PerkinElmer Pyris TGA-FTIR spectrometer. Thermograms were recorded in the temperature range 25 – 500°C with a heating rate of $10^\circ\text{C}/\text{min}$ under a 20-mL/min nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of PUOH

Several models of hydroxyl-terminated prepolymers were prepared, and the chemical compositions of the prepolymers are given in Table I. The influence of the diisocyanate structure on the final morphology of the polyurethane prepolymers is important. The PUOH polymers were characterized by FTIR-ATR and NMR spectroscopy for structural changes. Characteristic urethane FTIR-ATR vibrations appeared in each spectrum, especially vibrations in the amide I region (1680–1715), which confirmed the urethane formation. The main vibration frequencies are tabulated in Table II. Infrared spectroscopy is a simple but powerful technique for the investigation of hydrogen bonding in carbonyl compounds. Moreover, it is used to identify the phase separation behavior of the polymers. All of the compounds showed well-defined, strong carbonyl bands in a fairly broad wave-number range, depending on their hydrogen bonding capacities. The carbonyl vibration frequency of PUOH2 and PUOH3 appeared in the range of the disordered and limited hydrogen bonded urethane carbonyl vibration band, whereas the same band for PUOH1 appeared at the free carbonyl side. The N–H vibration frequency of the PUOH2 and PUOH3 prepolymers showed a hydrogen-bonded structure between the N–H of urethane and the carbonyl oxygen. On the other hand, the N–H group of PUOH1 was hydrogen-bonded to the etheric oxygen. The C=C stretching band was

TABLE II
Characteristic FTIR-ATR Vibration Bands of the
PUOH Prepolymers

Group assignment	Frequency (cm^{-1})		
	PUOH1	PUOH2	PUOH3
$\nu(\text{C}=\text{O})$	1722	1713	1706
$\nu(\text{N}-\text{H})$	3298	3334	3310
$\nu(\text{C}=\text{C})$	1601	—	1600
$\delta(\text{C}-\text{N}-\text{H}) + \nu(\text{C}-\text{N})$	1536	1536	1534
$\delta(\text{N}-\text{H}) + \delta(\text{C}-\text{N})$	1224	1241	1221
$\nu(\text{C}-\text{O}-\text{C})$ ether group	1101	1102	1107
$\nu(\text{C}-\text{O}-\text{C})$ hard segment	1065	1061	1069

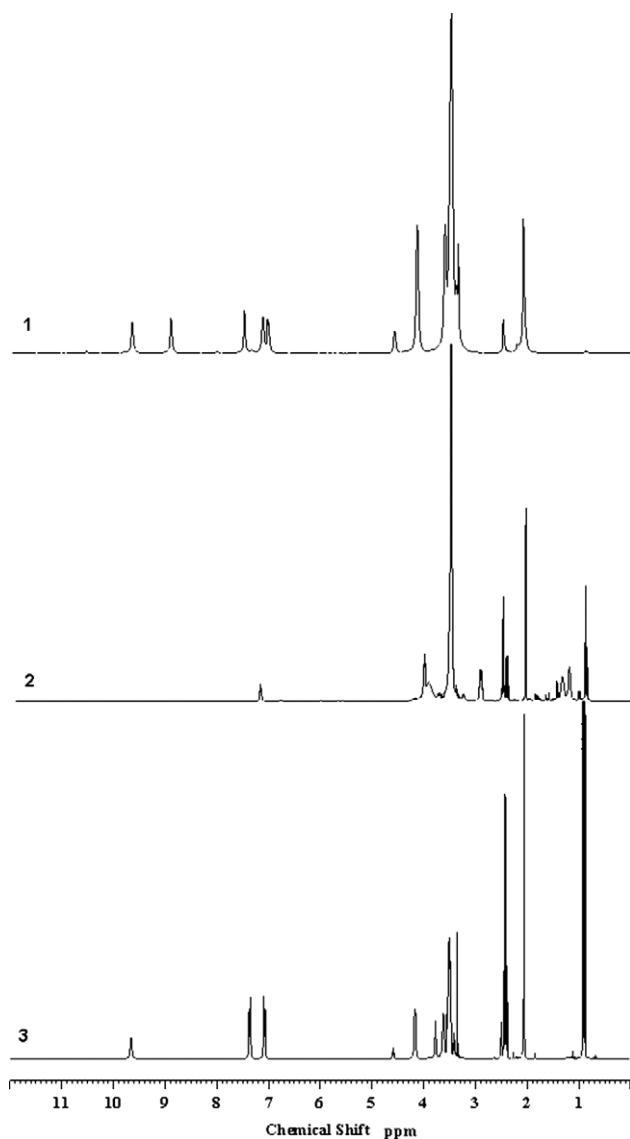


Figure 1 $^1\text{H-NMR}$ spectra of (1) PUOH1, (2) PUOH2, and (3) PUOH3.

not present in the PUOH2 spectrum, which was synthesized from aliphatic isocyanate, as expected. This band appeared almost at the same frequency for the prepolymers synthesized from aromatic diisocyanates (1600 cm^{-1}).

The $^1\text{H-NMR}$ spectra of the PUOH prepolymers are given in Figure 1. The urethane protons ($-\text{NH}$ in urethane) were observed at $\delta = 8.9$ and 9.7 ppm for PUOH1, at $\delta = 7.2$ – 7.3 for PUOH2, and at $\delta = 9.7$ ppm for PUOH3. The aromatic protons from TDI appeared at $\delta = 7$ – 7.6 ppm, and the methyl proton was assigned to the peak at $\delta = 2.5$ ppm. The hydroxyl proton ($-\text{OH}$) was at $\delta = 4.4$ ppm, and the $-\text{OCH}_2$ protons were found at $\delta = 4.3$ ppm. The CH_2 protons of PEG were at $\delta = 3.2$ – 3.7 ppm. The phenyl protons of the aromatic ring of PUOH3 are observed at $\delta = 7.1$ – 7.4 ppm. There existed small double-bond peaks from the resonance of the amide

groups at the area of 5.5 – 6.3 ppm in the $^1\text{H-NMR}$ spectrum of PUOH2.

The $^{13}\text{C-NMR}$ spectrum of PUOH1 is given in Figure 2. The carbonyl peak from the urethane group was at $\delta = 153$ ppm, and the aromatic carbons appeared at δ values between 114 and 137 ppm. The ether carbon peaks ($-\text{OCH}$) were at $\delta = 68$ ppm, and that of $-\text{CH}_3$ was at $\delta = 17$ ppm.

The thermal stability of the synthesized polymers was evaluated from the TGA in a nitrogen environment. The corresponding thermal stability curves are shown in Figure 3. The TGA thermogram of PUOH1 showed a smooth decrease, starting from 100°C with

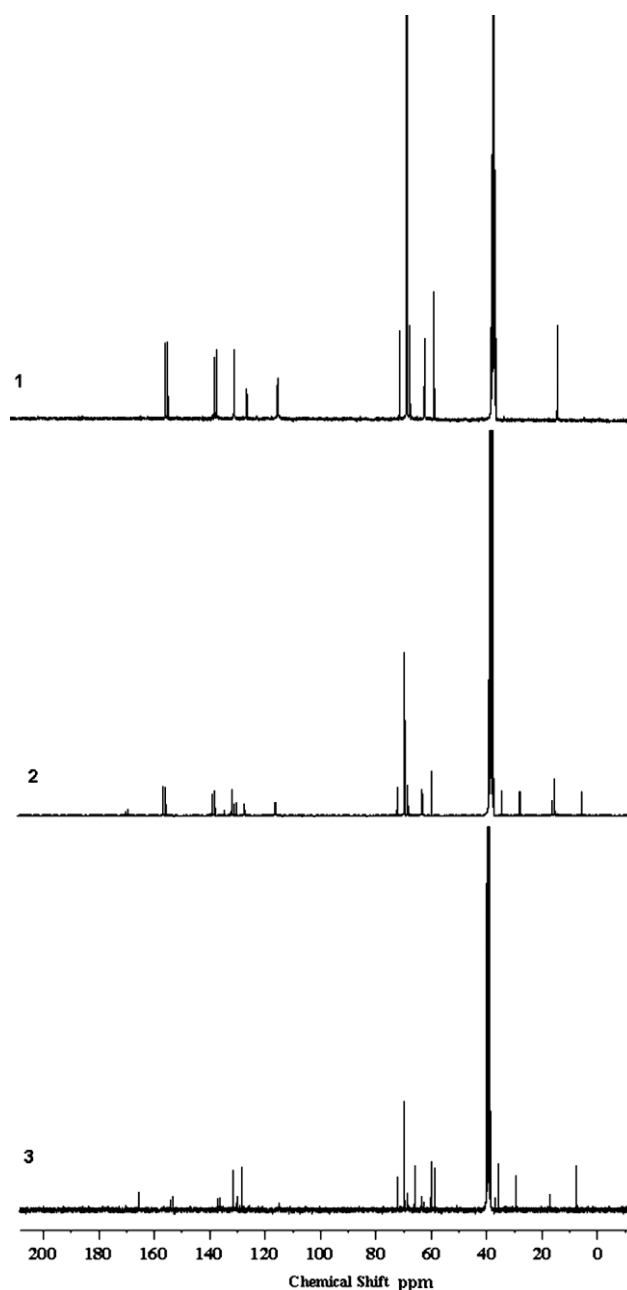


Figure 2 $^{13}\text{C-NMR}$ spectra of (1) PUOH1, (2) PUOHMMA1, and (3) PUOHHEMA1.

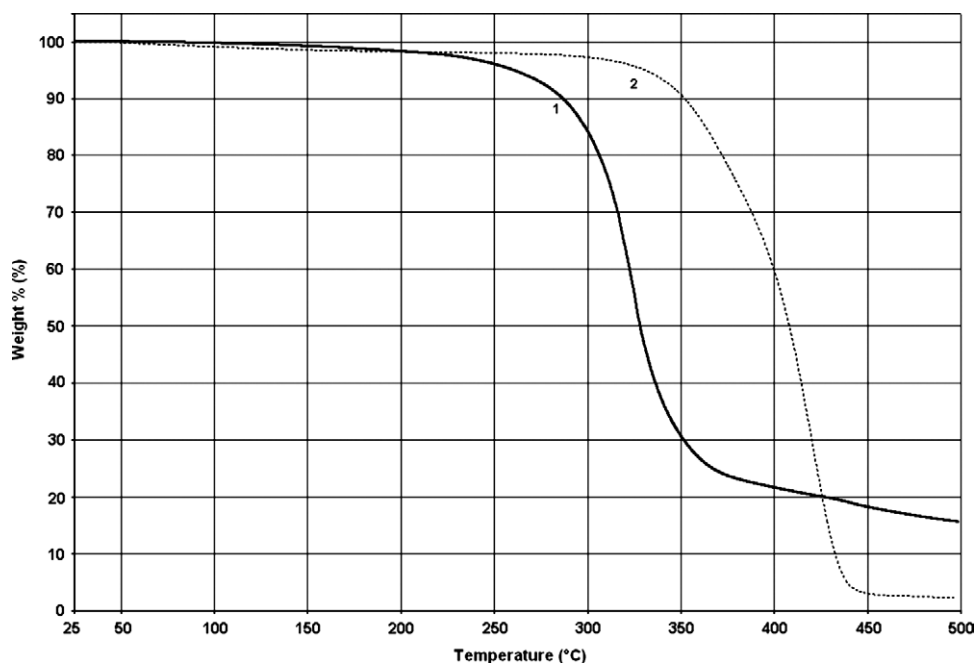


Figure 3 TGA thermogram of (1) PUOH1 and (2) PUOH2.

a weight loss of 10% up to 280°C; then, there was an increasing rate of degradation, which was maximized at 325°C, with a total weight loss of 83%. The char yield was about 15% and was stable up to higher temperatures, which was because of aromatization. This decomposition could be considered to be a random scission type with a limited amount of end group cyclization and depolymerization. How-

ever, the degradation of PUOH2 was sharp and most likely a depolymerization-type degradation. The main degradation was maximized at 420°C and had a shoulder at 375°C. The total weight loss was 97% at 450–500°C. The TGA thermogram of PUOH3 was identical to that of PUOH1.

DSC analysis was conducted to investigate the crystallization behavior of the prepared polymers.

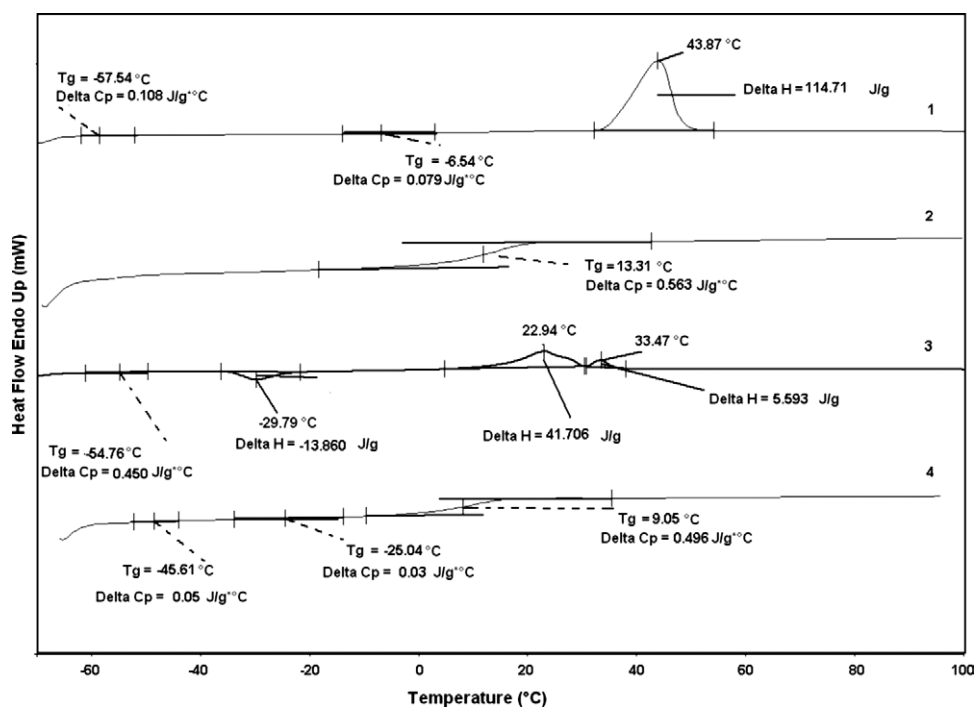


Figure 4 DSC thermograms of (1) PUOH2, (2) PUOHMMA1, (3) PUOHMMA2, and (4) PUOHMMA3. Cp and H refers to the heat capacity and the enthalpy of fusion, respectively.

It also gave us an idea about the extent of phase separation present in the prepolymers. The DSC thermogram of PUOH2 is given in Figure 4 for the temperature range between -70 and 100°C . Two glass-transition temperatures (T_g 's) were observed at -57.4 and -6.54°C ; these corresponded to the soft and hard domains, respectively. This also showed phase separation of the segments and liquid crystal nature. This result is in agreement with the FTIR-ATR vibration frequencies given in Table II. The heat capacity changes at the T_g values were 0.108 and 0.079 J/g $^\circ\text{C}$. The melting point (T_m) of PUOH2 was 43.87°C with an enthalpy of fusion 114.71 J/g. The presence of T_m (proven to be T_m from the second derivative) showed the T_m of the hard segment in the liquid-crystal phase.

Synthesis of the acrylate-end-capped hydroxyl-terminated polyurethane (PUOHA)

Acrylate end capping of the previously obtained prepolymers was achieved with two types of acrylates, MMA and HEMA. The compositions of the synthesized PUOHA prepolymers are given in Table I. The molecular weights and polydispersity index (P_d) values of the PUOHA polymers are given in Table I. The MMA-end-capped polymers had much higher M_n and weight-average molecular weight (M_w) values compared to the HEMA-end-capped polymer PUOHHEMA1. The P_d value of PUOHMMA3 was 7.19 . PUOHMMA2 had the highest M_n and M_w values.

The obtained prepolymers were not purified; therefore, it was possible that they may have contained some fractions of acrylate homopolymers in the final product. This gave rise to the difference between M_n and M_w as well as P_d . However, the observed differences were not too big, and therefore, they could be acceptable for application as soft liners.

The effect of acrylate end capping on the PUOH prepolymers was investigated with FTIR-ATR spectroscopy. The corresponding spectra are given in Figure 5. All of the polymers had the characteristic vibration bands of urethane. NH stretching vibration maxima of PUOHMMA1, PUOHMMA3, and PUOHHEMA1 appeared at 3295 – 3310 cm^{-1} , and these bands showed the presence of strong hydrogen bonding. This result was also consistent with the vibration frequency of the carbonyl band, that is, at 1705 – 1710 cm^{-1} . On the other hand, the N–H vibration for PUOHMMA2 was at the free-NH side, and the carbonyl vibration frequency was recorded at 1716 cm^{-1} , that is, close to the free carbonyl vibration band. All of the polymers except PUOHMMA2 had a C=C vibration band at 1602 cm^{-1} because of the aromatic ring present in the diisocyanate struc-

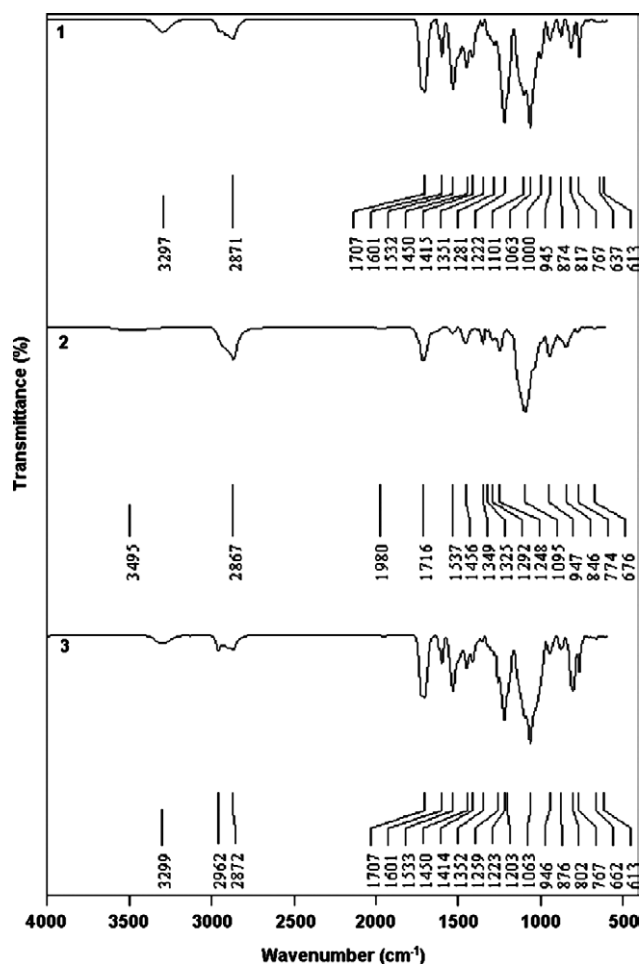


Figure 5 FTIR-ATR spectra of (1) PUOHMMA1, (2) PUOHMMA2, and (3) PUOHMMA3.

ture. The vinyl group stretching vibration band was at 1636 cm^{-1} for PUOHHEMA1.

The chemical structures of the PUOHAs were characterized by ^1H - and ^{13}C -NMR spectroscopy. The ^{13}C -NMR and ^1H -NMR spectra of PUOHMMA1 are given in Figures 2 and 6, respectively. Urethane protons ($-\text{NH}$ in urethane) were observed at $\delta = 8.9$ and 9.8 ppm, aromatic protons appeared at $\delta = 6.9$ – 7.9 ppm, the methyl proton was assigned to the peak at $\delta = 0.9$ ppm, the hydroxyl proton ($-\text{OH}$) was at $\delta = 2$ ppm, and the $-\text{OCH}_2$ protons were found at $\delta = 3.4$ ppm. Vinyl protons of MMA were observed at $\delta = 5.7$ and 5.9 ppm. In the ^{13}C -NMR spectrum, there were two carbonyl peaks at $\delta = 153$ and 154 ppm, which corresponded to the urethane and acrylic carbonyl. The aromatic carbons and carbons of the vinyl end group appeared at $\delta = 114$, 122 , 125 , 130 , 136 , and 137 ppm. The ether carbon peaks ($-\text{OCH}$) were at $\delta = 63$, and $-\text{CH}_2$ was at $\delta = 29$ ppm. The methyl carbon attached to the aromatic ring was observed at $\delta = 17$ ppm.

The ^{13}C -NMR and ^1H -NMR spectra of PUOHHEMA1 are presented in Figures 2 and 6,

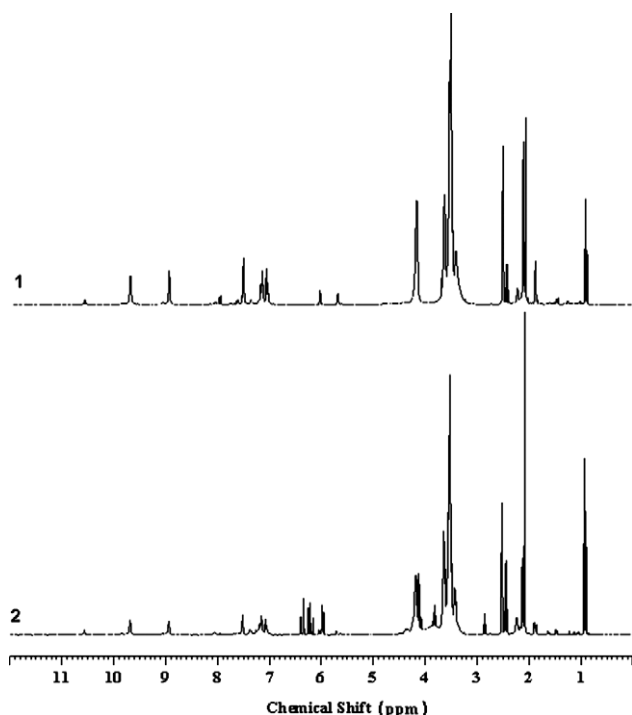


Figure 6 ^1H -NMR spectra of (1) PUOHMMA1 and (2) PUOHHEMA1.

respectively. Characteristic chemical shifts for the protons present in the polymer structure were observed at $\delta = 8.9$ and 9.6 ppm for NH protons, $\delta = 6.9$ – 7.6 ppm for aromatic protons, $\delta = 5.7$ – 6.4 ppm for the vinyl protons of HEMA, and $\delta = 2.1$ ppm for the hydroxyl proton ($-\text{OH}$). In the ^{13}C -NMR spectrum, there were three carbonyl peaks at δ

$= 153, 154,$ and 165 ppm, which corresponded to the urethane and acrylic carbonyl carbons. Vinyl carbons were present at $\delta = 114$ – 130 ppm, which were very near the aromatic carbons.

The nonisothermal stabilities of the PUOHA polymers were studied with TGA. The TGA thermograms of the PUOHA polymers are given in Figure 7. All of the polymers had two main degradation stages, which are described in Table III. PUOHMMA1 was degraded within two steps. First, a degradation with a weight loss of 10% was up to 130°C and might be attributed to solvent removal; it was followed by a second degradation maximized at 350°C (in the range of 300 – 375°C) with a total weight loss of 90%. The general trend of the thermogram resembled that of PUOH1 (Fig. 3). In this case, the acrylate ends led to a much higher thermally stable polymer. The thermal degradation of PUOHMMA1 could be considered a depolymerization mechanism type.

The thermal degradation of PUOHMMA2 started from 30 to 310°C with a smooth decrease that led to a weight loss of 10% and continued up to 400°C with a weight loss of about 32%. Then, the rate of degradation increased and was maximized at 420°C with a shoulder at 410°C due to decomposition of side groups. The total weight loss in stage 2 was 96%. A random-scission-type degradation behavior with some depolymerization was also observed in the PUOHMMA2 thermogram. The thermal degradation of PUOHMMA3 showed the same trend as was observed in the PUOHMMA1 thermogram. A smooth decrease by 10% due to possible end-group

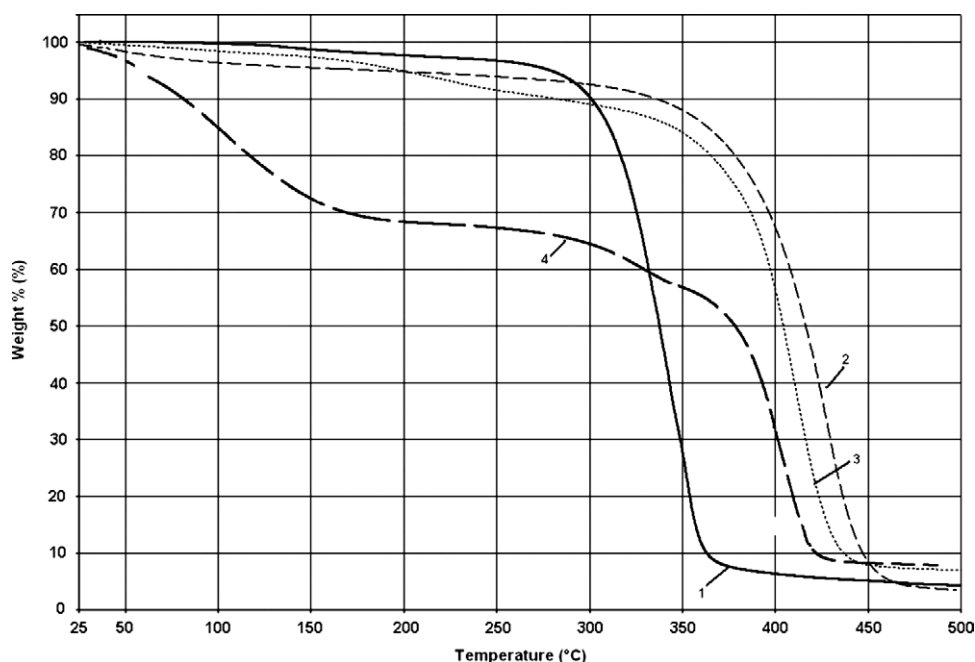


Figure 7 TGA thermograms of (1) PUOHMMA1, (2) PUOHMMA2, (3) PUOHMMA3, and (4) PUOHHEMA1.

TABLE III
TGA Results for the PUOHA Polymers

Polymer	Degradation stage	Temperature (°C)	Weight loss (%)
PUOHMMA1	1	130	10
	2	350	90
PUOHMMA2	1	410	45
	2	430	40
PUOHMMA3	1	216	6
	2	410	93
PUOHHEMA1	1	200	30
	2	430	95

cyclization was observed at 216°C, and the main-chain degradation with a total weight loss of 93% was maximized at 410°C.

PUOHHEMA1 decomposition (Fig. 7) started at room temperature, continued up to 200°C, and ended with a weight loss of 30% due to side-group degradation. This degradation could be regarded as a linkage type. This first degradation stage was followed by a random degradation with fluctuations due to end-group cyclization, and the second stage continued to 430°C and ended with a total weight loss of 95%. The TGA thermogram of PUOHHEMA1 had a similar characteristic to the typical TGA thermogram of poly(hydroxyethyl methacrylate). Therefore, it was possible to have a considerable amount of the homopolymer HEMA. Similarly, the PUOHMMA3 thermogram showed more depolymerization-type degradation, which was typical of poly(methyl methacrylate) homopolymers.

The thermal behaviors of PUOHMMA1, PUOHMMA2, and PUOHMMA3 were characterized by the DSC thermograms that are given in Figure 4. PUOHMMA1 exhibited a T_g value of 13.31°C with a heat capacity of 0.563 J/g °C. The single T_g value of the sample showed phase mixing of the sample rather than phase separation. The DSC thermogram of PUOHMMA2 showed a T_g at -54.76°C with a heat capacity change of 0.45 J/g °C. The crystallization peak was observed at -29.79°C. There were two T_m values, which were at 22.94 and 33.47°C, because of the polymorphic structures present. The enthalpy of fusion for the crystallization was -13.8 J/g, and those for melting were 41.7 and 5.6 J/g, respectively. The results of the DSC data show that there existed phase mixing and liquid-crystal formation in the polymer. The obtained T_m values indicated the presence of liquid crystals, whereas the observed single T_g value was an indication of phase mixing (no phase separation).

The T_g values observed for PUOHMMA3 were at -45.61, -25.04, and 9.05°C, as given in Figure 4. The negative T_g values may have corresponded to the transitions of the soft and hard segments present in

the acrylate-end-capped polyurethane, whereas the positive one may have been due to the homopolymer of the acrylate (oligomer). The molecular weight of the homopolymer was calculated from the Fox-Flory equation to be 3049 g/mol.²⁹ The limiting value of the T_g at a high molecular weight (T_g^∞) and constant K , which depends on the nature of polymer, were reported as $K = 4.3 \times 10^5$ and $T_g^\infty = 423$ K.³⁰

CONCLUSIONS

The commercial synthesis of polyurethane has received much attention from the very beginning, as low-cost synthesis is popular in many industries. However, there are some applications that require very special type of urethanes and require elaborate methods of synthesis. One of the main applications is the biomedical application to obtain materials such as soft liners, which can be used for the relining of removable prosthesis. For this purpose, a low-molecular-weight, hydroxyl-ended prepolymer has to be synthesized. It is then end-capped with acrylate to get a macromonomer, which can be cured to give a macromolecule of a final thermosetting polymer or a relatively more viscoelastic material of a soft liner. PUOHA polymers were synthesized with M_n values of 2590–6234 g/mol. In this synthesis, the effect of diisocyanate and acrylate were very important. The additions of acrylate to the urethane prepolymer required specific conditions, the rate of addition reaction by interesterification, temperature control, and the prevention of vinyl addition reactions. The interesterification reaction was highly exothermic, and the local temperature increase caused gelation. This could be controlled by an adjustment of the rate of the esterification reaction and the dissipation of the exothermic heat of reaction. Therefore, the reaction temperature was maintained between 30 and 70°C.

The DSC results show the liquid-crystal nature of some of the samples. Corresponding polymorphs for PUOHMMA2 were observed at 22.94 and 33.47°C. The FTIR-ATR investigation clarified the phase mixing and/or phase separation of some samples. The samples that showed phase mixing had more hydrogen bonding and more parallel linear chains, which showed liquid crystal properties. In the case of phase separation, the hard and soft samples showed two T_g values. Although acrylates are usually added to a reaction medium slowly, because of the mobility of the reaction medium, some acrylates gave a low-molecular homopolymer of the polyacrylates. The formation of the homopolymer could be predicted from the DSC thermogram, which could also be used to estimate the molecular weight of the homopolymer of acrylate. PUOHMMA3 with a P_d value

of 7.19 contained a poly(methyl methacrylate) with an M_n value of 3049 g/mol.

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