Synthesis and Characterization of Poly(urethane-ester)s Based on Calcium Salt of Mono(hydroxybutyl)phthalate

R. Arun Prasath,[1,2,*] **S. Nanjundan,**[1] **T. Pakula,**[2] **M. Klapper**[2]

[1]*Department of Chemistry, Anna University, Chennai 600 025, India*
[2]*Max-Planck Institute of Polymer Research, Postfach 3148, D-55021, Mainz, Germany*

ABSTRACT: Calcium-containing poly(urethane-ester)s (PUEs) were prepared by reacting diisocyanate (HMDI or TDI) with a mixture of calcium salt of mono(hydroxybutyl)phthalate [$Ca(HBP)_2$] and hydroxyl-terminated poly(1,4-butylene glutarate) [$HTPBG_{1000}$], using di-*n*-butyltin-dilaurate as catalyst. About six calcium-containing PUEs having different composition were synthesized by taking the mole ratio of $Ca(HBP)_2$:$HTPBG_{1000}$:diisocyanate (HMDI or TDI) as 3:1:4, 2:2:4, and 1:3:4. Two blank PUEs were synthesized by the reaction of $HTPBG_{1000}$ with diisocyanate (HMDI or TDI). The polymers were characterized by IR, ^{1}H NMR, Solid state ^{13}C-CP-MAS NMR, TGA, DSC, XRD, solubility, and viscosity studies. The T_g value of PUEs increases with increase in the calcium content and decreases with increase in soft segment content. The viscosity of the calcium-con-taining PUEs increases with increase in the soft segment content and decreases with increase in the calcium content. X-ray diffraction patterns of the polymers show that the HMDI-based polymers are partially crystalline and TDI-based polymers are amorphous in nature. The dynamic mechanical analysis of the calcium-containing PUEs based on HMDI shows that with increase in the calcium content of polymer, modulus (g' and g'') increases at any given temperature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1720–1727, 2006

Key words: poly(urethane-ester)s; calcium-containing polymer; NMR spectra; thermal properties; dynamic mechanical analysis

INTRODUCTION

Polymers having metal linkages in the polymer backbone are of interest from the scientific and industrial viewpoints, as these polymers have various applications such as aqueous thickeners, impregnates, textile seizers, adhesives, additives, resins, catalysts,[1–8] and in biomedical fields.[9–12] Metal-containing polyurethanes and copolyurethanes based on various divalent metal salts of mono(hydroxyalkyl)phthalate [$M(HAP)_2$] were reported in high purity and high yield.[13–42] Calcium and magnesium containing polyesters obtained by using calcium and magnesium salts of mono(hydroxyethyl)phthalate [$M(HEP)_2$] showed better physical and mechanical properties than those of commercial polyester without metal.[4–6,17–19,27] In general, polyurethanes, polyesters, polyureas, and polyethers or combination of the above polymers have a variety of biomedical applications.[43–52] Calcium-containing biodegradable polyurethanes and polyesters are known in biomedical implants, as it showed better physical and mechanical properties.[53–56] Calcium compounds blended with polymeric materials having carboxyl group are used as additives for dental cement to have good rigidity, as Ca^{2+} coordination or complexation with carboxyl group containing polymers to have high hardening with superior mechanical properties.[57] Calcium compounds filled hybrid polymeric materials are known to have unique properties such as good mechanical and optical properties.[58] We have reported about the synthesis and characterization of calcium-containing poly(urethane-ether)s using calcium salts of mono(hydroxybutyl)phthalate [$Ca(HBP)_2$].[59] In this article, we report about the synthesis and characterization of a new type of calcium-containing poly(urethane-ester)s (PUEs) by the reaction of diisocyanate (HMDI or TDI) with a mixture of calcium salt of $Ca(HBP)_2$ and hydroxyl-terminated poly(1,4-butylene glutarate) [$HTPBG_{1000}$].

EXPERIMENTAL

Materials

Phthalic anhydride (Aldrich), calcium acetate (Merck), 1,4-butanediol (Merck), hexamethylene diisocyanate (HMDI) [Merck], toluylene 2,4-diisocyanate (TDI) [Merck], and di-*n*-butyltin-dilaurate (DBTDL) [Al-

---

Correspondence to: R. A. Prasath (arun.ramaswamy@strath.ac.uk).

Present address: Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, Scotland, United Kingdom.

drich] were used as received. $HTPBG_{1000}$ of average molecular weight 1000 (Aldrich) was used after dehydration. Solvents such as methanol, ethanol, acetone, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate, ethyl methyl ketone, *n*-hexane, benzene, chlorobenzene, toluylene, xylene, and tetra hydrofuran are commercial and purified by standard methods. Dimethyl sulfoxide (DMSO), *N-N'*-dimethyl formamide (DMF), and dimethyl acetamide (DMAc) were obtained from Aldrich.

Synthesis of calcium-containing PUEs

Calcium salt of $Ca(HBP)_2$ was synthesized as reported in our earlier study.[40] Calcium-containing PUEs were prepared by taking a mixture of the monomers $Ca(HBP)_2$ (4.11 g, 0.008 mol) and hydroxyl-terminated polybutylene glutarate [$HTPBG_{1000}$] (8.00 g, 0.008 mol) dissolved in 250 mL DMF in a 500 mL three-necked round bottom flask fitted with an argon inlet, a condenser, and a dropping funnel. To this ~3 drops of DBTDL was added as catalyst. The reaction mixture was heated to 80°C over an oil bath under argon atmosphere with constant stirring using a magnetic stirrer. Then, a solution of HMDI (2.6 mL, 0.016 mol) or TDI (2.3 mL, 0.016 mol) in DMF (20 mL) was added slowly from a dropping funnel to the reaction mixture over a period of 30 min. After the addition, the reaction temperature was raised to 90°C and stirred at the same temperature for 8 h, and then the reaction vessel was taken out of the oil bath and set aside over night. DMF was added to the mixture to make the viscosity of the solution suitable for filtration. The filtrate was poured into an excess quantity of vigorously stirred acetone to precipitate the polymer. The copolymer was washed with water to remove the unreacted $Ca(HBP)_2$ and then with acetone and chloroform. The copolymer was dried in vacuum at 80°C for 24 h. PUEs having different compositions were prepared by taking the mole ratio of $Ca(HBP)_2$: $HTPBG_{1000}$: HMDI or TDI as 3 : 1 : 4, 2 : 2 : 4, and 1 : 3 : 4.

Instrumentation

IR spectra were recorded in a Perkin–Elmer Model 598 spectrophotometer using potassium bromide (KBr) pellet method. ^{1}H NMR spectra were recorded with Brucker MSL 300 MHz spectrometer. Solid State ^{13}C-CP-MAS-NMR spectra were recorded using Brucker MSL 75 MHz spectrometer with adamantine as chemical shift reference. Thermogravimetric analysis was carried out using Mettler TA-300-thermal analyzer in air atmosphere at the heating rate of 10°C/min. DSC measurements have been performed with the cooling and heating rate of 10°C/min using a Mettler 30 calorimeter with a cell purged with nitrogen. Dynamic mechanical measurements were performed by means of Rheometric Mechanical Spectrometer (RMS 800). Solubility of the polymers was tested in various polar and nonpolar solvents. The inherent viscosity, η_{inh}, of the polymers was determined using Ubbelohde-Viscometer in DMSO at 40°C. X-ray diffractograms were recorded according to powder method with a Philips PW 1710 diffractrometer using Cu kα radiation.

RESULTS AND DISCUSSION

Synthesis of calcium-containing PUEs

Calcium-containing PUEs were prepared by reacting diisocyanate (HMDI or TDI) dissolved in DMF with a mixture of $Ca(HBP)_2$ and $HTPBG_{1000}$ in DMF at 90°C, using DBTDL as catalyst. By taking the mole ratio of $Ca(HBP)_2$: $HTPBG_{1000}$: diisocyanate as 3 : 1 : 4, 2 : 2 : 4, and 1 : 3 : 4, calcium-containing PUEs having different compositions were prepared. Using the monomers, $Ca(HBP)_2$ and $HTPBG_{1000}$ in different ratios, six PUEs were prepared based on HMDI and TDI. Scheme 1 shows the reaction involved in the preparation of PUEs. The polymers are coded as $Ca(HBP)_2$-$HTPBG_{1000}$-HMDI (3 : 1 : 4) **(1)**, $Ca(HBP)_2$-$HTPBG_{1000}$-HMDI (2 : 2 : 4) **(2)**, $Ca(HBP)_2$-$HTPBG_{1000}$-HMDI (1 : 3 : 4) **(3)**, $Ca(HBP)_2$-$HTPBG_{1000}$-TDI (3 : 1 : 4) **(4)**, $Ca(HBP)_2$-$HTPBG_{1000}$-TDI (2 : 2 : 4) **(5)**, and $Ca(HBP)_2$-$HTPBG_{1000}$-TDI (1 : 3 : 4) **(6)**. The results of synthesis of PUEs are given in Table I. Blank PUEs without $Ca(HBP)_2$ were also prepared by using the aforementioned procedure. Two blank PUEs coded $HTPBG_{100}$-HMDI **(7)** and $HTPBG_{1000}$-TDI **(8)** were used for comparing their properties with that of calcium-containing PUEs. The synthesis data for PUEs are given in Table I.

Characterization of calcium-containing PUEs

The IR spectra of calcium-containing PUEs (polymers **2** and **5**) are shown in Figure 1. The broad band at 3389–3346 cm^{-1} is due to the N—H stretching. The two bands at 2957–2934 and 2869–2859 cm^{-1} are due to the asymmetrical and symmetrical C—H stretching of methylene groups. The peaks about 1733–1710 cm^{-1} are attributed to the carbonyl stretching of urethane and ester groups. The two broad bands at 1591–1548 and 1412–1400 cm^{-1} confirm the presence of static linkages between COO— and Ca^{2+} in the PUEs. The C—O stretching was observed at 1077–1069 cm^{-1}.

The ^{1}H NMR spectra of PUEs (polymers **2** and **5**) are shown in Figure 2. The ^{1}H NMR spectra of TDI-based PUEs show peaks about 9.35–9.28 and 8.55–8.45 ppm due to the urethane N—H protons while that of HMDI-based PUEs show the corresponding peaks about 6.52–6.45 ppm. The peaks about 8.00–6.95 ppm are due to aromatic protons. The peaks at 4.21–3.95 ppm are due to the methyleneoxy group attached to —COPh, —CONH,
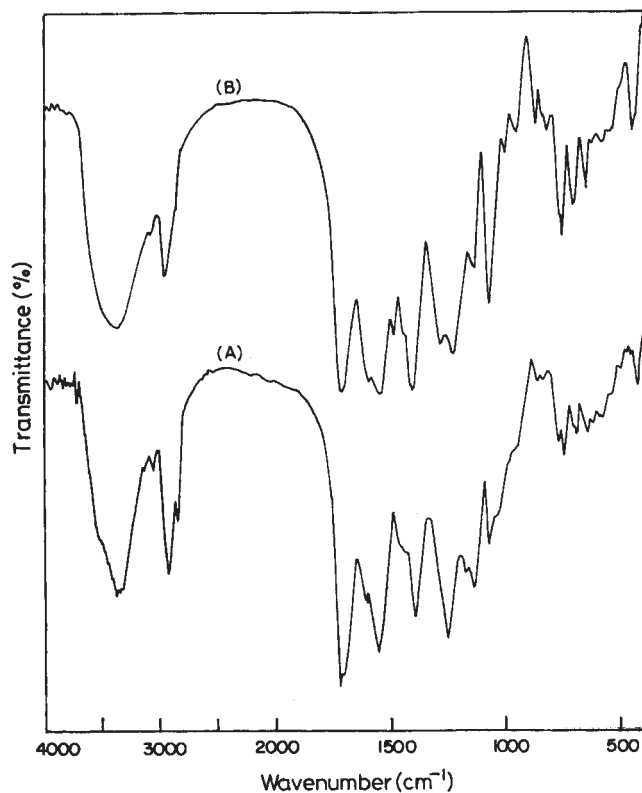
Scheme 1

Polymer	1	2	3	4	5	6
Ca(HBP)$_2$-HTPBG$_{1000}$-Diisocyanate	3:1:4	2:2:4	1:3:4	3:1:4	2:2:4	1:3:4
R	I	I	I	II	II	II
R^1	III	III	III	III	III	III

and —COCH$_2$ groups. The methylene group attached to —NH shows peak at 2.98 ppm. The methylene group attached to —COO shows peak at 2.31–2.29 ppm. The peak about 2.12–2.10 ppm is due to the methyl group attached to aromatic ring of TDI-based PUEs. The methylene group attached to —CH$_2$COO, —CH$_2$OCONH, —CH$_2$OCOPh, —CH$_2$NHCOO, and —CH$_2$COOCH$_2$ shows resonance peak about 1.83–1.55 ppm. The other methylene group attached to —(CH$_2$)$_2$NHCOO shows a resonance peak about 1.42–1.20 ppm.

Figure 3 shows the solid state ^{13}C-CP-MAS NMR spectra of Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4). The solid state ^{13}C-CP-MAS NMR spectra of PUEs show their carboxylate carbon and ester carbonyl carbon peak at 173.24–172.59 ppm. The urethane carbon peaks of HMDI-based polymers were observed about

157.62–157.21 ppm and that of TDI-based polymers were observed about 153.71–153.33 ppm. The TDI-based copolymer shows broad peaks about 136.33–114.59 ppm that is attributed to the aromatic carbons. HMDI-based copolymers show the corresponding broad peak about 130.02–129.67 ppm. The methyleneoxy carbon attached to —COCH$_2$, —COPh, and —CONH shows peak about 65.92–64.81 ppm. The methylene group attached to —NHCOO group shows peak about 41.73–41.37 ppm in the case of HMDI-based polymer. This peak is not seen in the ^{13}C NMR spectra of the polymer in solution state. The broad peak about 27.27–26.24 ppm is due to the other methylene groups in the polymer chain. The methyl group of TDI-based polymer shows resonance signals about 20.12–20.10 ppm.

TABLE I
Synthesis and Viscosity of Calcium-Containing Poly(urethane-ester)s

Polymer no.	Polymer	External appearance	η_{inf}
1	Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (3 : 1 : 4)	White	0.1107
2	Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4)	White	0.1478
3	Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (1 : 3 : 4)	Rubber white	0.2062
4	Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (3 : 1 : 4)	Yellowish white	0.0972
5	Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (2 : 2 : 4)	Yellowish white	0.1257
6	Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (1 : 3 : 4)	Waxy yellow	0.1972
7	HTPBG$_{1000}$-HMDI	White	0.3125
8	HTPBG$_{1000}$-TDI	Slightly yellow	0.2874

DMF was used as solvent for polymer synthesis; reaction time, 8 h; reaction temperature, 90°C.

Figure 1 IR spectra of (A) $Ca(HBP)_2$-$HTPBG_{1000}$-HMDI (2 : 2 : 4) and (B) $Ca(HBP)_2$-$HTPBG_{1000}$-TDI (2 : 2 : 4).

The TGA traces of calcium-containing PUEs (polymers **1–6**) along with blank PUEs (polymers **7** and **8**) are shown in Figure 4. Calcium-containing PUEs show 2–3 stage decompositions. Blank PUEs show single stage decomposition. Initial decomposition temperature (IDT) of PUEs decreases with increase in the calcium content, also the rate of decomposition of PUEs decreases with increase in the calcium content. The blank PUEs show slightly higher IDT than calcium-containing PUEs but the decomposition rate of blank PUEs is higher than that of calcium-containing PUEs. The TDI-based PUEs show higher thermal stability than HMDI-based PUEs. In general, the residual weight at 750°C corresponds to CaO formed for the PUEs, based on $Ca(HBP)_2$. Thermal data for PUEs are given in Table II. Thermal stability of metal-containing polyesters decreases with increase in the metal salt content in the feed and this was reported.[19] It was also known that the presence of various metallic ions in the polyurethanes or copolyurethanes reduce the initial thermal stability of the polymer and enhance the thermal stability of its intermediate decomposition products.[60–63]

DSC traces of calcium-containing PUEs (polymers **1, 2, 4,** and **5**) along with blank PUEs (polymers **7** and **8**) are given in Figure 5. The PUEs derived from $Ca(HBP)_2$, $HTPBG_{1000}$, and HMDI or TDI show two T_g values when the composition of $Ca(HBP)_2$:$HTPBG_{1000}$:

The calcium-containing PUEs were insoluble in methanol, ethanol, acetone, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate, ethyl methyl ketone, *n*-hexane, benzene, chlorobenzene, toluylene, xylene, and tetra hydrofuran. However, they are soluble in highly polar solvents such as DMF, DMSO, and DMAc at 40°C. The inherent viscosity data for the PUEs in DMSO (1 g/dL) at 40°C are given in Table I. The value of inherent viscosity is lower when compared with that of blank PUEs containing no $Ca(HBP)_2$ units. A similar behavior was reported earlier for polymers with ionic bonds in the backbone.[40–42] The viscosity of the PUEs increases with increase in soft segment content and decreases with increase in the calcium content. This reveals that at higher amount of calcium content, the polymeric backbone will have more ionic linkages, which would dissociate into lower molecular weight fragments in DMSO to have lower viscosity.[35] The higher the soft segment content and lower the calcium content of the polymer, higher would be the viscosity due to the presence of less ionic linkages, which would give higher molecular weight fragments after dissociation in DMSO. The HMDI-based PUEs show higher viscosity than TDI-based PUEs because the chain length for a given molecular weight of the polymer is higher in the HMDI-based PUEs than in the TDI-based PUEs.

Figure 2 ^1H NMR spectra of (A) $Ca(HBP)_2$-$HTPBG_{1000}$-HMDI (2 : 2 : 4) and (B) $Ca(HBP)_2$-$HTPBG_{1000}$-TDI (2 : 2 : 4).

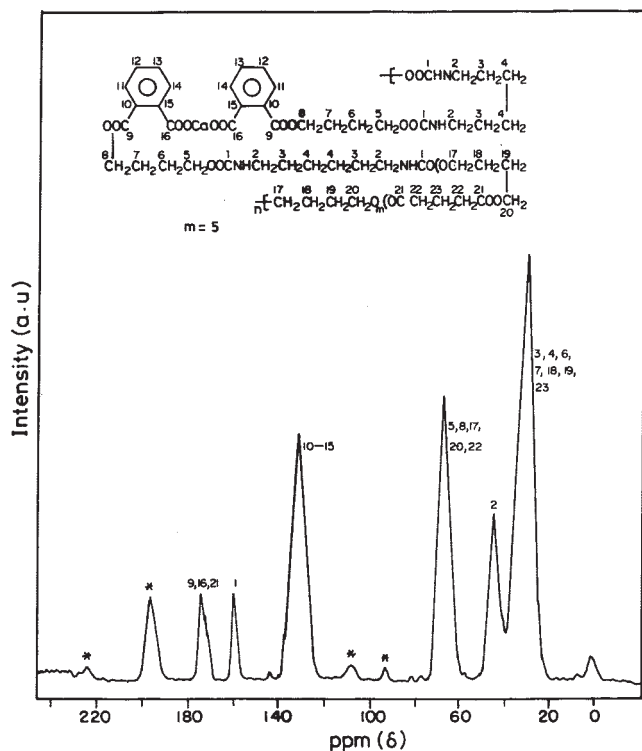**Figure 3** Solid state ^{13}C-CP-MAS NMR spectrum of Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4).

diisocyanate in the feed was 3 : 1 : 4, 2 : 2 : 4, and 1 : 3 : 4. The blank PUEs gave T_g values of -50 and $-41°C$ for HMDI- and TDI-based polymers, respectively. The higher T_{g2} values of 95 and 101°C are observed, respectively, for the PUEs based on HMDI and TDI when the composition of Ca(HBP)$_2$: HTPBG$_{1000}$: diisocyanate (HMDI or TDI) in the feed was 3 : 1 : 4. In general, it is observed that TDI-based PUEs showed higher T_g value than that of HMDI-based PUEs. Barbeau et al.[64] reported that the TDI-based polymer showed higher T_g value than that of HMDI-based polymer. The T_g data for PUEs are given in Table II. From the T_g data, it is clear that the calcium-containing PUEs are in heterogeneous phase. The T_{g2} and T_{g1} values decrease with decrease in the calcium content. The T_{g2} value can be considered for the phase with ionic species, hard segment with little soft segment and T_{g1} value can be considered due to soft segment with little ionic species. It is reported that poly(ester-siloxane)-urethanes show two T_{gs} with respective to hard and soft segments.[65,66]

Figure 6 presents the XRD pattern of Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4) and Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (2 : 2 : 4). XRD pattern of the PUEs based on HMDI shows broad peak about $2\theta = 20$–25 and some sharp peaks that revealed the partial crystalline nature of the PUEs. TDI-based PUEs do not show any sharp peaks, indicating that they are amorphous in nature. The HMDI-based PUEs owe their tendency to

crystallize in the presence of —(CH$_2$)$_6$— units in the backbone of the PUEs. The molecular weight of calcium-containing PUEs could not be determined by GPC due to the possible deposition of the calcium salt in the GPC column. However, the number and weight average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of PUEs were determined using GPC.

The polymer **7** gives $\bar{M}n = 1.2493 \times 10^4$; $\bar{M}w = 3.2707 \times 10^4$; $\bar{M}w/\bar{M}n = 2.6315$

The polymer **8** gives $\bar{M}n = 1.1863 \times 10^4$; $\bar{M}w = 3.1691 \times 10^4$; $\bar{M}w/\bar{M}n = 2.6714$

Figure 7 shows the effect of temperature on the storage modulus (g') and loss modulus (g'') for the PUEs derived from Ca(HBP)$_2$, HMDI, and HTPBG$_{1000}$. Figure 7(A–D) correspond to the copolymer formed when the feed composition of Ca(HBP)$_2$: HTPBG$_{1000}$: HMDI were 3 : 1 : 4, 2 : 2 : 4, 1 : 3 : 4, and 0 : 1 : 1, respectively. Figure 7(A) shows that storage modulus (g') and loss modulus (g'') increases as the amount of ionic species increases. As the ionic species decreases [Fig. 7(B)] the modulus decreases, still lower modulus was observed for the system containing only soft segment without ionic species [Fig. 7(D)]. As the ionic concentration in the polymer increases the ionic cluster (physical crosslinks) forming capacity also increases, which in turn increases the modulus.[67] The magnitude of g' decreases gradually with increase in temperature. This is because at higher temperature the greater mobility of the polymer chain helps in a faster dissipation of applied strain, leading to lower g' value.[68] Higher the ionic content in the system lower will be the change in the magnitude of g', as the mobility of the polymer chain is more arrested. All the copolymer
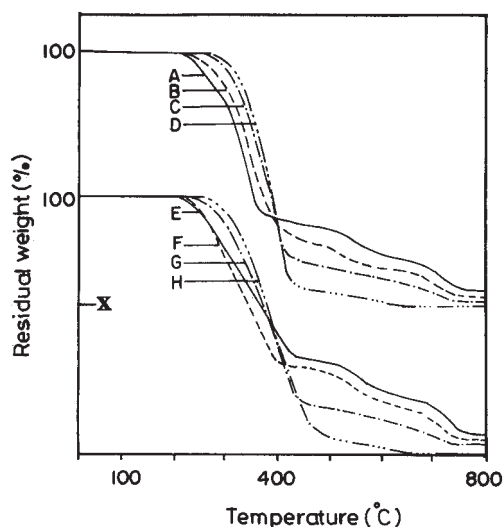

Figure 4 TGA traces of (A) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (3 : 1 : 4), (B) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4), (C) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (1 : 3 : 4), (D) HTPBG$_{1000}$-HMDI, (E) Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (3 : 1 : 4), (F) Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (2 : 2 : 4), (G) Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (1 : 3 : 4), and (H) HTPBG$_{1000}$-TDI.

TABLE II
Thermal Data for Poly(urethane-ester)s

Polymer	T_{g1} (°C)	T_{g2} (°C)	IDT (°C)	Temperature at different weight loss (°C)					Weight loss at 800 °C (%)
				20%	40%	60%	80%	90%	
Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (3 : 1 : 4)	−35	95	190	289	321	354	590	721	93
Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4)	−43	81	223	305	338	370	525	688	96
Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (1 : 3 : 4)	−45	55	262	321	354	387	413	609	97
HTPBG$_{1000}$-HMDI (1 : 1)	−50	—	279	331	361	387	400	420	100
Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (3 : 1 : 4)	−18	101	230	288	364	423	694	747	93
Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (2 : 2 : 4)	−27	88	238	298	337	383	608	727	94
Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (1 : 3 : 4)	−34	61	259	324	370	403	463	661	96
HTPBG$_{1000}$-TDI (1 : 1)	−41	—	285	340	377	397	409	463	100

systems show a rubbery plateau above its first T_g. The height of the rubbery plateau is influenced by the variable composition of the copolymer system.[69] Hard rubbery with higher plateau value of g' is observed for the system with higher ionic content [Figs. 7(A,B)], and soft rubbery with lower plateau value of g' is observed for the system with lower ionic content or with higher soft segment content [Figs. 7(C,D)]. It is observed that the peak of the loss modulus curve broaden with increase in the ionic content of the copolymer, while the peak of the loss modulus curve for

PUEs with higher soft segment content and lower ionic species become narrow.[70] These peaks indicate the T_g of the polymers. The T_g values measured from DSC are shown with an arrow mark in the Figure 7. The T_g values measured by DSC and DMA are in good agreement with each other. The copolymers formed when the feed composition of Ca(HBP)$_2$: HTPBG$_{1000}$: HMDI were 3 : 1 : 4, 2 : 2 : 4, and 1 : 3 : 4 show a heterogeneous phase in which the lower value of T_g can be considered due to the phase with higher soft segment with little dissolved hard-ionic species, and the higher T_g value can be considered due to hard segments-ionic species, with little soft segment dissolved in it. Thus, using soft segment units having higher molecular weight increases the degree of phase separation.[71,72]
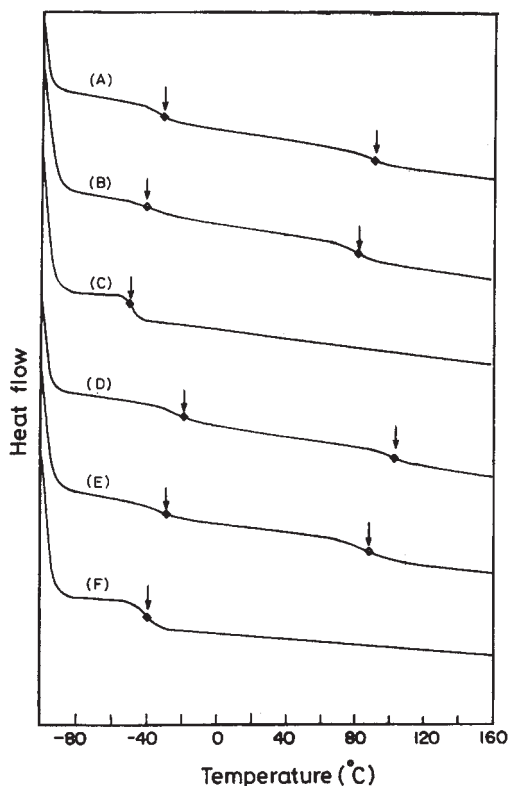
CONCLUSIONS

Calcium-containing PUEs with different composition were synthesized by taking the mole ratio of Ca(HBP)$_2$:

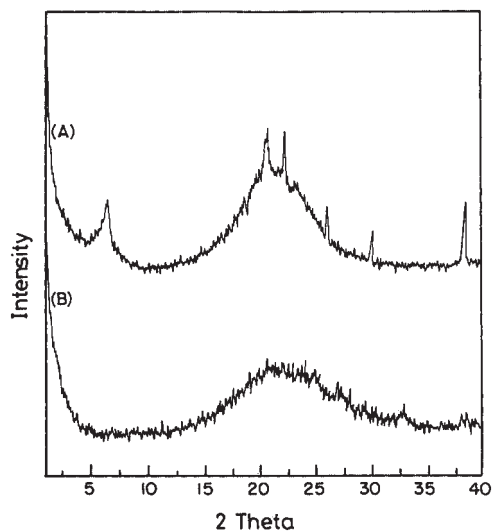**Figure 5** DSC traces of (A) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (3 : 1 : 4), (B) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4), (C) HTPBG$_{1000}$-HMDI, (D) Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (3 : 1 : 4), (E) Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (2 : 2 : 4), and (F) HTPBG$_{1000}$-TDI.

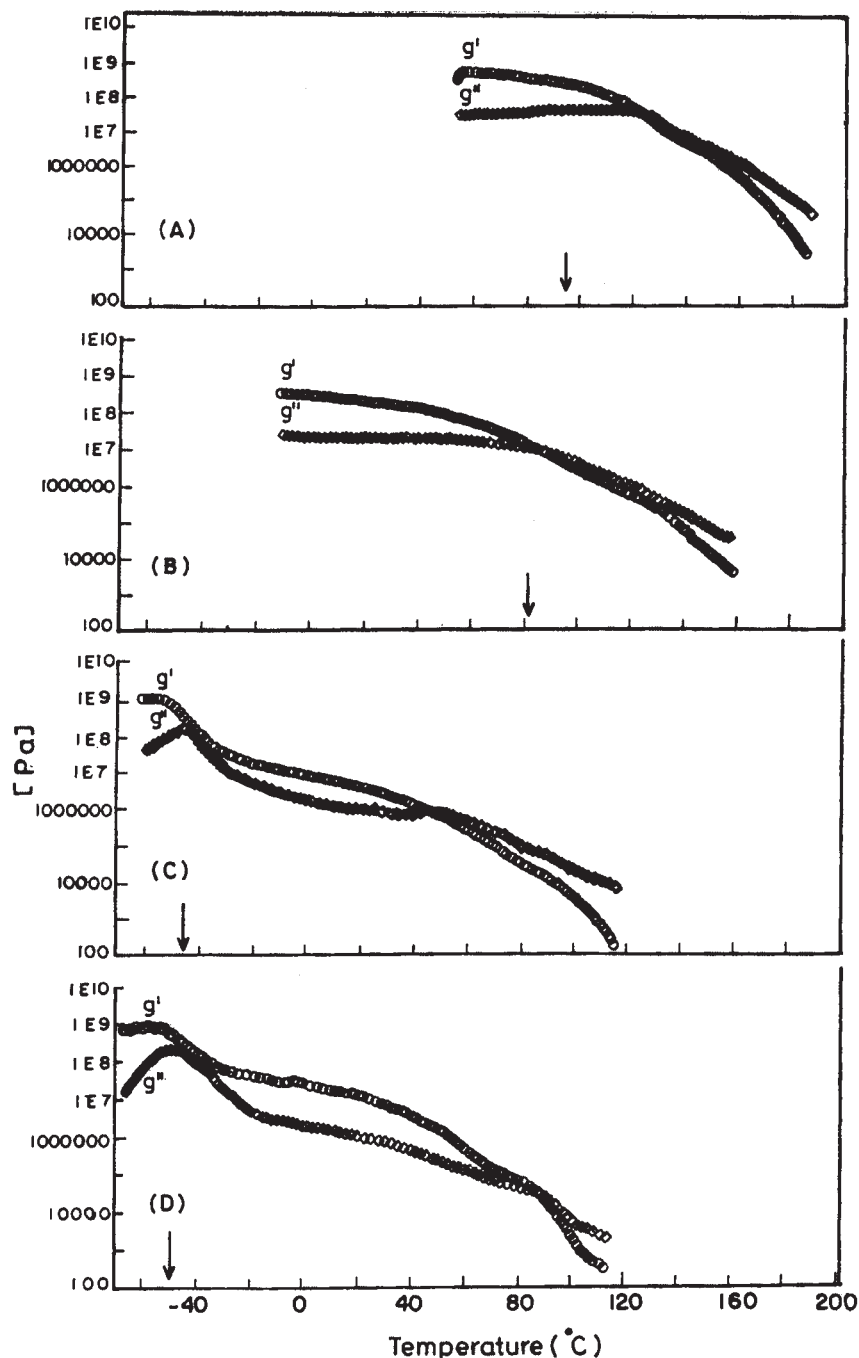**Figure 6** XRD pattern of (A) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4) and (B) Ca(HBP)$_2$-HTPBG$_{1000}$-TDI (2 : 2 : 4).

Figure 7   Plot of storage modulus and loss modulus versus temperature for (A) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (3 : 1 : 4), (B) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (2 : 2 : 4), (C) Ca(HBP)$_2$-HTPBG$_{1000}$-HMDI (1 : 3 : 4), and (D) HTPBG$_{1000}$-HMDI.

HTPBG$_{1000}$: diisocyanate (HMDI or TDI) as 3 : 1 : 4, 2 : 2 : 4, and 1 : 3 : 4. Blank PUEs were synthesized by the reaction of HTPBG$_{1000}$ with diisocyanate (HMDI or TDI). The calcium-containing PUEs were characterized by IR, ^{1}H NMR, and Solid state ^{13}C-CP-MAS NMR for structural confirmation. Molecular weights of blank PUEs were determined by GPC. Calcium-containing PUEs are insoluble in most of the organic solvents and soluble in highly polar solvents, which infer the presence of ionic linkages. The inherent viscosity of calcium-containing

PUEs are found to be low when compared with that of blank PUEs, which reveal that static linkages between COO$^-$ and Ca^{2+} in the polymer chain dissociate to low molecular weight fragments. The HMDI-based PUEs show slightly higher viscosity than that of TDI-based PUEs. The viscosity of the calcium-containing PUEs increases with increase in the soft segment content [HTPBG$_{1000}$] and decreases with increase in the calcium content. PUEs with higher amount of calcium content and lower amount of soft segment content dissociate into

small molecular weight fragments in DMSO and hence exhibit lower viscosity. With increase in the soft segment content [HTPBG$_{1000}$] and decrease in the calcium content in the PUEs, the viscosity increases due to presence of lower number of ionic linkages. The IDT of blank PUEs are higher than that of the calcium-containing PUEs. Also, the IDT of TDI-based PUEs are higher than HMDI-based PUEs, as the former case has rigid aromatic ring. The T_g value of PUEs increases with increase with calcium content and decreases with increase in the soft segment content. Two T_g values of PUEs based on HT-PBG$_{1000}$ for various composition of Ca(HBP)$_2$: HT-PBG$_{1000}$: diisocyanate (HMDI or TDI) show the presence of heterogeneous phase. The dynamic mechanical analysis of the calcium-containing PUEs based on HMDI shows that with increase in the ionic content of polymer, modulus (g' and g'') increases at any given temperature. After first $T_{g'}$ a rubbery plateau is noted for all the polymers. The variable composition of ionic and soft segment content in the polymer system has influence on the plateau height in the rubbery state.

References

1. Matsuda, H.; Kanaoka, K. J Appl Polym Sci 1985, 30, 1229.
2. Matsuda, H. J Appl Polym Sci 1979, 23, 2603.
3. Matsuda, H.; Takechi, S. J Polym Sci Polym Chem 1990, 28, 1895.
4. Matsuda, H. J Appl Polym Sci 1978, 2093, 22.
5. Matsuda, H. J Polym Sci Polym Chem 1977, 15, 2239.
6. Matsuda, H. J Appl Polym Sci 1978, 22, 3371.
7. Manners, I. Polym Mater Sci Eng 2002, 86, 85.
8. Czuprynski, B.; Paciorek-Sadowska, J.; Liszkowska, J. Polimery 2002, 47, 727.
9. James, H. S.; Arlene, P. S.; Elot, C. W.; Stuart, L. C.; Coopersaid, C.; Denis, L.; Marcel, J. Biomaterials 1992, 13, 339.
10. Acharya, V.; Prabha, C. R.; Murthy, C. N. J Polym Mater 2003, 20, 83.
11. Ogawa, R.; Watanabe, J.; Ishihara, K. Sci Tech Adv Mater 2003, 4, 523.
12. Thomas, R. J.; Tan, F. R.; Phillips, R. E. J Biomat Appl 1988, 3, 180.
13. Matsuda, H. J Polym Sci Polym Chem 1974, 12, 455.
14. Matsuda, H. J Polym Sci Polym Chem 1974, 12, 469.
15. Matsuda, H. J Macromol Sci Chem 1975, A9, 397.
16. Matsuda, H. J Appl Polym Sci 1976, 14, 1783.
17. Matsuda, H. J Macromol Sci Chem 1976, A10, 1143.
18. Matsuda, H. J Appl Polym Sci 1976, 20, 995.
19. Matsuda, H. J Macromol Sci Chem 1977, A11, 431.
20. Matsuda, H. Okamato, T. Polym Eng Sci 1978, 18, 628.
21. Matsuda, H. J Appl Polym Sci 1979, 24, 811.
22. Durairaj, B.; Venkatarao, K. Polym Bull 1979, 1, 723.
23. Durairaj, B.; Venkatarao, K. Eur Polym Mater 1980, 16, 941.
24. Matsuda, H. J Appl Polym Sci 1980, 25, 2339.
25. Matsuda, H. J Appl Polym Sci 1980, 25, 1915.
26. Matsuda, H. Polym Eng Sci 1981, 21, 360.
27. Matsuda, H. J Macromol Sci Chem 1981, A15, 1521.
28. Matsuda, H.; Dohi, H. J Appl Polym Sci 1981, 26, 1931.
29. Matsuda, H. J Appl Polym Sci 1982, 27, 757.
30. Matsuda, H.; Miyoshi, N. J Appl Polym Sci 1982, 27, 3877.
31. Matsuda, H. J Macromol Sci Chem 1983, A19, 1.
32. Matsuda, H.; Miyoshi, N. J Appl Polym Sci 1983, 28, 3793.
33. Kothandaraman, H.; Venkatarao, K.; Raghavan, A.; Chandrasekaran, V. Polym Bull 1985, 13, 353.
34. Matsuda, H. Polym Eng Sci 1987, 27, 233.
35. Rajalingam, P.; Radhakrishnan, G.; Vasudevan, C.; Tamare, S. K.; Venkatarao, K. Polym Commun 1990, 31, 243.
36. Matsuda, H.; Takechi, S. J Polym Sci Polym Chem 1991, 29, 83.
37. Rajalingam, P.; Radhakrishnan, G. Polymer 1992, 33, 2214.
38. Soundararajan, S.; Palanivelu, K.; Ramamurthy, K. Popular Plast Packag 1994, 39, 45.
39. Matsuda, H. Polym Adv Tech 1997, 8, 616.
40. Arun, P. R.; Nanjundan, S. J. Macromol Sci Pure Appl Chem 1998, A35, 821.
41. Arun, P. R.; Nanjundan, S. Eur Polym Mater 1999, 35, 1939.
42. Arun, P. R.; Jayakumar, R.; Nanjundan, S. J Macromol Sci Pure Appl Chem 2000, A37, 469.
43. Gunatillake, P.; Martin, D. J.; Meijs, G. F.; McCarthy, S. J.; Adhikari, R. Aus J Chem 2003, 56, 545.
44. Levesque, S.; Rodrigue, D.; Vermette, P.; Gunatillake, P. Biomed Appl Polyurethanes 2001, 6, 22.
45. Dong-An, W.; Ji, J.; Gao, C.; Guan-Hua, Y.; Lin-Xian, F. Biomaterials 2001, 22, 1549.
46. Dong-An, W.; Ji, J.; Lin-Xian, F. Macromol Chem Phys 2000, 201, 1574.
47. Jayabalan, M.; Lizymol, P. P.; Thomas, V. Polym Int 2000, 49, 88.
48. Zdrahala, R. J.; Zdrahala, I. J. J Biomat Appl 1999, 14, 67.
49. Corneillie, S.; Lan, P. N.; Schacht, E.; Davies, M.; Shard, A.; Green, R.; Denyer, S.; Wassall, M.; Whitfield, H.; Choong, S. Polym Int 1998, 46, 251.
50. Jui-Hsiang, C.; Jeng, W.; Chung-Yi, L.; Ru-Fong, L.; Yu-Der, L. J Biomed Mater Res 1998, 41, 633.
51. Han, D. K.; Park, K. D.; Kim, Y. H. J Biomat Sci Polym Ed 1998, 9, 163.
52. Spaans, C. J.; Groot, J. H.; Dekens, F. G.; Pennings, A. J Polym Bull 1998, 41, 131.
53. Carsten, S.; Christian, R.; Michael, W.; Felix, B.; Harald, E.; Matthias, E.; Stephan, W. Biomaterials 2004, 25, 1239.
54. Gorna, K.; Gogolewski, S. J. Biomed Mater Res 2003, 67A, 813.
55. Maeda, H.; Kasuga, T.; Nogami, M.; Hibino, Y.; Hata, K. I.; Ueda, M.; Ota, Y. Key Eng Mater 2003, 240–242, 163.
56. Guan-Nan, C.; Kan-Nan, C. J Appl Polym Sci 1999, 71, 903.
57. Yamamoto, H.; Yamaguchi, M.; Sugawara, T.; Suwa, Y.; Ohkawa, K.; Shinji, H.; Kurata, S. Key Eng Mater 2004, 254–256, 603.
58. Takashi, K.; Ayae, S.; Naoya, H. Adv Mater 2002, 14, 869.
59. Arun, P. R.; Nanjundan, S.; Pakula, T.; Klapper, M. Eur Polym J 2004, 40, 1767.
60. Moroi, G. J Anal Appl Pyrol 2004, 71, 485.
61. Moroi, G. J Anal Appl Pyrol 2003, 70, 879.
62. Moroi, G. Polym Degrad Stabil 2002, 78, 287.
63. Moroi, G. Thermochim Acta 2002, 385, 1539.
64. Barbeau, P. H.; Gerand, J. F.; Magny, B.; Pascaul, T. J. J Polym Sci Polym Phys 2000, 38, 2750.
65. Ioan, S.; Grigorescu, G.; Stanciu, A. Polymer 2001, 42, 3633.
66. Ioan, S.; Grigorescu, G.; Stanciu, A. Eur Polym Mater 2002, 38, 2295.
67. Eisenberg, A.; Navratil, M. Macromolecules 1973, 6, 604.
68. Bhatt, C. U.; Royer, R. J.; Hwang, R. C.; Khan, A. S. J Polym Sci Polym Phys 1999, 37, 1045.
69. Fengkui, L.; Jianan, H.; Wie, Z.; Xian, Z.; Mao, X.; Xiaolie, L.; Dezhu, M.; Byung, K. K. J Appl Polym Sci 1996, 62, 631.
70. Visser, A. S.; Cooper, L. S. Polymer 1992, 33, 920.
71. Mix, R.; Goering, H.; Schulz, G.; Grudemann, E.; Gahde, J. J Polym Sci Polym Chem 1995, 33, 1523.
72. Lin, J. R.; Chen, L. W. J Appl Polym Sci 1998, 69, 1575.