

Synthesis and Characterization of Calcium-Containing Poly(urethane-urea)s

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ABSTRACT: A calcium salt of mono(hydroxyethoxyethyl)phthalate [Ca(HEEP)2] was synthesized by the reaction of diethylene glycol, phthalic anhydride, and calcium acetate. Four different bisureas like hexamethylene bis(ω ,N-hydroxyethylurea), tolylene 2,4-bis(ω ,N-hydroxyethylurea), hexamethylene bis(ω ,N-hydroxypropylurea), and tolylene 2,4-bis(ω ,N-hydroxypropylurea) were prepared by reacting ethanolamine or propanolamine with hexamethylene diisocyanate (HMDI) or tolylene 2,4-diisocyanate (TDI). Calcium-containing poly(urethane-urea)s (PUUs) were synthesized by reacting HMDI or TDI with 1:1 mixtures of Ca(HEEP)2 and each of the bisureas using di-*n*-butyltin dilaurate as a

catalyst. The PUUs were well characterized by Fourier transform infrared, ¹H- and ¹³C-NMR (nuclear magnetic resonance), solid-state ¹³C cross-polarization–magic angle spinning NMR, viscosity, solubility, elemental, and X-ray diffraction studies. Thermal properties of the polymers were also studied by using thermogravimetric analysis and differential scanning calorimetry. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3488–3496, 2003

Key words: polyurethanes; viscosity; thermogravimetric analysis; X-ray

INTRODUCTION

Poly(urethane-urea)s (PUUs) are of considerable technical importance and have been widely used for coatings, impregnations, and manufacture of sheets and films. The introduction of metal to a urethane–urea backbone results in a considerable decrease in the decomposition temperature.¹ The PUUs are widely applicable to a number of industrial products as functional plastics due to their outstanding elastic properties; elastomers, foams, adhesives, and paints, etc., and have been extensively used in medical and/or industrial fields, including artificial heart blood vessels, shock absorbers, textiles, paints, additives, and soil conditioners.^{2,3}

Polyurethanes and PUUs possess excellent mechanical and physical properties, high combustion resistance, high wear resistance with a broad temperature range for use, and good blood and tissue compatibility.⁴ These polymers are usually composed of multiphase segments. These alternating hard and soft segment structures are suitable for many applications by

imparting various properties. Incorporation of metal and functional groups into the polymers has led to wide applications such as aqueous thickeners, impregnates, textile sizings,^{5,6} resins,^{7–9} and catalysts.¹⁰ Ionic diols containing ionic linkages between COO' and M²⁺ are of interest and are very important starting materials for the synthesis of ionic polymers in which the metal is firmly incorporated into the backbone of the polymer chain.^{11–16}

PUUs are the important class of copolymers. They are composed of a class of elastomers exhibiting superior extensibility, toughness, and durability over segmented polyurethanes and are used extensively, ranging from textile fibers to medical prosthesis.¹⁷ Introduction of urea group into the polymer backbone is expected to improve the solubility of the polymer without decreasing the thermal stability significantly. So in this article we report the synthesis and characterization of calcium-containing PUUs derived from a calcium salt of mono(hydroxyethoxyethyl)phthalate {[Ca(HEEP)2]Ca(HEEP)2}, diisocyanates [hexamethylene diisocyanate (HMDI) or tolylene 2,4-diisocyanate (TDI)], and bisurea diols.

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EXPERIMENTAL

Materials

Phthalic anhydride (BDH, India), diethylene glycol (Merck, India), di-*n*-butyltin dilaurate (DBTDL) (Fluka, Switzerland), ethanolamine (Merck), propano-

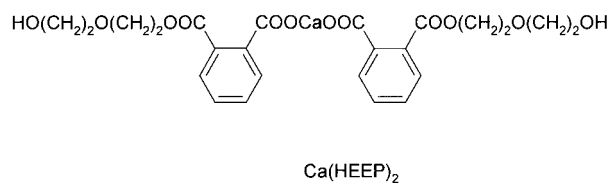
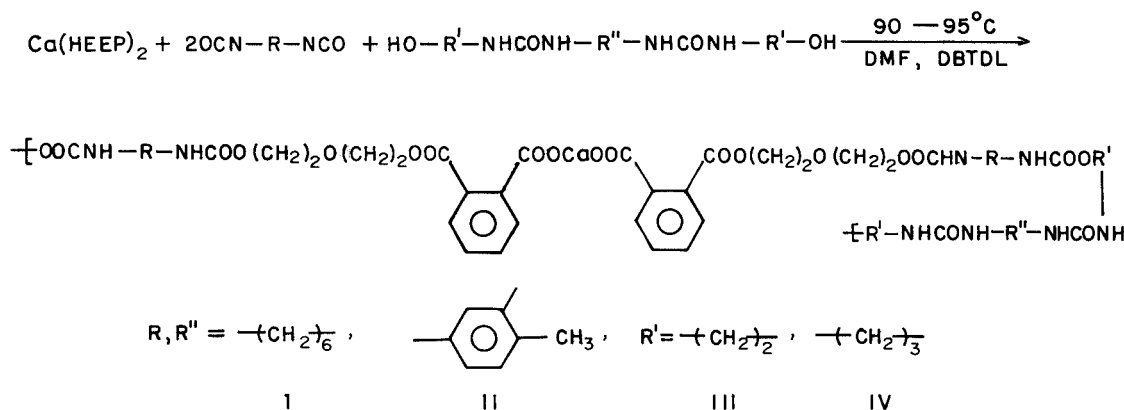


Figure 1 Chemical structure of Ca(HEEP)₂.

lamine (Merck), HMDI and TDI (Fluka), and calcium acetate (BDH) were used without any purification. The solvents such as acetone, methanol, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide (DMAc), benzene, toluene, *m*-cresol, and chloroform were purified by standard procedures. Ca(HEEP)₂ and four different bisureas were synthesized as reported in our previous articles.^{15,18} The chemical structure of Ca(HEEP)₂ is shown in Figure 1.

Synthesis of PUUs

Calcium-containing PUUs were synthesized by reacting Ca(HEEP)₂ (0.008 mol) and hexamethylene bis(ω ,N-hydroxyethylurea) (HBHEU), hexamethylene bis(ω ,N-hydroxypropylurea) (HBHPU), tolylene 2,4-bis(ω ,N-hydroxyethylurea) (TBHEU), or tolylene 2,4-bis(ω ,N-hydroxypropylurea) (TBHPU) (0.008 mol) dissolved in 200 mL of DMF with HMDI or TDI (0.016 mol) dissolved in 25 mL of the same solvent using 2–3 drops of DBTDL as a catalyst. The reaction was carried out under a nitrogen atmosphere at 90–95°C. After stirring the reaction mixture for 4 h, 50 mL of DMF was added to the mixture and the solution was filtered. The filtrate was poured into a large excess of vigorously stirred chloroform to precipitate the product. The product was further washed with acetone several times and dried at 60°C in vacuum. The reactions involved in the poly-



Polymer	I	II	III	IV	V	VI	VII	VIII
R		I	I	I	II	II	II	II
R'	III	IV	III	IV	III	IV	III	IV
R''	I	I	II		I	I	II	II

Scheme I Synthesis of calcium-containing PUUs.

TABLE I
Synthesis, Viscosity, and Analytical Data of Calcium-Containing PUUs

Polymer no.	Polymer code	Yield (%)	η_{inh}	Repeating unit	Analytical data found Calculated (%)		
					C	H	Ca
I	Ca(HEEP) ₂ -HBHEU-HMDI	76	0.105	CaC ₅₂ H ₇₆ O ₂₀ N ₈	53.67 (53.24)	6.75 (6.53)	3.14 (3.42)
II	Ca(HEEP) ₂ -HBHPU-HMDI	75	0.109	CaC ₅₄ H ₈₀ O ₂₀ N ₈	54.32 (53.99)	6.94 (6.71)	3.08 (3.34)
III	Ca(HEEP) ₂ -TBHEU-HMDI	85	0.101	CaC ₅₃ H ₇₀ O ₂₀ N ₈	54.41 (53.99)	6.18 (5.98)	3.15 (3.40)
IV	Ca(HEEP) ₂ -TBHPU-HMDI	82	0.100	CaC ₅₅ H ₇₄ O ₂₀ N ₈	55.18 (54.72)	6.33 (6.18)	3.04 (3.32)
V	Ca(HEEP) ₂ -HBHEU-TDI	72	0.096	CaC ₅₄ H ₆₄ O ₂₀ N ₈	55.12 (54.73)	5.62 (5.44)	3.11 (3.38)
VI	Ca(HEEP) ₂ -HBHPU-TDI	71	0.098	CaC ₅₆ H ₆₈ O ₂₀ N ₈	55.87 (55.44)	5.74 (5.65)	3.06 (3.30)
VII	Ca(HEEP) ₂ -TBHEU-TDI	80	0.091	CaC ₅₅ H ₅₈ O ₂₀ N ₈	55.92 (55.46)	5.12 (4.91)	3.15 (3.37)
VIII	Ca(HEEP) ₂ -TBHPU-TDI	78	0.093	CaC ₅₇ H ₆₂ O ₂₀ N ₈	56.52 (56.16)	5.34 (5.13)	3.02 (3.29)

TABLE II
Synthesis and Viscosity Data of Blank PUUs

Polymer no.	Polymer code	Yield (%)	η_{inh}
IX	HBHEU-HMDI	88	0.264
X	HBHPU-HMDI	86	0.271
XI	TBHEU-HMDI	93	0.190
XII	TBHPU-HMDI	91	0.198
XIII	HBHEU-TDI	83	0.203
XIV	HBHPU-TDI	80	0.209
XV	TBHEU-TDI	85	0.170
XVI	TBHPU-TDI	84	0.177

mer synthesis are presented in Scheme I. The synthesis data of are given in Table I.

The blank PUUs were also prepared by the same method without calcium-containing ionic diol. The synthesis data of blank PUUs are given in Table II.

Measurements

The infrared (IR) spectra of the polymers were recorded in a Testscan Shimadzu FT-IR 8000 series spec-

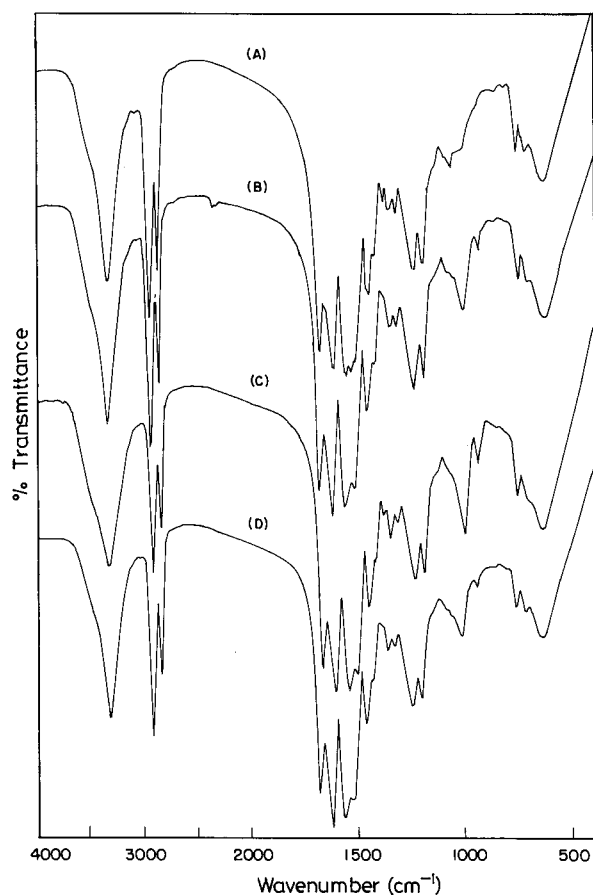


Figure 2 FTIR spectra of PUUs: (A) I, (B) II, (C) III, and (D) IV.

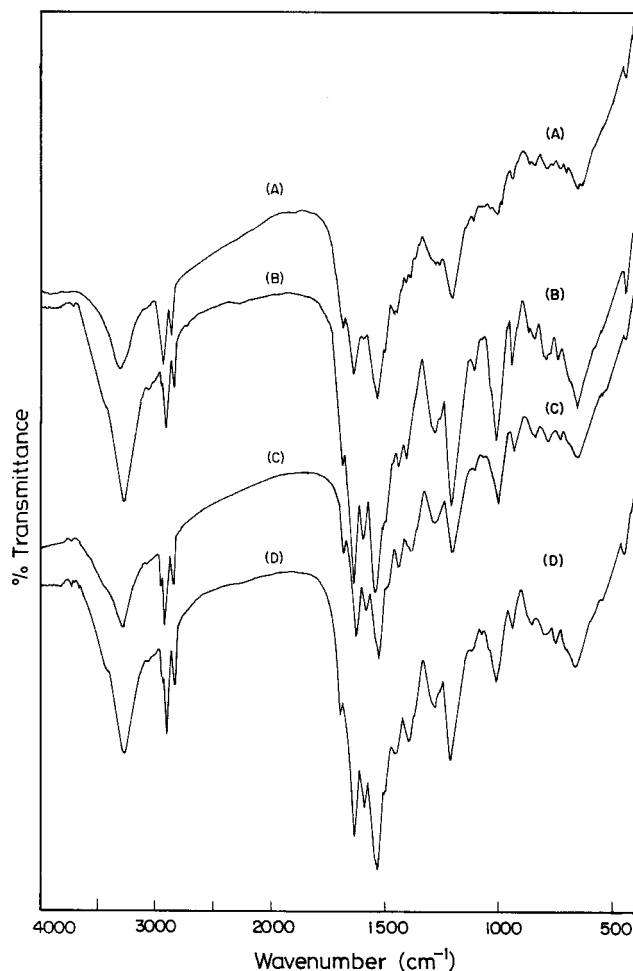


Figure 3 FTIR spectra of PUUs: (A) V, (B) VI, (C) VII, and (D) VIII.

trophotometer at room temperature with the KBr pellet method. The ^1H - and ^{13}C -NMR (NMR: nuclear magnetic resonance) and distortionless enhancement by polarization transfer (DEPT) spectra of the polymers were recorded in a JEOL GSX-400 MHz spectrometer in $\text{DMSO-}d_6$ using tetramethylsilane (TMS) as an internal standard. The solid-state ^{13}C cross-polarization-magic angle spinning (^{13}C -CP-MAS) NMR spectra were obtained using Bruker MSL 75 MHz spectrometer with adamantane as a chemical shift reference. The thermogravimetric analysis (TGA) was performed with a Mettler-3000 thermal analyzer using 2 mg of the sample at a heating rate of $20^\circ\text{C}/\text{min}$ in air. The differential scanning calorimetric analysis was carried out using a DSC V4.OB Dupont 2100 model differential scanning calorimeter at the heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The X-ray diffractograms were recorded according to a powder method with a Philips PW 1710 diffractometer using CuK_α radiation. A Perkin-Elmer 2400 carbon-hydrogen analyzer was used for elemental analysis. The inherent viscosity η_{inh} of the polymers in DMSO

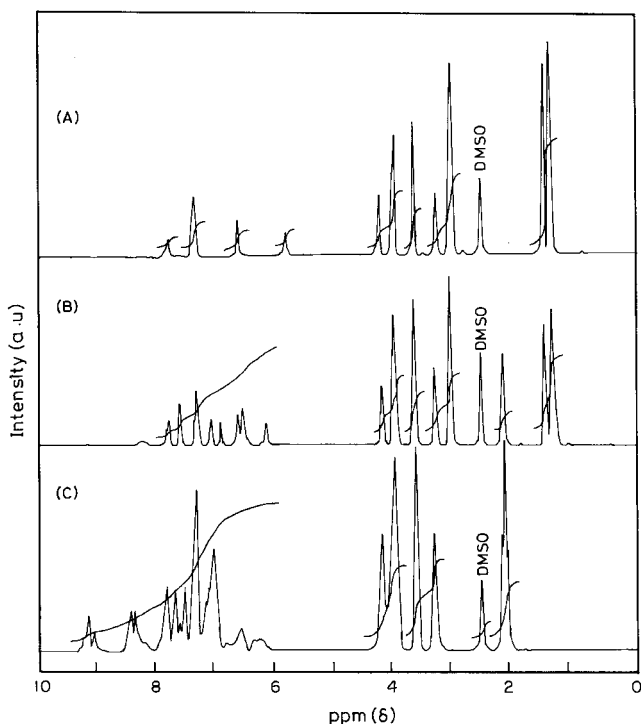


Figure 4 $^1\text{H-NMR}$ spectra of PUUs: (A) I, (B) II, (C) III, and (C) VII.

was determined using an Ubbelohde viscometer at 40°C . The flow time for the solvent as well as the polymer solution (1.0 g/dL) was determined. The solubility of the polymers was tested in various polar and nonpolar solvents by taking 10 mg of the polymers in 2 mL of different solvents in a closed test tube and set aside for one day.

RESULTS AND DISCUSSION

Synthesis and characterization of PUUs

The syntheses of calcium-containing PUUs were carried out in DMF solvent. In the synthesis of the polymers, the mole ratio of diisocyanate:diol [$\text{Ca}(\text{HEEP})_2$ and bisurea] was taken as 1:1 to avoid side reactions such as ring formation of dimeric and trimeric diisocyanates, branching, and crosslinking due to the formation of allophanate linkages. The crosslinked product formed if any was filtered off after mixing the product with excess of DMF to dissolve the linear polymer. Subsequently, the dissolved linear polymer was reprecipitated by the addition of nonsolvents. The yield was found to be between 71 and 85%. Using the $\text{Ca}(\text{HEEP})_2$ and four different bisureas, eight calcium-containing PUUs were prepared based on HMDI and

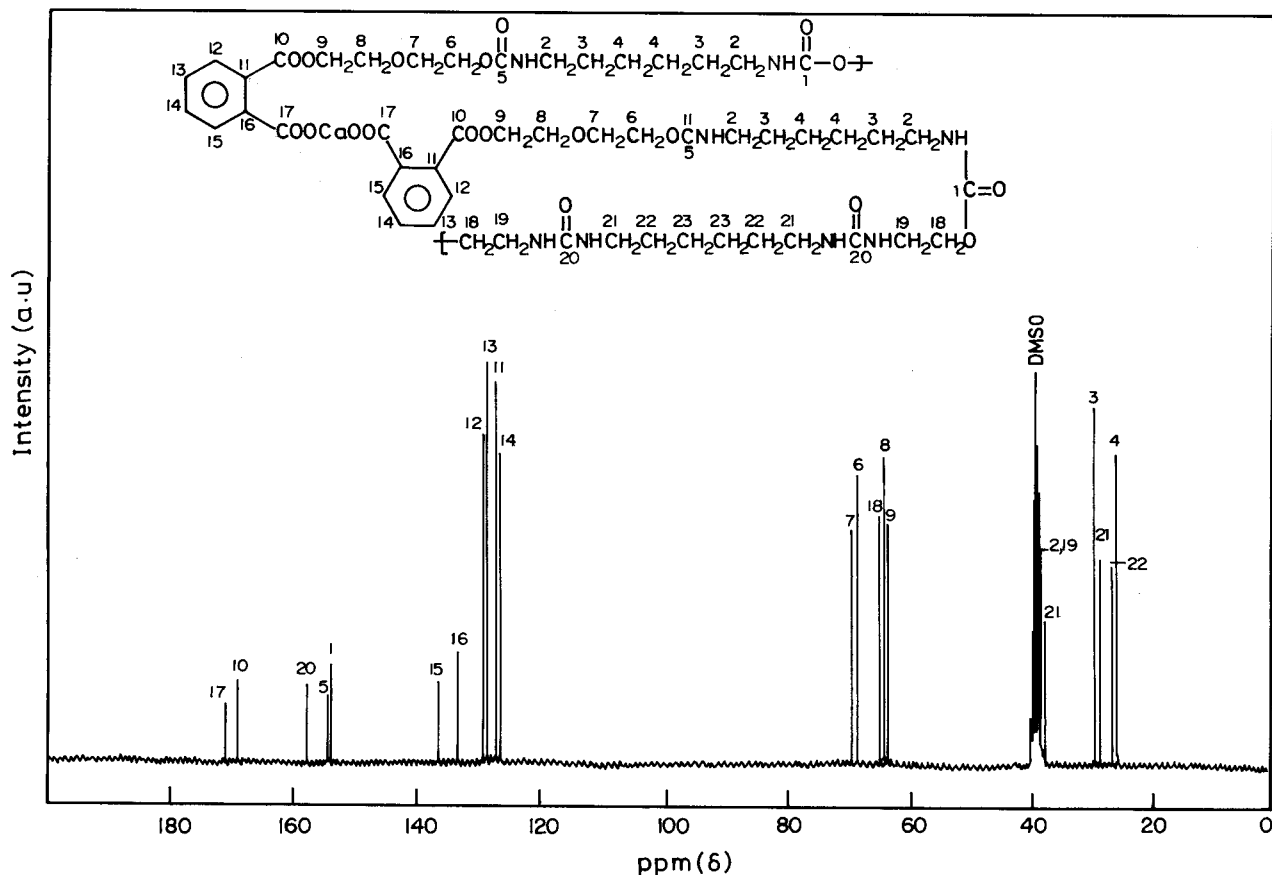


Figure 5 $^{13}\text{C-NMR}$ spectrum of $\text{Ca}(\text{HEEP})_2\text{-HBHEU-HMDI}$ (I).

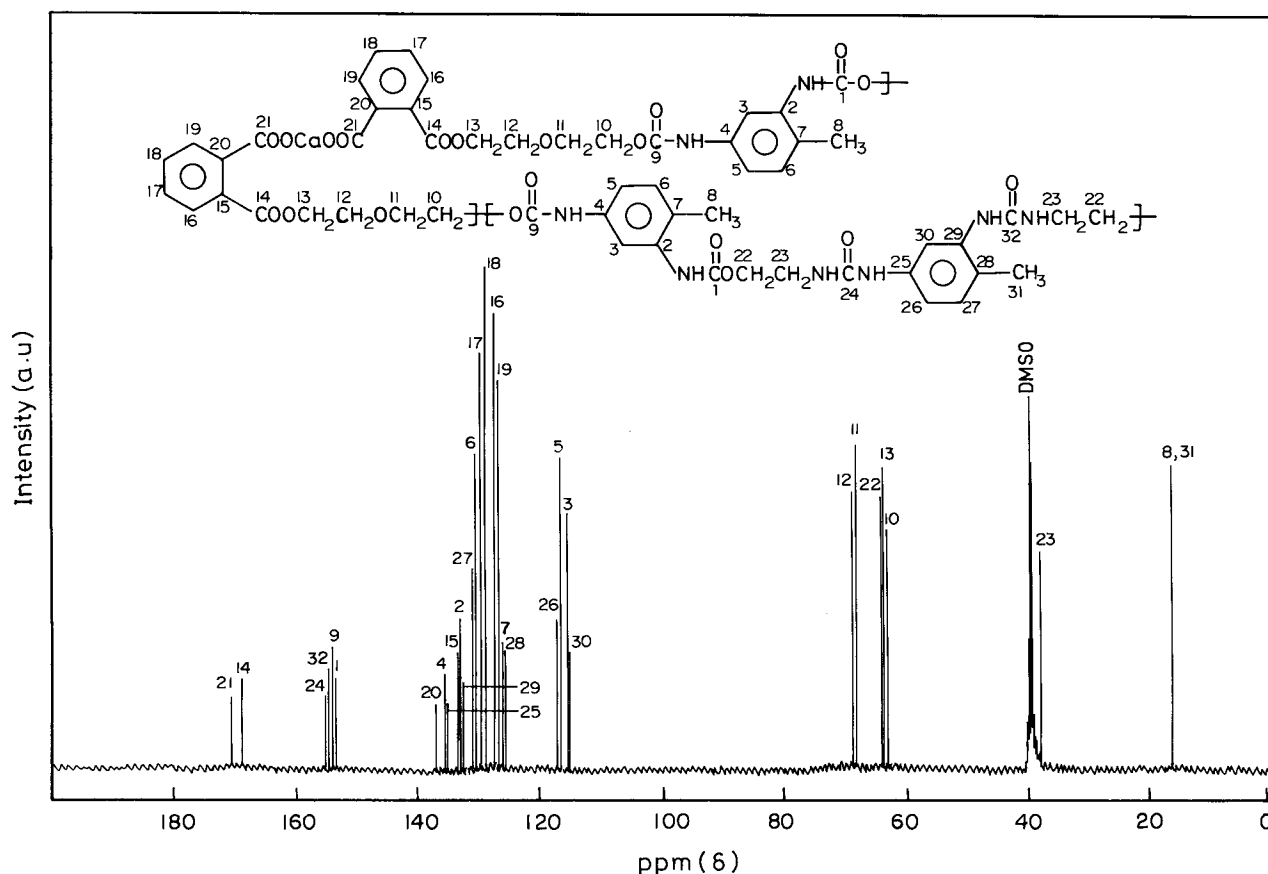


Figure 6 ^{13}C -NMR spectrum Ca(HEEP) $_2$ -TBHEU-TDI (VII).

TDI. They are coded as Ca(HEEP) $_2$ -HBHEU-HMDI (I), Ca(HEEP) $_2$ -HBHPU-HMDI (II), Ca(HEEP) $_2$ -TBHEU-HMDI (III), Ca(HEEP) $_2$ -TBHPU-HMDI (IV), Ca(HEEP) $_2$ -HBHEU-TDI (V), Ca(HEEP) $_2$ -HBHPU-TDI (VI), Ca(HEEP) $_2$ -TBHEU-TDI (VII), and Ca(HEEP) $_2$ -TBHPU-TDI (VIII), respectively.

Blank PUUs without the calcium-containing ionic diol were also synthesized by applying the above procedure. Eight blank PUUs were synthesized and they are coded as HBHEU-HMDI (IX), HBHPU-HMDI (X), TBHEU-HMDI (XI), TBHPU-HMDI (XII), HBHEU-TDI (XIII), HBHPU-TDI (XIV), TBHEU-TDI (XV), and TBHPU-TDI (XVI).

The PUUs were soluble in aprotic polar solvents like DMSO, DMF, and DMAc, but they were insoluble in water, acetone, ethyl methyl ketone, ethyl acetate, toluene, benzene, xylene, dioxane, chloroform, carbon tetrachloride, carbon disulfide, *n*-hexane and tetrahydrofuran. The elemental analysis data of PUUs are given in Table I. The elemental analysis data reveals that the percentage value of carbon and hydrogen were higher than the calculated values assuming that there were 1:1 ratio of ionic diol and urea units in the PUUs. But the calcium content in PUUs is found to be less than the calculated values, showing that the reactivity of bisureas (HBHEU, HBHPU, TBHEU, and TB-

HPU) is higher than that of calcium-containing ionic diol towards the diisocyanates.

IR spectra

The IR spectra of PUUs are shown in Figures 2 and 3. The peak at $3334\text{--}3290\text{ cm}^{-1}$ is due to N—H stretching. The C—H asymmetrical and symmetrical stretching due to methylene and methyl groups are observed between $2931\text{--}2919$ and $2857\text{--}2849\text{ cm}^{-1}$, respectively. The aromatic C—H stretchings show signals at $3062\text{--}3026\text{ cm}^{-1}$. The carbonyl stretching of the urethane, urea and ester groups shows peaks at $1697\text{--}1684\text{ cm}^{-1}$. The carboxylate ions of calcium salts give two broad peaks observed at 1623 and 1372 cm^{-1} . This confirms the presence of the ionic linkage in the polymer. The peak at $1027\text{--}1021\text{ cm}^{-1}$ is due to C—O stretching. The peaks for the C—H out of plane bending vibrations of the aromatic rings are seen at $772\text{--}739\text{ cm}^{-1}$.

^1H -NMR spectra

The ^1H -NMR spectra of PUUs are shown in Figure 4 (I, III, and VII). The NMR spectra of PUUs derived from TDI show resonance signals at $9.35\text{--}9.20$ and

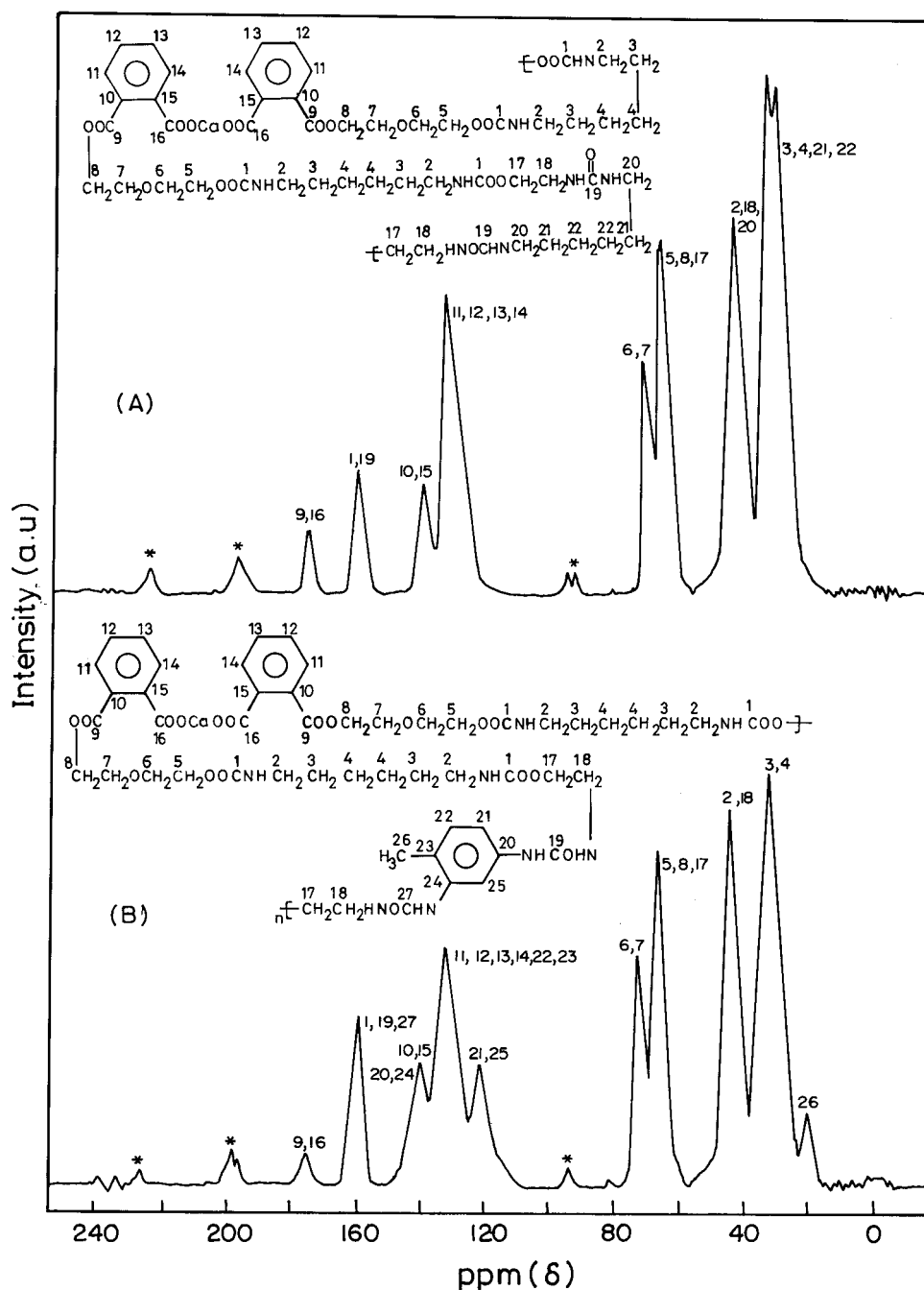


Figure 7 Solid state ^{13}C -CP-MAS NMR spectra: (A) I and (B) III.

8.45–8.24 ppm due to the N—H protons of the urethane groups. The resonance signals based on HMDI and TDI are observed at 7.85–6.95 and 7.97–6.98 ppm, respectively, due to the aromatic protons of PUUs. The HMDI-based PUUs show signals around 6.68–6.65 ppm due to N—H protons of the urethane groups. The methyleneoxy group attached to the —COPh and —CONH groups shows signals between 4.24 and 3.94 ppm. The peaks at 3.56–3.54 ppm are due to the —CH₂OCH₂— group. The signal at 3.44–3.00 ppm is due to the methylene group attached to the —tNH

group. In the case of TDI-based PUUs, the methyl group attached to aromatic ring shows signal at 2.14–2.12 ppm. The peaks at 1.83–1.63 ppm are due to the methylene group attached to the —CH₂OOC group. The other methylene groups are observed between 1.46 and 1.17 ppm.

^{13}C -NMR spectra

The ^{13}C -NMR spectra of PUUs (I and VII) are shown in Figures 5 and 6. The ^{13}C -NMR spectra of PUUs

TABLE III
Viscosities Data of PUUs in DMF and DMSO

Polymer no.	η_{inh} in DMF	η_{inh} in DMSO
I	0.111	0.105
II	0.112	0.109
III	0.104	0.101
IV	0.106	0.100
V	0.101	0.096
VI	0.104	0.098
VII	0.097	0.091
VIII	0.099	0.093

show peaks at 170.75–170.08 ppm due to the carboxylate carbon and another peak at 168.82–168.62 ppm due to the ester carbonyl carbon. The signal due to urea carbonyl carbon for HMDI- and TDI-based PUUs is observed at 157.65–157.30 and 155.58–154.36 ppm, respectively. The HMDI- and TDI-based PUUs show the urethane carbonyl carbon at 154.70–153.78 and 154.32–153.67 ppm, respectively. The aromatic carbons of HMDI-based PUUs show resonance signals around 136.68–115.26 ppm while those of TDI-based PUUs show signals at 136.66–115.28 ppm. The peak at 68.79–68.03 ppm is attributed to the $-\text{CH}_2\text{OCH}_2-$

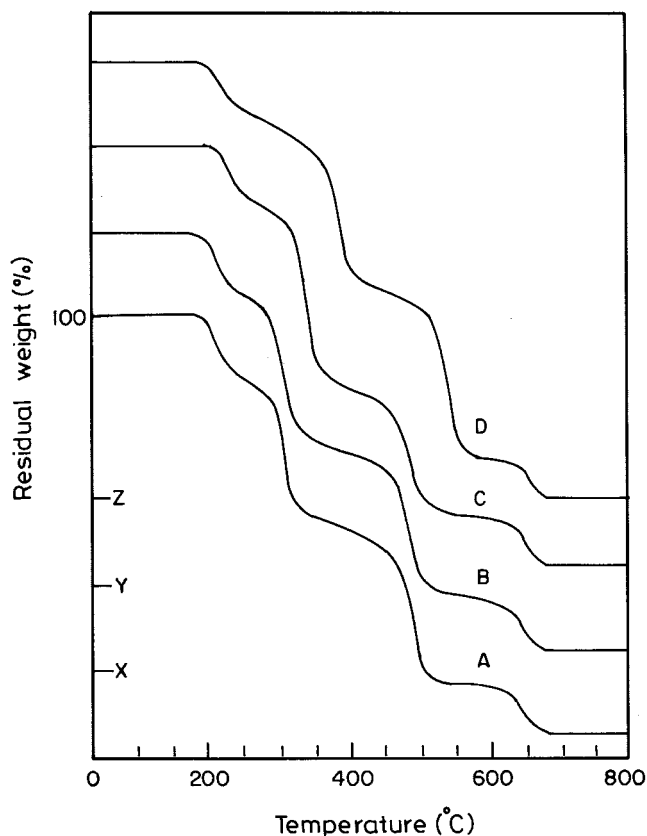


Figure 8 TGA traces of PUUs: (A) I, (B) II, (C) III, and (D) IV. Note: Baseline for B, C, and D are shifted to X, Y, and Z.

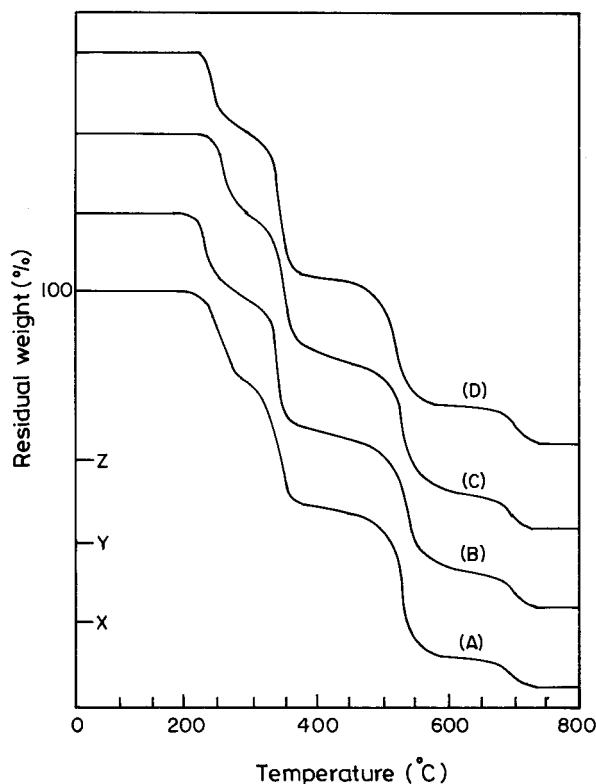


Figure 9 TGA traces of PUUs: (A) V, (B) VI, (C) VII, and (D) VIII. Note: Base line for B, C, and D are shifted to X, Y, and Z.

group. The methyleneoxy groups attached to $-\text{COPh}$ and $-\text{CONH}$ are observed at 64.92–64.41 and 65.12–61.14 ppm, respectively. The peak due to methylene group attached to $-\text{NH}$ group is overlapped with DMSO peaks. The other methylene carbons in the PUUs are observed at 30.04–25.29 ppm. In the case of TDI-based PUUs the methyl group attached to the aromatic ring shows peaks at 17.41–17.21 ppm.

Solid state ^{13}C -CP- MAS NMR spectra

Figure 7 shows the ^{13}C -CP-MAS NMR spectra of PUU, I and III. The PUUs show a broad peak around 172.89–172.30 ppm due to the carboxylate carbon and ester carbonyl carbon. The urethane and urea carbonyl carbons show resonance signals around at 157.54–156.15 ppm. The PUUs based on HMDI show resonance signals between 136.75 and 130.15 ppm due to the aromatic carbons while TDI-based PUUs show two broad resonance peaks at 136.73 and 116.34 ppm. The methyleneoxy group attached to the $-\text{COPh}$ and $-\text{CONH}$ groups shows broad peaks at 70.81–70.35 and 64.53–64.12 ppm, respectively. The signal due to the methylene group attached to $-\text{NHCONH}$ and $-\text{NHCOO}$ is observed between 41.53 and 41.28 ppm. This peak is not observed in the ^{13}C -NMR spectra of liquid samples as it is hidden with the DMSO peaks.

TABLE IV
TGA and DSC Data of Calcium-Containing PUUs

Polymer no.	T_g (°C)	IDT (°C)	Temperature at weight loss (°C)					Weight loss at 800°C (%)
			20%	40%	60%	80%	90%	
I	101.3	187	287	309	474	508	647	95.2
II	98.5	183	292	316	473	502	645	95.3
III	108.4	202	318	333	458	499	648	95.2
IV	106.7	196	342	391	507	526	610	95.3
V	113.9	210	272	341	499	535	672	95.2
VI	111.4	206	298	336	506	548	678	95.3
VII	119.6	228	313	348	510	552	684	95.3
VIII	116.7	223	288	347	501	537	698	95.3

The other methylene carbons are observed between 30.73 and 27.15 ppm. The methyl group attached to the aromatic ring shows peaks at 17.86–17.35 ppm.

Inherent viscosity

The inherent viscosity data are shown in Table I. The inherent viscosities of the polymers are considerably lower than their corresponding nonmetal analogues (Table II), which is general for all metal-containing polyurethanes and PUUs.^{12–16,19,20} The reason for the low viscosities may be that in these PUUs the molecular weight built up may not be very high and there may also be partial reversible dissociation of the metal oxygen bonds leading to lower molecular weight fragments in solutions.^{19,20} This was supported by the decrease in viscosity with increasing the polarity of the solvents (Table III). In addition, the viscosity increase is higher in DMF than in DMSO, probably owing to the lower depression of ionic association in DMF because of its lower dielectric constant (ϵ 36.7) than in DMSO (ϵ 46.6). The HMDI-based polymers showed higher inherent viscosities than TDI-based polymers, since the chain lengths of HMDI-based polymers were higher than those of TDI-based polymers. Also, the hydrodynamic volume of HMDI-based polymers may be larger than that of TDI-based polymers.

Thermal properties

The TGA curves of calcium-containing PUUs are shown in Figures 8 and 9. The TGA data of PUUs and blank PUUs are given in Table IV and V, respectively. Introducing metals into the PUU produces some decrease in decomposition temperature. The initial decomposition temperatures (IDT) of the PUUs show the ranges between 183 and 228°C, which are lower than those of blank PUUs. However, their decomposition rates are less than those of blank PUUs. This result indicates that the calcium metal acts as a catalyst and facilitates the first-stage decomposition, but retards the rate of decomposition on further stages. All the PUUs showed multiple-stage decomposition. The first stage may be considered to be urethane–urea scission (hard segment) followed by the formation of isocyanate and hydroxyl components.²¹ The second stage perhaps involves cyclization and secondary degradation. The third stage corresponds to the formation of CaCO₃. In all the cases of polymers, the residual weight at 800°C roughly corresponds to the amount of CaO formed (fourth stage). All the PUUs showed slightly higher stability than polyurethanes, due to the presence of a greater number of hydrogen bonding and the lesser number of metal ion in the PUUs.^{15,16} The blank PUUs showed 100% weight loss at 650°C,

TABLE V
TGA Data of Blank PUUs

Polymer no.	IDT (°C)	Temperature at weight loss (°C)					Weight loss at 650°C (%)
		20%	40%	60%	80%	90%	
IX	191	284	325	414	446	484	100
X	185	252	298	372	422	467	100
XI	209	257	287	373	419	486	100
XII	202	248	280	374	420	498	100
XIII	214	289	335	383	436	479	100
XIV	210	268	297	364	459	496	100
XV	231	297	326	354	396	462	100
XVI	226	268	298	322	397	460	100

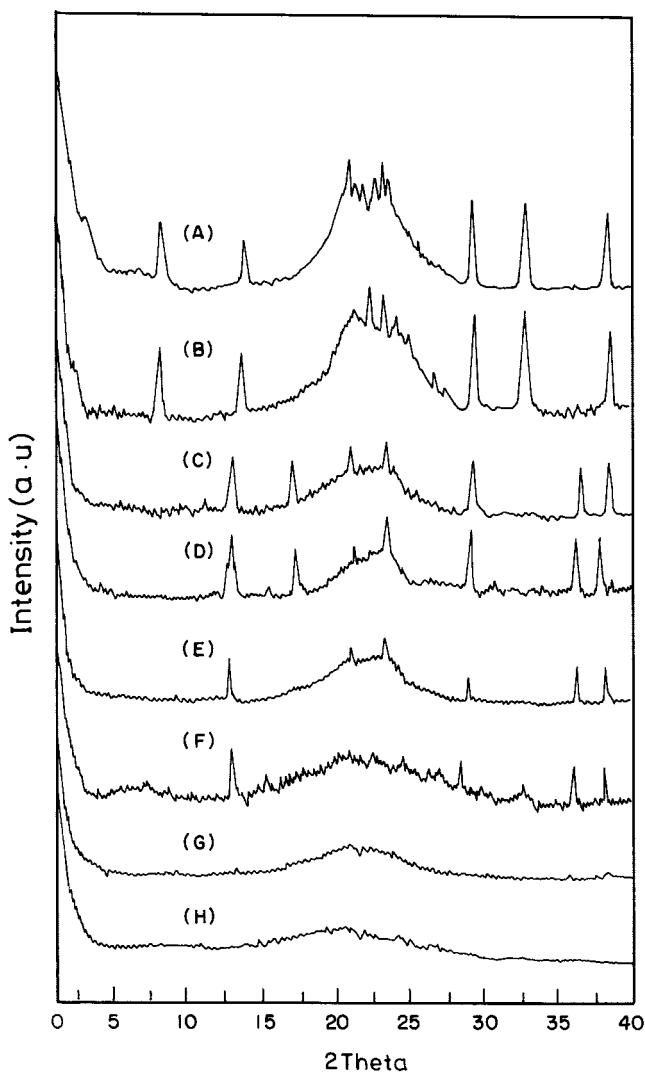


Figure 10 XRD patterns of PUUs: (A) I, (B) II, (C) III, (D) IV, (E) V, (F) VI (G) VII, and (H) VIII.

indicating that PUUs exhibit a good thermal stability than the blank polymers.

The glass transition temperature (T_g) data are given in Table IV. The T_g values of the calcium-containing PUUs range from 98.5 to 119.6°C. All the polymers showed a single T_g value. This may be due to the absence of formation of mixture of homopolymer or a block copolymer. This may also be due to the absence of heterogeneous mixing of hard and soft segments in the polymer matrix. The PUUs prepared from HMDI-based bisureas have lower T_g values than those derived from TDI-based bisureas due to the flexible hexamethylene group.

X-ray diffraction

Figure 10 shows the X-ray diffraction pattern of the PUUs. The X-ray diffraction patterns show that the

HMDI-based PUUs are partially crystalline in nature, whereas the TDI-based PUUs are amorphous in nature. This may be due to the folding of the hexamethylene groups present in the backbone of the PUUs. The crystalline nature of HMDI-based polymers was also confirmed by the solubility studies of the PUUs in DMSO. The TDI-based PUUs were more easily soluble in DMSO than the HMDI-based PUUs. The HMDI-based PUUs, III and IV, exhibit slightly low crystallinity because the bisurea unit contains a tolylene ring and not a hexamethylene unit.

CONCLUSIONS

The calcium-containing PUUs were synthesized by the reaction of HMDI or TDI with 1:1 mixtures of Ca-(HEEP)₂ and the four different bisureas by using DBTDL as a catalyst. The PUUs were soluble in DMF, DMSO, and DMAc. The HMDI-based polymers showed higher viscosity than the TDI-based polymers. The TDI-based polymers showed higher thermal stability than the HMDI-based polymers. The X-ray diffraction studies of the polymers showed that the HMDI-based polymers are partially crystalline but TDI-based polymers are amorphous in nature.

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