STUDIES ON ODD-EVEN EFFECT OF METHYLENE SPACERS IN POLY(PYROMELLITIMIDE-URETHANE)S

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ABSTRACT

Three series of poly(pyromellitimide-urethanes)s were synthesized from various N,N′-bis(ω-hydroxyalkyl)pyromellitimides (HAPMIs) and various dicarbooxyloxyl diazides namely terephthaloyl diazide (TPDA), 4,4′-diphenyldiacid azide (BPDAA) and 4,4′-azobenzenediacid azide by solution polycondensation in DMSO at 75°C in the presence of di-n-butyltin dilaurate as catalyst. The polymers were characterized by elemental analysis, IR, ^{1}H and ^{13}C-NMR and X-ray diffraction analysis. Thermal stability and phase transition behavior were studied by TGA, DSC, and hot-stage optical polarized microscopy (HOPM). T_g values decrease linearly as the number of methylene spacer increases while T_m shows odd-even effect. In a given series, polymers with even number of methylene spacers possess higher T_m values than the neighboring polymers with odd number of methylene spacers and thermal stability decreases with increase in number of methylene spacers. Thermal stability is also influenced by the aromatic segment present in the polymer backbone, order being : phenyl > biphenyl > azobenzene.

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INTRODUCTION

Polypyromellitimides (PPMIs) have gained considerable interest as heat-resistant polymers because of their high thermal stability, good chemical resistance and excellent mechanical properties [1-4]. The main drawback of the polymers is that they need special techniques for processing. To overcome this drawback, PPMIs were suitably modified by incorporation of ether, ester, carbonate, urethane, sulfone or amide segments into the polymers. These modified systems not only provide heat resistance but also showed other interesting properties like improved solubility, processability and in a few cases, liquid crystalline (LC) behavior. Composite membrane/electrode for electrochemical cell was made by Copeland *et al.* using poly(imide-ether) sheet laminated with aqueous dispersion of PTFE blend containing Ir-Ru oxide [5]. Kannan *et al.* synthesized a new series of aromatic heterocyclic poly(arylpyromellitimide-ether)s which showed high thermal stability [6]. They also synthesized flame-retardant poly(pyromellitimide aryl phosphoramide-ester)s [7, 8]. Gilbert and Andre prepared poly(pyromellitimide-urethane) (PPMIU) fibre-elastomers from substituted pyromellitimide diols with poly(ethylene adipate) and 1,6-hexamethylene diisocyanate (HMDI) in nitrogen at 170°C [9]. Kiselva *et al.* synthesized PPMIUs from various pyromellitimide diols with HMDI and 2,4-tolylene diisocyanate [10]. Mustafa *et al.* reported that poly(pyromellitimide-ester)s (PPMIEs) prepared from N,N′-dihydroxypyromellitimide and aliphaticdiacid chlorides with various methylene spacers, showed thermotropic LC behavior [11]. Hung and Chang synthesized PPMIEs from N-(4-carboxyphenyl) trimellitimide with pyromellitimide diols with various methylene spacers. Polymers with an even number of methylene spacers showed a smectic mesophase [12]. Sato *et al.* synthesized poly(imide-carbonate)s, of which the polymer with the biphenyl unit, exhibited LC [13]. In continuation of our research in this domain [14, 15], we are herein reporting the synthesis and characterization of three series of poly(pyromellitimide-urethane)s containing phenyl, biphenyl and azobenzene units.

EXPERIMENTAL

Materials

3-Amino-1-propanol (Merck), 4-amino-1-butanol (Sigma), 5-amino-1-pentanol (Sigma), 6-amino-1-hexanol (Sigma), sulphuric acid (36N, Qualigens),

biphenyl (Merck), anhydrous aluminium chloride (Merck), acetyl chloride (Qualigens), glacial acetic acid (BDH), chromium (VI) oxide (Qualigens), p-nitrobenzoic acid (BDH), glucose (Qualigens), terephthalic acid (Merck) and sodium azide (Merck) were used as received. 2-amino ethanol (BDH) was purified by distillation under reduced pressure. PMDA (Merck) was purified by sublimation under reduced pressure [16].

N,N'-bis(ω-hydroxyalkyl)pyromellitimides (HAPMIs)

HAPMIs (i-v) were prepared using PMDA and ω-aminoalcohols namely 2-aminoethanol, 3-amino-1-propanol, 4-amino-1-butanol, 5-amino-1-pentanol and 6-amino-1-hexanol by a modified procedure [17]. A typical procedure for the preparation of N,N'-bis(2-hydroxyethyl)pyromellitimide (i) is as follows : PMDA (20 mmol) in DMF was refluxed with 2-aminoethanol (40 mmol) at 135-140°C for 8 hours with stirring. The resultant product was poured into water. The precipitated diol was filtered, washed and dried. Similarly, other monomers (ii-v) were prepared. The yield of the monomers were more than 80%. The melting points of HAPMIs (i-v) are 274, 246, 225, 206, and 200°C respectively (lit. m.p. 277, 248, 224, 209, and 201°C, respectively) [12].

4,4'-Biphenyldicarboxylic Acid (BPDA)

Biphenyl was acetylated using excess acetyl chloride according to the procedure reported by Silver and Lowy in the presence of excess of anhydrous aluminium chloride in carbondisulphide [18]. 4,4'-Diacetylbiphenyl (DABP) thus obtained was oxidized by chromium (VI) oxide in the presence of glacial acetic acid and concentrated sulphuric acid at 60°C to give BPDA. Yield 88%, melting point of the diacid was > 300°C. m.p. of dimethyl ester 212°C (lit. m.p. 212-213°C) [18].

4,4'-Azobenzenedicarboxylic Acid (ABDA)

ABDA was synthesized by the reported procedure [19]. 4-Nitrobenzoic acid (0.01 mol) in aqueous caustic soda was reacted with aqueous glucose (0.05 mol) at 50°C and aerated for 8 hours with vigorous stirring. It was acidified to get the diacid. It was purified by converting into its dipotassium salt and then liberating the diacid. Yield 65% m.p. > 300°C, m.p. of dimethyl ester was 241°C (lit. m.p. 241°C) [20].

Diacid Azides

Diacid azides were prepared from the corresponding diacids by a modified procedure reported by Petersen [21]. A typical procedure for the preparation

of terephthaloyl diazide (TPDA) is as follows: Terephthalic acid (TPA) (10 mmol) was converted to the di-acid chloride by refluxing with excess of thionyl chloride (30 mmol) and a drop of pyridine, at 100°C for 2 hours and the excess thionyl chloride was removed by distillation under reduced pressure. The terephthaloyl dichloride (10 mmol) was dissolved in dry acetone, treated with aqueous sodium azide (25 mmol) with vigorous stirring at 20°C for 2 hours. The precipitated diacid azide was filtered, washed, and dried *in vacuo* at room temperature. Yield was 85%. The melting point was not determined as it decomposed around 75°C. Similarly 4,4′-biphenyldiacid azide (BPDAA) and 4,4′-azobenzenediacid azide (ABDAA) were also synthesized from the corresponding diacids via the formation of diacid chlorides. Melting points were not determined as they decomposed around 75°C.

Polymerization

Poly(imide-urethane)s (I-XV) were synthesized by solution polycondensation technique [22] employing various HAPMIs (10 mmol) and the three diacid azides (10 mmol) namely TPDA, BPDAA, and ABDAA in DMSO using a few drops of di-n-butyltin dilaurate (DBTDL) as catalyst under nitrogen atmosphere. The temperature was maintained at 75°C during addition and raised to 110°C and maintained for 20 hours. The mixture was poured into a large quantity of water. The precipitated polymer was filtered, washed, dried, and dissolved in hot THF and reprecipitated by dry chloroform, and finally dried under vacuum at 60°C.

Characterization

Solubility of the polymers was tested with various solvents. Inherent viscosity was determined using Ubbelohde viscometer at 30°C. Elemental analysis was carried out on a Heraeus CHN analyzer. IR spectra of the polymers were recorded on a Hitachi 270-50 IR spectrophotometer using KBr pellet. ^{1}H and ^{13}C-NMR spectra of the polymers were recorded on a Bruker AMX 400 FT NMR (400 MHz) spectrometer in DMSO-d$_6$ using TMS as internal standard. XRD powder patterns of the polymers were obtained on a Sierfert 3000 TT X-ray diffractometer using Ni filtered Cu/K radiation of wavelength 1.5406Å. Thermal transitions of the polymers were determined using Delta series DSC 7 differential scanning calorimeter. Thermogravimetric analysis of the polymers was carried out on a Mettler TA 3000 thermogravimetric analyser. Hot-stage optical polarized microscopic studies was carried out using a Leitz Ortholux 2 POL BK

polarizing microscope equipped with a Linkam THMS 600 heating stage and a camera.

RESULTS AND DISCUSSION

HAPMIs were prepared from PMDA and various ω-aminoalcohols in DMF in good yield. BPDA and ABDA were obtained in good yield. Diacid azides namely TPDA, BPDAA and ABDAA were obtained in good yield from the corresponding diacids via the formation of diacid chlorides. The monomers were characterized by elemental analysis, IR and ^{1}H-NMR which were consistant with the assigned structure. Elemental analysis for the diacid azides was not carried out since they decomposed with explosion around 75°C. Poly(imide-urethane)s (I-XV) were obtained in > 83% yield by solution polycondensation in DMSO from various HAPMIs with various diacid azides using DBTDL as catalyst (Scheme 1). It is noteworthy to mention that in the present studies, diacid
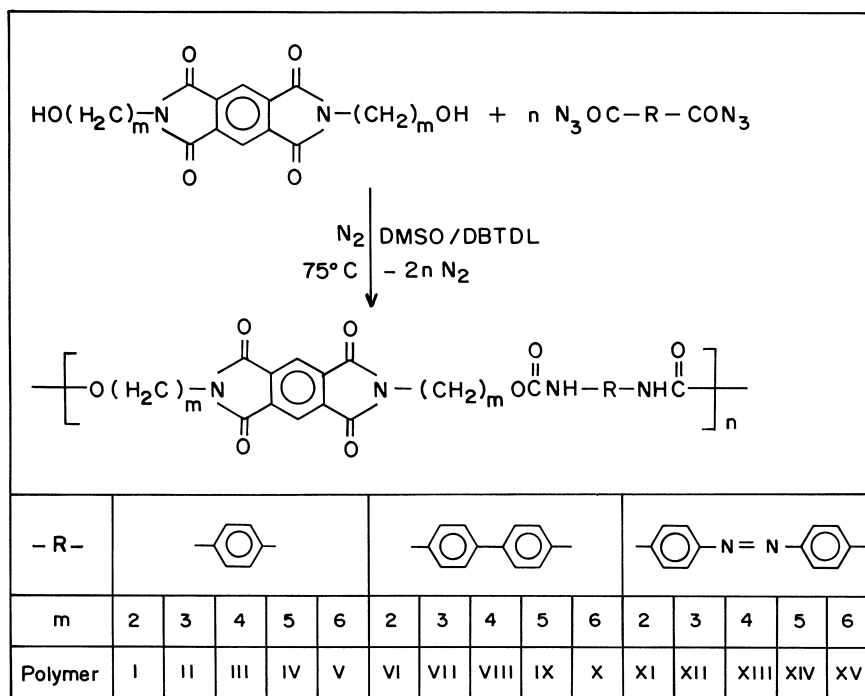
Scheme 1. Synthesis of Poly(pyromellitimide-urethane)s I-XV.

azides were used because they possess several superior characteristics over the corresponding diisocyanate counter parts viz. stability towards hydrolysis or polymerization, less toxic, easy to synthesize, easy to handle and economically feasible [23]. Yield and elemental analysis data of the polymers are shown in Table 1. The elemental analysis data is in good agreement with the calculated values. All the polymers are soluble in concentrated sulphuric acid, sparingly soluble in DMSO at room temperature and completely soluble on heating. They are soluble in hot THF, DMAc, m-cresol and DMF and insoluble in benzene, chloroform and nitrobenzene. Inherent viscosity of the polymers was carried out in concentrated sulphuric acid at 30°C and the results are presented in Table 1. The results reveal that the polymers are of moderately high molecular weight.

The representative IR spectra of polymers VI and XV are shown in Figure 1. The polymers show absorption bands around 1780-1770 and 1740-1710 cm^{-1} due to imide and urethane carbonyl linkages [24]. Absorption bands around 1620-1600 and 2980-2925 cm^{-1} are due to aromatic ring vibrations and methylene stretchings, respectively. As the number of methylene spacer increases, a band around 2900-2860 cm^{-1} appears distinctly which is due to symmetric stretching vibration of -CH$_2$. Polymers VI-X show broad bands around 3400-3350 and 1540-1525 cm^{-1} due to urethane N-H stretching and bending vibrations, respectively.

The representative ^{1}H-NMR spectra of polymers IV and VIII are shown in Figure 2. Aromatic proton of pyromellitimide (PMI) ring resonate at 8.07-8.20 δ as singlet [6]. The aromatic ring protons of polymers I-V, VI-X and XI-XV resonate in the region 6.95-7.20, 7.32-7.67 (AB quartet) and 7.52-7.88 δ (multiplet) respectively. The resonance signals of N-H protons appear around 7.40-7.90 δ as a broad peak. The resonance signals for methylene protons of the polymers appear in the region 1.28-4.40 δ depending upon the position of the methylene protons from the neighboring urethane and imide groups [25]. The representative proton decoupled ^{13}C-NMR spectra of polymers V and XI are shown in Figure 3 and the chemical shift values of the polymers I-XV are shown in Table 2. The resonance signals around 166.3-167.8 and 153.4 δ correspond to the carbonyl carbons of imide and urethane respectively [26, 27] Phenyl carbons of PMI resonate around 118.1-118.3 and 136.9-137.9 δ. The aromatic carbons of phenyl, biphenyl and azobenzene resonate in the region around 128.6-139.5, 110.5-132.3, and 112.5-126.6 δ, respectively. The methylene carbons resonate in the region 22.6-65.7 δ [25].

Representative X-ray diffractograms of polymers I, II, VI, VII, XI and XII are shown in Figure 4. X-ray diffraction patterns of the polymers reveal that

TABLE 1. Yield, Inherent Viscosity and Elemental Analysis Data of Polymers I-XV

Polymer No.	Molecular formula	Yield (%)	Inherent[a] viscosity (dLg⁻¹)	Elemental analysis (wt %)					
				Carbon		Hydrogen		Nitrogen	
				Found	Calcd.	Found	Calcd.	Found	Calcd.
I.	$(C_{22}H_{16}N_4O_8)_n$	85	0.73	56.82	56.89	3.43	3.47	12.08	12.06
II.	$(C_{24}H_{20}N_4O_8)_n$	83	0.75	58.60	58.53	4.03	4.10	11.40	11.38
III.	$(C_{26}H_{24}N_4O_8)_n$	87	0.82	60.02	60.00	4.57	4.65	10.80	10.77
IV.	$(C_{28}H_{28}N_4O_8)_n$	90	0.86	61.37	61.31	5.10	5.15	10.25	10.22
V.	$(C_{30}H_{32}N_4O_8)_n$	92	0.84	62.47	62.50	5.54	5.60	9.79	9.72
VI.	$(C_{28}H_{20}N_4O_8)_n$	83	0.72	62.18	62.22	3.68	3.73	10.43	10.37
VII.	$(C_{30}H_{24}N_4O_8)_n$	86	0.65	63.34	63.38	4.20	4.26	9.89	9.86
VIII.	$(C_{32}H_{28}N_4O_8)_n$	84	0.68	64.40	64.43	4.68	4.73	9.46	9.39
IX.	$(C_{34}H_{32}N_4O_8)_n$	83	0.69	65.33	65.38	5.10	5.17	8.99	8.97
X.	$(C_{36}H_{36}N_4O_8)_n$	89	0.68	66.32	66.26	5.50	5.56	8.63	8.59
XI.	$(C_{28}H_{20}N_6O_8)_n$	85	0.52	59.16	59.15	3.49	3.55	14.83	14.79
XII.	$(C_{30}H_{24}N_6O_8)_n$	87	0.62	60.38	60.40	4.00	4.06	14.13	14.09
XIII.	$(C_{32}H_{28}N_6O_8)_n$	87	0.63	61.50	61.54	4.44	4.52	13.50	13.46
XIV.	$(C_{34}H_{32}N_6O_8)_n$	92	0.62	62.53	62.57	4.87	4.94	12.92	12.88
XV.	$(C_{36}H_{36}N_6O_8)_n$	91	0.64	63.60	63.53	5.27	5.33	12.39	12.35

[a] Measured at a concentration of 0.5 gdL⁻¹ in Conc. H_2SO_4 at 30°C
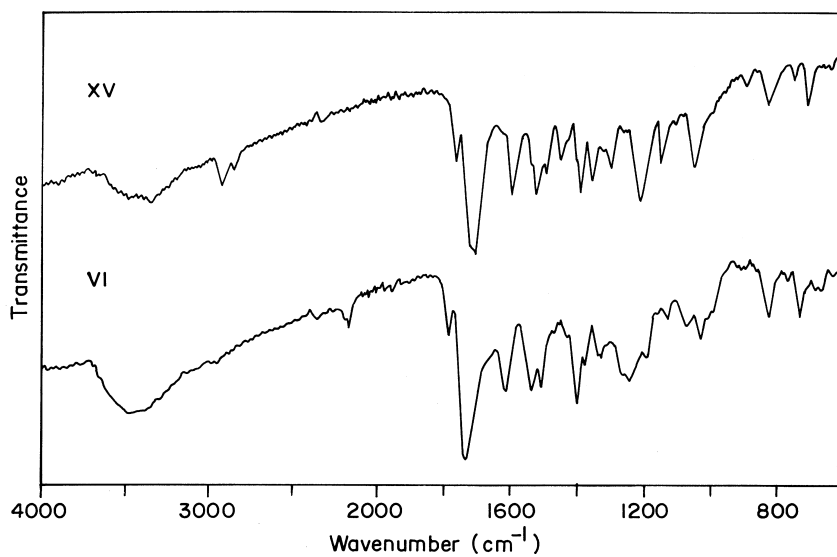
Figure 1.   IR spectra of polymers VI and XV.

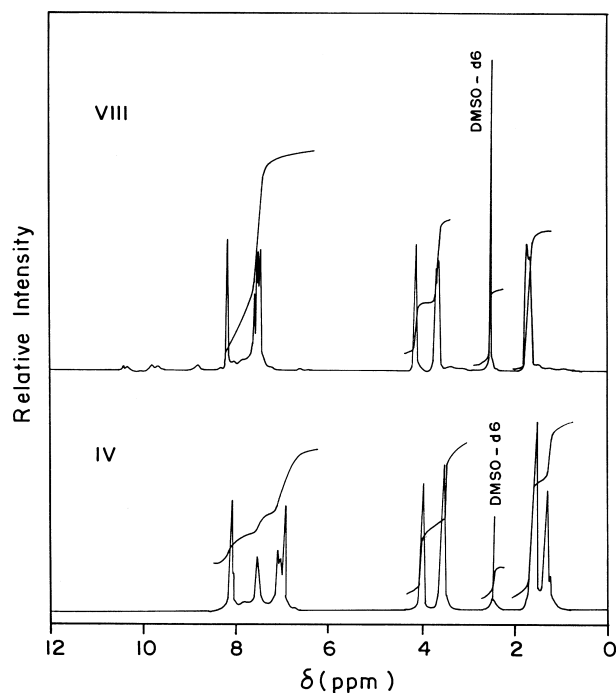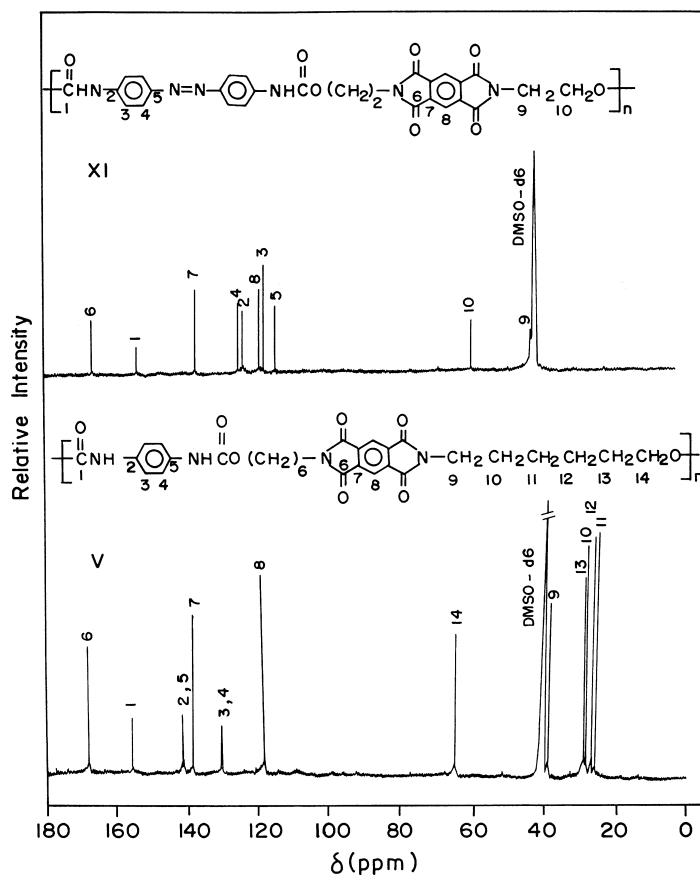**Figure 2.** ^{1}H-NMR spectra of polymers IV and VIII.

Figure 3.   Proton decoupled ^{13}C-NMR spectra of polymers V and XI.

they are partially crystalline. Crystallinity of the polymers slightly varies depending on the aromatic segment present in the polymer back-bone. Azobenzene based polymers are more crystalline than biphenyl polymers which in turn more crystalline than phenyl polymers.

DSC thermograms of polymers II, III, VII, VIII, XII, and XIII are shown in Figure 5 and the DSC data of the polymers is presented in Table 3. For a given set of polymers, T_g values decrease linearly as the number of methylene spacer increases and T_m values show odd-even effect. The variations of T_g and T_m with respect to number of methylene spacers are shown in Figure 6. Polymers with even number of methylene spacers show higher T_m values than the neighboring polymers with odd number of methylene spacers [28]. This odd-even effect is

TABLE 2. Proton Decoupled ^{13}C-NMR Spectral Data of Polymers I-XV

| Polymer No.	Chemical shift value δ (ppm)													
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
I.	153.4	139.5	128.6	128.6	139.5	166.3	136.8	117.0	40.9	57.8	-	-	-	-
II.	153.4	139.5	128.6	128.6	139.5	166.3	136.8	117.0	36.7	27.7	64.5	-	-	-
III.	153.4	139.5	128.6	128.6	139.5	166.3	136.8	117.0	37.7	24.4	26.0	63.5	-	-
IV.	154.5	140.6	129.6	129.6	140.6	167.3	137.9	118.1	38.8	28.2	23.7	28.6	65.7	-
V.	154.5	140.6	129.6	129.6	140.6	167.3	137.9	118.1	39.0	28.7	26.1	27.0	29.4	65.0
VI.	153.4	120.4	117.1	132.3	110.5	166.3	136.9	118.2	35.0	57.0	-	-	-	-
VII.	153.4	120.4	117.1	132.3	110.5	166.3	136.9	118.2	36.8	27.8	64.3	-	-	-
VIII.	153.4	120.4	117.1	132.3	110.5	166.3	136.9	118.2	39.1	25.7	30.8	61.3	-	-
IX.	153.4	120.4	117.1	132.3	110.5	166.3	136.9	118.2	37.7	27.6	22.6	31.9	60.4	-
X.	153.4	120.4	117.1	132.3	110.5	166.3	136.9	118.2	37.9	27.6	25.0	26.0	32.2	60.6
XI.	153.4	123.2	117.1	126.6	113.4	166.3	136.9	118.2	40.9	57.3	-	-	-	-
XII.	153.4	123.2	117.1	126.6	113.4	166.3	136.9	118.2	35.8	26.6	58.6	-	-	-
XIII.	153.4	123.2	117.1	126.6	113.4	166.3	136.9	118.2	37.8	24.6	29.8	60.1	-	-
XIV.	153.4	123.2	117.1	126.6	113.4	166.2	136.8	118.1	37.8	27.2	22.6	27.9	60.4	-
XV.	153.4	122.7	117.1	126.4	112.5	166.2	138.3	117.6	37.9	27.6	24.9	25.8	28.2	60.6

Solvent = DMSO - d_6
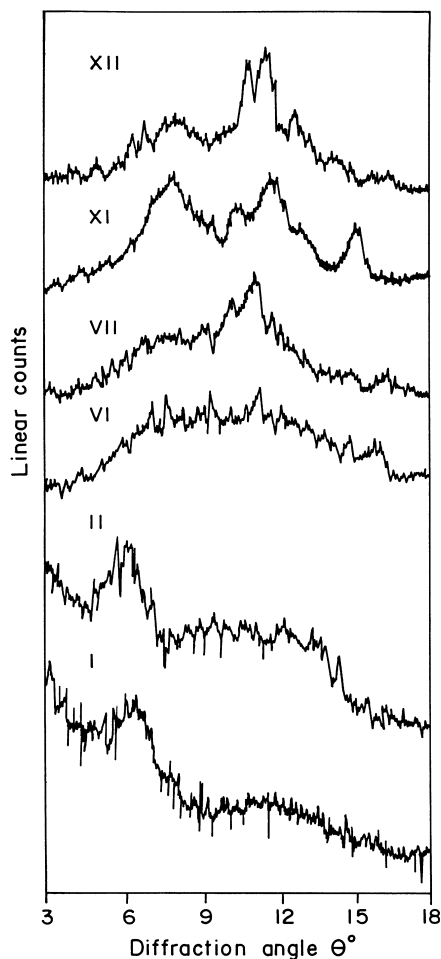
Figure 4. X-ray diffractograms of I, II, VI, VII, XI, and XII.

attributed to the zig-zag packing of the polymer chains. Polymers with even number of methylene spacers possess planar zig-zag packing of methylene chain while polymers with odd number of methylene spacers possess non-planar zig-zag packing which leads to less good packing and hence lower T_m. The non-planar zig-zag packing in polymers with odd number of methylene spacers would have resulted by the tilting of PMI and other aromatic segments in the polymer back-bone, relative to the layer planes [29]. Some of the polymers showed exotherms prior to the melting temperature. This may be attributed to solid-solid transition (Ts). The thermal stability and decomposition temperature of the polymers were studied by TGA in nitrogen atmosphere. The weight loss and char
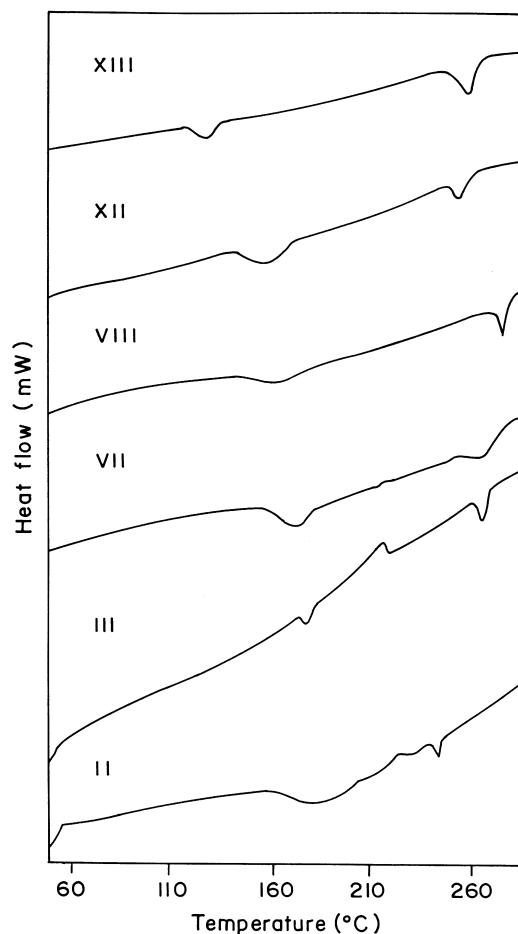
Figure 5. DSC thermograms of polymers II, III, VII, VIII, XII, and XIII.

residue at 600°C are given in Table 3. The temperature corresponding to 5% weight loss is considered as initial decomposition temperature (IDT). IDT of these polymers are in the range 269-294°C (Figure 7). In a given set of polymers, the thermal stability decreases with increasing number of methylene spacers. This may be attributed to the presence of thermally sensitive aliphatic segments. Aromatic segment of the polymers also influences the thermal stability. The order of stability being phenyl > biphenyl > azobenzene. High thermal stability of phenyl polymers I-V (285-294°C) compared to other two series, may be due to the more symmetrical nature of the polymer structure. Biphenyl based polymers show higher thermal stability (272-288°C) than the azobenzene polymers

TABLE 3. DSC and TGA Data of Polymers I-XV

Polymer No.	T_g^a (°C)	T_s^a (°C)	T_{ml}^a (°C)	Temperature (°C) corresponding to Weight loss			Char yield at 600°C (%)
				5%	15%	50%	
I.	228	-	270	294	309	406	13.1
II.	196	220	243	292	309	394	12.0
III.	178	217	265	290	303	343	10.5
IV.	160	196	242	288	303	412	10.1
V.	130	184	257	285	302	356	8.7
VI.	190	227	278	288	306	375	12.6
VII.	174	217	269	285	306	344	12.6
VIII.	167	-	275	279	302	350	8.0
IX.	155	-	263	277	300	350	7.3
X.	139	-	270	272	294	419	5.6
XI.	170	-	264	285	303	338	8.1
XII.	157	-	253	282	306	331	7.0
XIII.	142	-	255	277	300	325	7.0
XIV.	128	-	225	274	296	325	7.0
XV.	114	-	240	269	281	325	5.0

[a] The data pertaining to first heating
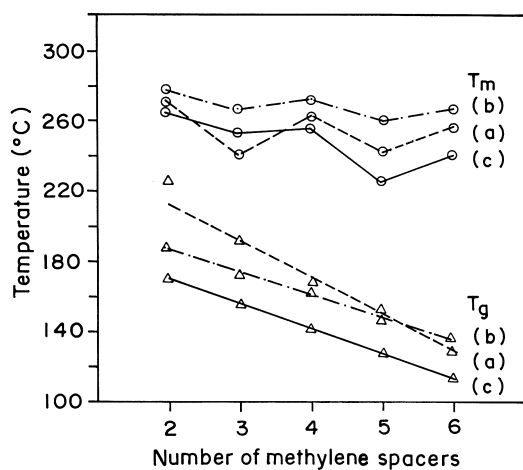
(269-285°C). This may be attributed to the higher percentage of aromaticity of biphenyl. A two step degradation pattern is observed for all the polymers. First step corresponds to the formation of various small fragments which subsequently carbonized in the second step. The char at 600°C for all the polymers are in the range of 5-13%.
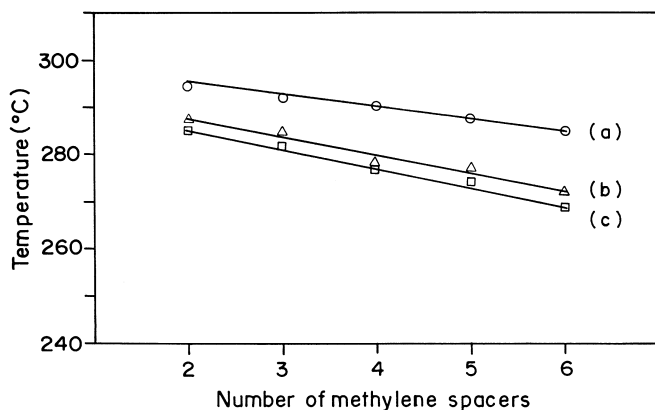
Figure 7.   Change of IDT of polymers I-V (a); VI-X (b), and XI-XV (c) with number of methylene spacers.

Sun and Chang had reported that poly(pyromellitimide-carbonate)s with biphenyl units rich copolymer exhibited a nematic melt and the mesogenic character of PMI ring was very low [30]. Hirato *et al.* prepared thermotropic LC aromatic-aliphatic PPMICs with biphenyl unit rich copolymers [31]. Hence, HOPM studies were performed for these polymers at elevated temperatures. However, the studies revealed that none of the polymers exhibited liquid crystalline behavior. This was in agreement with the reports of Kricheldorf *et al.* [32]. In the event that these systems might possess a latent liquid crystalline phase hidden by a stable crystalline state, the structures may be modified suitably to reduce the stability of the crystalline phase [33].

CONCLUSION

Three series of poly(pyromellitimide-urethane)s were synthesized and characterized by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR and XRD measurements. XRD studies reveal that these polymers possess little crystallinity. Crystallinity slightly varies according to the nature of the aromatic segment present in the polymer backbone, the order being azobenzene > biphenyl > phenyl polymers. DSC studies reveal that in a given set of polymers, T_g values decrease as the number of methylene spacers increases and T_m values show odd-even effect. Polymers with an even number of methylene spacers show higher T_m values than the neighboring polymers with odd number of methylene spacers. TGA studies reveal that in a given set of polymers, the thermal stability decreases as the number of methylene spacer increases and the thermal stability is also influenced by the aromatic segment present in the polymers, the order being phenyl > biphenyl > azobenzene polymers. HOPM studies show that these polymers do not show any liquid crystalline behavior. This indicates that pyromellitimide segment is a weak mesogen.

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