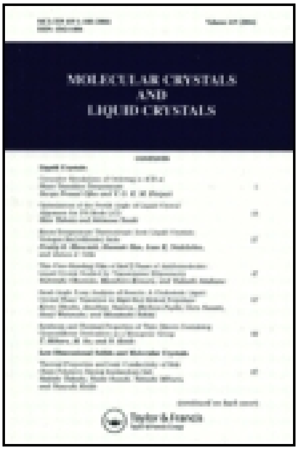

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Studies on Thermotropic Main Chain Liquid Crystalline Segmented Polyurethanes. II. Synthesis and Properties of H 12 MDI- and MDI-Based Polyurethanes from High Aspect Ratio Mesogenic Diol as Chain Extender

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Studies on Thermotropic Main Chain Liquid Crystalline Segmented Polyurethanes. II. Synthesis and Properties of H_{12}MDI- and MDI-Based Polyurethanes from High Aspect Ratio Mesogenic Diol as Chain Extender

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Previous studies on thermotropic main chain liquid crystalline polyurethanes (TLCPUs) prepared from 4-{[4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-benzoic acid 4-{[4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-phenyl ester (mesogenic diol) as chain extender were continued. In this article, the main chain liquid crystalline polyurethanes are based on the mesogenic diol as chain extender, poly(tetramethylene oxide)glycol (PTMG) soft segment of different molecular weight PTMGs ($M_n = 650$, 1000, 2000), different diisocyanates including 4,4′-methylene bis(cyclohexyl isocyanate) (H_{12}MDI) and 4,4′-methylene bis(phenyl isocyanate) (MDI). The polyurethanes were investigated by FTIR spectroscopy for structural confirmation and DSC and hot stage optical polarizing microscope to study the mesomorphic properties. The molecular weight distribution was determined by GPC. The effect of partial replacement of the mesogenic diol by 20–50 mol% PTMG and the effect of the diisocyanates on the liquid crystalline properties were studied. It was observed that the partial replacement of the mesogenic diol by PTMG of varying molecular weights and also the diisocyanates influenced the phase transitions and the occurrence of mesophase textures. Characteristic liquid-crystalline textures were observed when sufficient content of the mesogenic diol was present. If the flexible spacer was longer, a higher content of mesogenic agent was needed to obtain LC properties. Depending on the flexible spacer length and the mesogenic content, grained and threadlike textures were obtained for the H_{12}MDI series

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polymers while the PUs prepared from MDI showed only grained texture for all the compositions. Elastomeric behavior was observed in the polymers from PTMG 2000 and H_{12}MDI with mesogen content 20–40 mol%.

Keywords: high aspect ratio mesogenic unit, chain extender, segmented liquid crystal polyurethanes

INTRODUCTION

Themoplastic liquid crystalline polyurethanes (TLCPUs) are being investigated with much interest owing to their application potential. Due to the strong intermolecular interaction arising from hydrogen bonding of the urethane linkages, the synthesis of the TLCPUs seems more difficult than the synthesis of the other LC polymers. To prepare a LCPU, many methods of minimizing the hydrogen bonding effect have been developed, such as (1) inserting flexible spacers into the mesogenic units [1], (2) introducing substituted mesogenic segments [2], or (3) using secondary amines reacted with dichloroformates [3]. Among these methods, the introduction of long flexible spacers such as poly (tetramethylene oxide) glycol, PTMG 1000, and PTMG 2000 into the polymer main chains was effective in decreasing the phase transition temperature, increasing solubility, reducing hydrogen bonding [4], and showing elastic properties. However, the use of long flexible spacers could result in partial or complete loss of liquid crystalline properties. Hence, we envisage that the incorporation of a high axial ratio mesogenic unit into the polymer backbone could help to balance the mesogenic property and elastic nature of the polyurethane.

Most of the literature references on liquid crystal PU elastomers report the use of low axial ratio mesogenic diols such as 4,4′-bis(hydroxy alkoxy) biphenyl [5–12], N,N′-bis(6-hydroxyhexyl)-3,4,3′,4′-biphenyl dicarboximide [13], 4,4′-bis(hydroxyhexyloxy)azobenzene [14], and very few reports on triad mesogenic diol benzene 1,4-di(4-iminophenoxy-n-hexanol) [15,16] as chain extenders. In their study, Sun et al. have reported that polyurethane elastomers with low axial ratio mesogenic unit and long soft segment diol do not easily exhibit mesophase and suggested that the axial ratio of the mesogenic unit has to be increased to obtain a liquid crystal polymer with long flexible spacers [16].

In a previous article [17], we synthesized and studied the properties of liquid crystalline polyurethanes based on the mesogenic diol 4-{[4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-benzoic acid 4-{[4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-phenyl ester as chain extender, PTMG soft segment of different molecular weights (M_n = 650, 1000, 2000), and an aliphatic linear diisocyanate, 1,6-hexamethylene diisocyanate (HMDI). The effect of partial replacement of the mesogenic diol by 20–50 mol% PTMG on the LC properties was studied.

In continuation of this work, this article reports the synthesis and properties of segmented polyurethanes from soft segement PTMG of different molecular weights (M_n = 650, 1000, 2000), with the diisocyanates (H_{12}MDI and MDI) and high-aspect ratio tetrad mesogenic diol 4-{[4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-benzoic acid 4-{[4-(6-hydroxyhexyloxy)-phenylimino]-methyl}-phenyl ester as a chain extender. The effect of partial replacement of the mesogenic diol by PTMG, the effect of the chain length of the PTMG and the effect of the diisocyanates on the liquid crystalline properties are reported.

EXPERIMENTAL SECTION

Materials

Poly(tetramethylene oxide) glycol (PTMG) of molecular weights 650, 1000, and 2000 were purchased from Aldrich, USA. The polyol was dried and degassed at 90–100°C under vacuum for 6–7 h before use. 4,4′-methylene bis(cyclohexyl isocyanate) 90% isomers (H_{12}MDI), 4,4′-methylene bis (phenyl isocyanate) (MDI) (Aldrich), and dibutyltin dilaurate (DBTDL) (Merck) were used as received. The solvent N,N′-dimethylformamide (DMF) was purified by distillation under reduced pressure over calcium hydride before use.

Characterization

The FTIR spectra of the polymers were recorded using NICOLET Impact 400 spectrophotometer by casting film of KBr disks. A Seiko model SSC 5200 H attached to a Differential Scanning Calorimetry (DSC) module was used to determine the second heating thermograms. The equipment was calibrated using indium and tin as standards. The measurements were carried out at a heating rate of 10°C/min in nitrogen atmosphere. Molecular weights were calculated relative to polystyrene standards in tetrahydrofuran using an Ultrastyragel column (Waters). Visual observation of liquid crystal transitions were studied by using an OLYMPUS BX 50 polarizing microscope equipped with a LINKAM THMS 600 heating stage. Stress-strain measurements of polyurethane films were measured by INSTRON Universal Testing Machine at a constant speed of 50 mm/min. The specimens were conditioned before testing and the measurements were performed at room temperature with dumb bell–shaped specimens with dimensions of $3.5 \times 2.5 \times 0.16\,mm^3$.

Monomer Synthesis

The detailed synthetic procedure and properties of the mesogenic diol 4-{[4-(6-hydroxyalkoxy)-phenylimino]-methyl}-benzoicacid4-{[4-(6-hydroxyalkoxy)-phenylimino]-methyl}-phenyl ester is reported elsewhere [18].

Polymer Synthesis

The polyurethanes were synthesized by the polyaddition reaction of the diisocyanates, namely H_{12}MDI and MDI with the dihydroxy compounds (polyol and mesogenic diol) at a molar ratio of 1:1. The molar ratio of the dihydroxy compounds, namely the polyol and the mesogenic diol were varied as per the compositions described in Table 1. The polymerization was carried out by a two step process. In the first step, an NCO terminated prepolymer was prepared by the polyaddition reaction of the polyol and an excess amount of diisocyanate, which was then chain extended in the next step with the mesogenic diol in the presence of DBTDL catalyst to yield the polyurethanes.

A typical procedure for the synthesis of PU is as follows: In a 50 ml three-necked flask, equipped with a mechanical stirrer and nitrogen inlet, PTMG

TABLE 1 Codes and the compositions (mol) of the polyurethanes

		PTMG molecular weight			
*Polymer code**	*Mesogenic diol*	650	1000	2000	*Diisocyanate (RDI)*
PG-6-R-50	0.50	0.50	—	—	1.00
PG-1-R-50	0.50	—	0.50	—	1.00
PG-2-R-50	0.50	—	—	0.50	1.00
PG-6-R-40	0.40	0.60	—	—	1.00
PG-1-R-40	0.40	—	0.60	—	1.00
PG-2-R-40	0.40	—	—	0.60	1.00
PG-6-R-30	0.30	0.70	—	—	1.00
PG-1-R-30	0.30	—	0.70	—	1.00
PG-2-R-30	0.30	—	—	0.70	1.00
PG-6-R-20	0.20	0.80	—	—	1.00
PG-1-R-20	0.20	—	0.80	—	1.00
PG-2-R-20	0.20	—	—	0.80	1.00

*PG, PTMG; 6, M_n 650; 1, M_n 1000; 2, M_n 2000 of PTMG; R = H_{12} for H_{12}MDI; and M for MDI. The last two digits refer to the mesogenic content.

650 (0.5 mmol) was reacted with H_{12}MDI (1 mmol) at 80°C in inert atmosphere to prepare a NCO-terminated prepolymer. When the theoretical NCO content was reached (confirmed by dibutylamine titration), the prepolymer was chain extended with the mesogenic diol (0.5 mmol) in dry DMF using 0.1 wt% DBTDL as catalyst at 70°C for 12 h. Films were obtained by casting the hot polymer solution on prewarmed silicon molds (60–80°C) and vaporizing the solvent at this temperature under vacuum. The yields obtained for the polymers were in the range of 70–80%.

RESULTS AND DISCUSSION

The general reaction route for the synthesis of all the polyurethanes in this study is shown in Figure 1. The thermotropic LCPUs were synthesized by the polyaddition of the diisocyanates with PTMG of various molecular weights and chain extended with the mesogenic diol in the presence of DBTDL catalyst by a two-step method. In order to study the effect of the soft segment on the properties of the LCPUs, three different molecular weights of the soft segment PTMG were chosen (M_n = 650, 1000, 2000). The mesogen content and the diisocyanates were also varied in order to study the influence of the hard segment on the thermal and physical properties. In contrast to conventional chain extenders such as 1,2-ethylene glycol or 1,4-butane diol, the synthesized polyurethanes could exhibit mesophase transition by using a high-aspect ratio mesogenic diol as a chain extender.

PROPERTIES OF POLYETHERURETHANES

The structure of all polyetherurethanes synthesized was confirmed by FTIR spectroscopy. Representative IR spectrum (Figure 2) shows the characteristic absorption of the carbonyl band of the urethane groups at 1700 cm^{-1}, -NH stretching of urethane groups at 3320 cm^{-1}, $-CH_2-$ stretching at 2929 cm^{-1} and 2855 cm^{-1}, and azomethine group (-CH=N-) at 1626 cm^{-1}.

In contrast to the unsegmented polyurethanes [18], for which molecular weight data could not be obtained due to the poor solubility of the polymers in common organic solvents, the molecular weights of the segmented PUs were determined by gel permeation chromatography, and the results are presented in Tables 2 and 3. Thus it is evident that the incorporation of soft segment improves the solubility characteristics of the polymers.

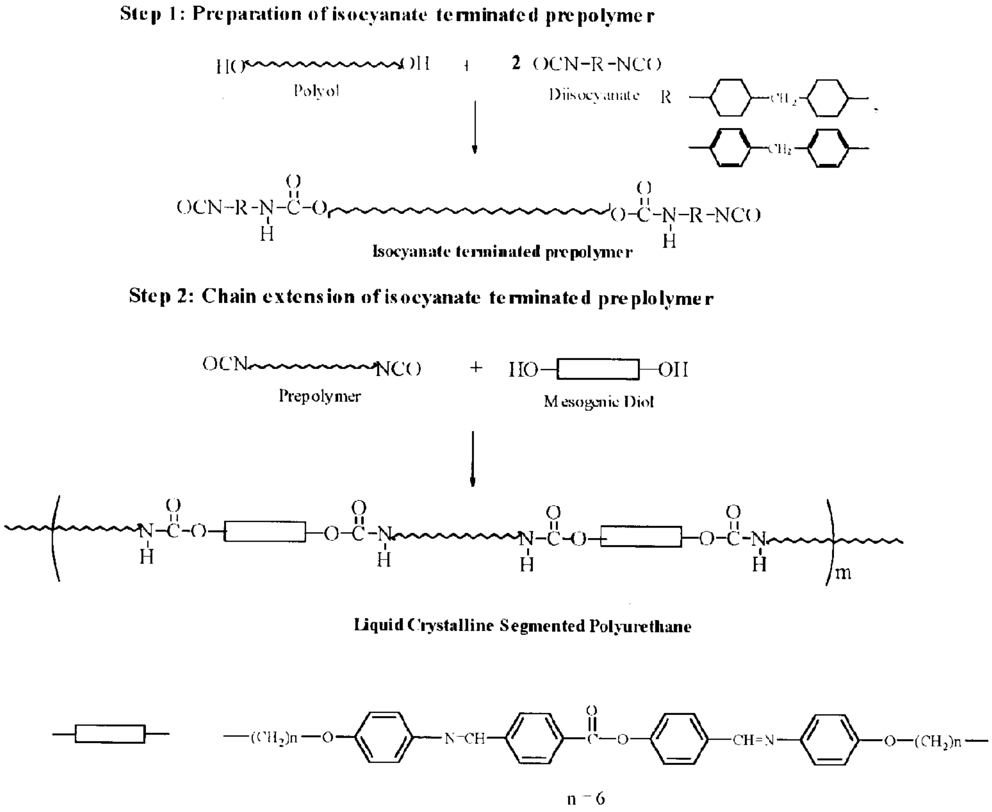

FIGURE 1 Synthesis of segmented liquid crystalline polyurethanes.

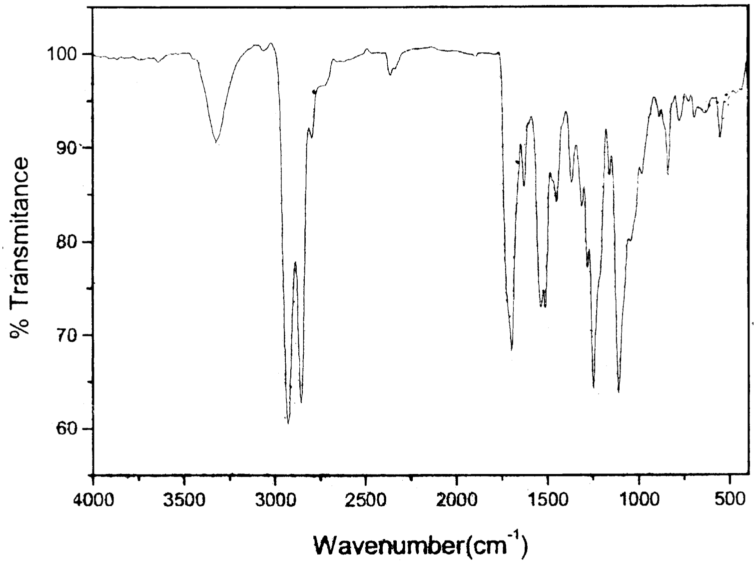

FIGURE 2 FTIR spectrum of PG-6-H_{12}-50.

Liquid Crystalline and Thermal Properties

The mesophase transitions of the PUs were determined by DSC measurements and the second heating scans are reported. The mesophase textures were observed under the optical polarizing microscope. The results are summarized in Tables 4 and 5. The DSC heating traces of the PUs displayed

TABLE 2 Molecular weights and molecular weight distribution of H_{12}MDI series polyurethanes

Polymer code	M_n	M_w	M_w/M_n
PG-6-H_{12}-50	12300	27300	2.21
PG-1-H_{12}-50	36200	62400	1.72
PG-2-H_{12}-50	48700	87660	1.80
PG-6-H_{12}-40	14400	34200	2.37
PG-1-H_{12}-40	40300	67200	1.66
PG-2-H_{12}-40	60400	106900	1.77
PG-6-H_{12}-30	15900	36700	2.30
PG-1-H_{12}-30	47100	108200	2.29
PG-2-H_{12}-30	63400	117200	1.85
PG-6-H_{12}-20	17300	36400	2.10
PG-1-H_{12}-20	52600	108900	2.07
PG-2-H_{12}-20	78800	158200	2.00

TABLE 3 Molecular weights and molecular weight distribution of MDI series polyurethanes

Polymer code	M_n	M_w	M_w/M_n
PG-6-M-50	13700	23800	1.73
PG-1-M-50	20900	37700	1.89
PG-2-M-50	27000	53200	1.97
PG-6-M-40	18100	31700	1.80
PG-1-M-40	24100	46600	1.74
PG-2-M-40	27100	50100	1.74
PG-6-M-30	24900	46000	1.81
PG-1-M-30	25600	48300	1.84
PG-2-M-30	38500	66400	1.85
PG-6-M-20	29700	54300	1.82
PG-1-M-20	33800	61400	1.92
PG-2-M-20	39800	69500	1.72

glass transition T_g, melting temperature T_m, isotropization temperature T_i, and hard segment melting T_{hm}. The DSC heating cycle showed phase transition temperatures for the polyurethanes, while in the cooling cycle no transitions were observed, which could be due to the partial decomposition of the polymers. However, the polarizing optical microscope showed the formation of a mesophase on cooling.

Representative DSC thermograms for the H_{12}MDI series are shown in Figure 3. The DSC trace of PG-6-H_{12}-50 exhibited a transition at 34.6°C, corresponding to the glass transition temperature of the PTMG soft segment, and another transition at 115.8°C, corresponding to the glass transition of the hard segments which is derived from isocyanate and mesogenic units. The thermogram shows three endotherms positioned at 157.0, 169.0, and 186.1°C. The endotherms at 157 and 169°C were the result of crystal-mesophase transition temperature and isotropization temperature respectively as confirmed by polarizing optical microscope. The higher temperature melting endotherm at 186.1°C is a result of melting of microcrystalline hard segments which is commonly observed in materials having longer aromatic urethane segements.

In the MDI series, some of the polymers displayed very weak T_m and T_i transitions, and in most of the polymers these transitions could not be detected with DSC and were determined by optical polarizing microscope. In all the thermograms, the most prominent transition is that of the hard segment melting T_{hm}. Figure 4 shows representative DSC thermograms of PG-6-M-40, PG-1-M-40 and PG-2-M-40 as representatives for the MDI series. As can be seen, the T_m and T_i behavior of the PUs are obscure except in the case of PG-1-M-40, where in the T_i transition is seen at 207°C.

TABLE 4 Thermal properties of H_{12}MDI series polyetherurethanes

Polymer code	Hard segment content (%)	DSC (°C)							Microscope (°C)	
		T_{sg}	T_{sm}	T_{hg}	T_c	T_m	T_i	T_{hm}	T_m	T_i
PG-6-H_{12}-50	64	34.6	—	115.8	—	157.0	169.0	186.1	155	175
PG-1-H_{12}-50	54	−21.2	—	89.4	—	143.7	166.9	—	145	169
PG-2-H_{12}-50	36	−40.0	19.0	78.7	—	138.0	158.0	—	132	162
PG-6-H_{12}-40	57	22.2	—	100.2	—	142.3	165.5	190.5	149	168
PG-1-H_{12}-40	46	−23.7	—	73.7	—	137.4	163.7	185.0	135	165
PG-2-H_{12}-40	30	−47.0	18.4	65.4	—	135.8	156.0	—	129	158
PG-6-H_{12}-30	50	15.7	—	88.0	—	138.6	155.7	—	142	160
PG-1-H_{12}-30	39	−26.9	—	61.2	—	—	153.6	—	130	157
PG-2-H_{12}-30	24	−49.0	18.3	59.2	—	—	—	—	—	—
PG-6-H_{12}-20	43	−2.5	—	77.7	—	—	—	—	135	156
PG-1-H_{12}-20	33	−28.3	—	—	—	—	—	—	123	153
PG-2-H_{12}-20	20	−51.8	17.8	—	—	—	—	—	—	—

T_{sg}, soft segment glass transition; T_{sm}, soft segment melting; T_{hg}, hard segment glass transition; T_c, crystal-crystal transition; T_m, melting temperature; T_i, isotropisation temperature; T_{hm}, hard segment melting.

TABLE 5 Thermal properties of MDI series polyetherurethanes

Polymer code	*Hard segment content (%)*	*DSC (°C)*							*Microscope (°C)*	
		T_{sg}	T_{sm}	T_{hg}	T_c	T_m	T_i	T_{hm}	T_m	T_i
PG-6-M-50	64	—	—	86.0	—	—	—	192.1	164	223
PG-1-M-50	53	−9.0	—	78.5	—	155.6	—	190.7	155	217
PG-2-M-50	36	−30.9	16.1	71.0	—	—	—	193.5	150	210
PG-6-M-40	56	23.7	—	80.0	—	—	—	190.8	148	217
PG-1-M-40	46	−19.3	—	76.9	—	—	207	192.1	143	205
PG-2-M-40	30	−32.7	20.0	69.0	—	—	—	194.2	140	198
PG-6-M-30	49	−15.6	—	72.4	—	141.1	—	195.0	144	202
PG-1-M-30	39	−23.3	—	70.8	—	—	—	195.7	137	184
PG-2-M-30	24	−34.6	16.5	64.3	—	—	—	193.6	—	—
PG-6-M-20	42	−23.3	—	67.0	—	—	—	186.9	137	180
PG-1-M-20	32	−28.5	—	—	—	—	—	191.0	128	178
PG-2-M-20	19	−41.2	16.0	—	—	—	—	194.5	—	—

T_{sg}, soft segment glass transition; T_{sm}, soft segment melting; T_{hg}, hard segment glass transition; T_c, crystal-crystal transition; T_m, melting temperature; T_i, isotropisation temperature; T_{hm}, hard segment melting.

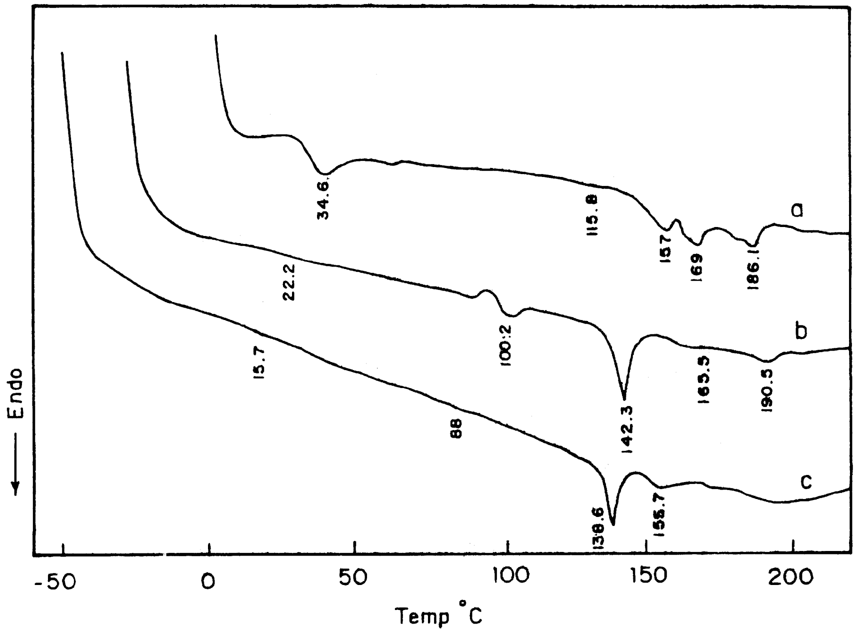

FIGURE 3 DSC thermograms of (a) PG-6-H_{12}-50, (b) PG-6-H_{12}-40, and (c) PG-6-H_{12}-30.

Effect of Mesogen Content

The effect of partial replacement of the mesogenic diol by PTMG ($M_n = 650$, 1000, 2000) on the liquid crystalline properties was studied. Comparing the PUs with the same soft segment and different mesogen content, it can be observed that the transition temperatures increase with increasing mesogen content. As the mesogen content is increased, the average length of hard segment is increased, and this seems to cause the increase in transition temperatures [19]. For instance, for PUs prepared from PTMG 650 and H_{12}MDI, as the mesogen content is raised from 30–50 mol% the T_m increases from 138–157.0°C and the T_i increases from 155.7–169.0°C, as shown in Figure 3. Although there is a trend, the variation in the transition temperatures is not much. This could possibly be attributed to the correspondingly less variation in the hard segment content of the polymers.

Visual observation of mesophase transitions in H_{12}MDI series polyurethanes under the optical microscope revealed that 20 mol% of mesogen content was sufficient to impart LC for PTMG 650 and PTMG 1000 polymers, whereas a minimum of 40 mol% was required for PTMG 2000. In the case of MDI series, observations similar to that of H_{12}MDI series were

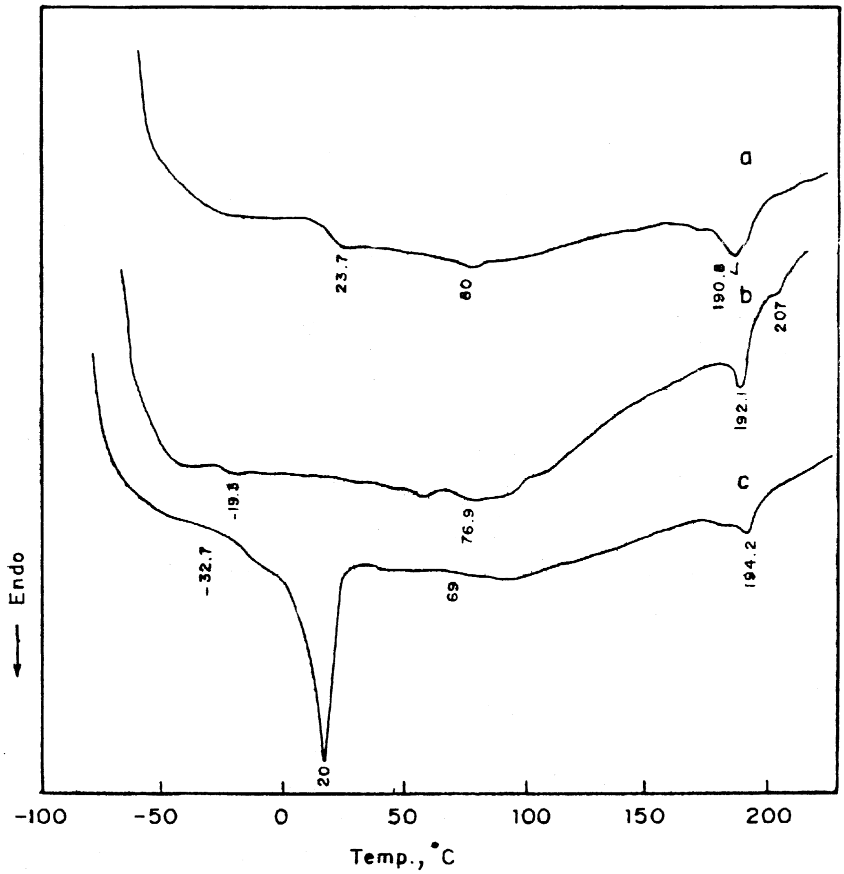

FIGURE 4 DSC thermograms of (a) PG-6-M-40, (b) PG-1-M-40, and (c) PG-2-M-40.

seen, whereas in the case of a HMDI series reported in another article [17], a minimum of 20 mol% mesogen content was sufficient to impart LC in PTMG 650, whereas a minimum of 30 mol% was required for PTMG 1000 and 40 mol% for PTMG 2000. When the mesogen content was 40 mol% and above, liquid crystalline behavior was exhibited by all the polymers. Therefore, a higher content of the mesogen component was required to impart LC properties on increasing the PTMG soft segement spacer length.

Apart from the transition temperatures, the mesophase texture of the polymers also varied with mesogen content. Lower mesogen contents displayed grained texture, and threadlike texture was observed as the mesogen content was raised. Representative optical photomicrograph of the polymers is shown in Figure 5. In the H_{12}MDI series, the PUs prepared from PTMG

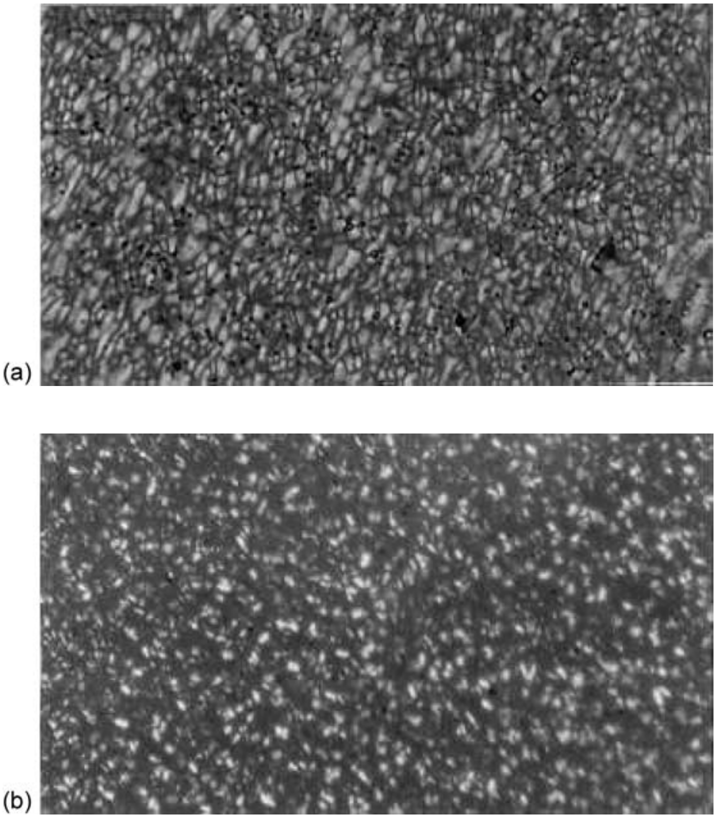

FIGURE 5 Optical photomicrograph of (a) threadlike texture PG-6-H_{12}-50 and (b) grained texture of PG-1-M-40.

650 and PTMG 1000 containing 20, 30, and 40 mol% showed grained texture, while 50 mol% showed threadlike texture, and the PUs prepared from PTMG 2000 containing 40 and 50 mol% showed threadlike texture. Such observations of texture variation with mesogen content were also made by Szczepaniak et al. [7] and also in the polyurethanes prepared with HMDI reported in the previous article [17]. In the MDI series, all the compositions exhibited only grained texture.

Effect of the Soft Segment

The data given in Tables 4 and 5 show that the phase transition temperatures of the segmented polyurethanes shift to lower temperatures compared to the unsegmented polyurethanes [18] as a result of the flexible soft segment. An increase in the molecular weight of the soft segment from 650 to 2000 results in lowering of T_g, T_m, and T_i. However, the changes in mesophase temperature ranges were not so evident. Figure 6 depicts the DSC thermograms of 40 mol% mesogenic content PUs made from PTMG, 650, 1000, and 2000 and $H_{12}MDI$.

Effect of Diisocyanate

A comparison of thermal characteristics shows that the HMDI [17] and MDI series materials exhibit a considerable degree of hard-segment crystallinity, whereas the $H_{12}MDI$ series materials are amorphous or slightly

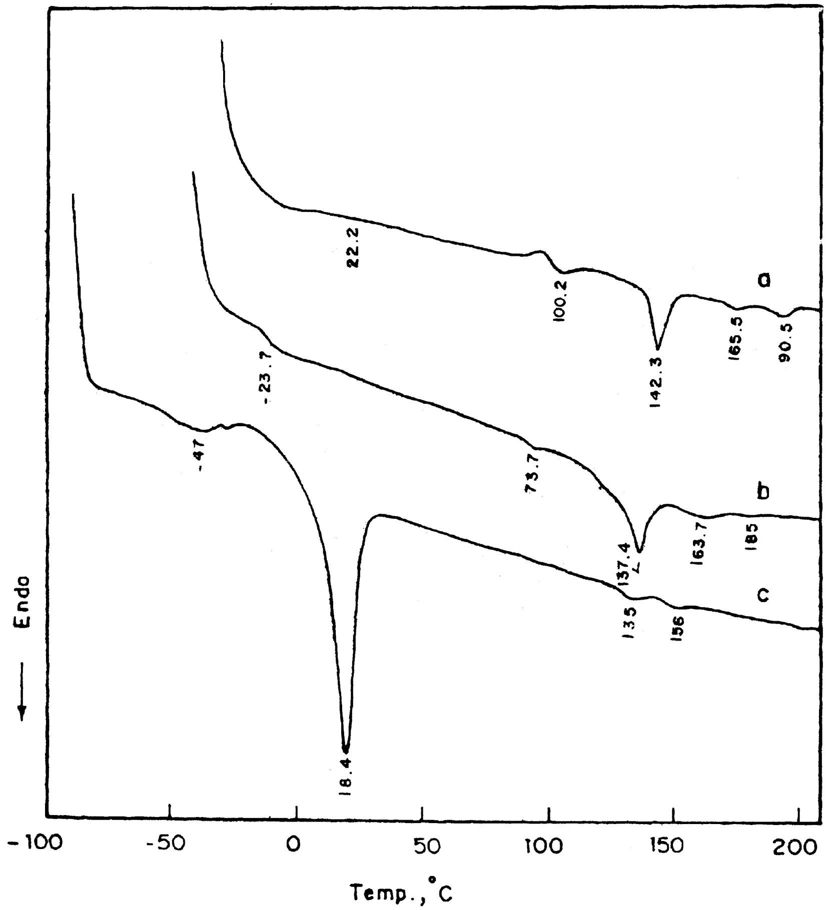

FIGURE 6 DSC thermograms of (a) PG-6-H_{12}-40, (b) PG-1-H_{12}-40, and (c) PG-2-H_{12}-40.

crystalline at best. The limited crystallizability of H_{12}MDI series materials is due to the *cis-cis*, *trans-trans*, and *cis-trans* configurational isomers of the hard segment. In preparation of a hard segment from the typical mixture of the three isomers, a random hard-segment structure forms which substantially inhibits crystallization [20]. Thus, the MDI/mesogenic diol and the HMDI/mesogenic diol hard segments of the MDI and HMDI series PUs, which have a regular repeat structure capable of a high degree of crystallinity, exhibit sharp melting peaks (very sharp in the case of MDI series), whereas the H_{12}MDI/mesogenic diol hard segments of the H_{12}MDI series show only slight evidence of hard-segment crystallinity.

The LC phase transition is in the order of $PU_{MDI} > PU_{HMDI} > PU_{H12MDI}$. This could be due to the MDI and HMDI hard segments exhibiting a more symmetric and rigid structure than H_{12}MDI. Similar observations were made by Jia et al. [14]. The thermal data show that the PUs based on MDI have wider LC transition region than the polymer based on HMDI [17] and H_{12}MDI. This could be due to the better compatibility between the hard and soft segments in the HMDI and H_{12}MDI-based PUs than the MDI-based Pus, which results in a decrease of the phase transition temperatures of LC phases. Also, the mesophase interval becomes narrower, as seen in the case of HMDI and H_{12}MDI.

Mesophase texture variation is observed when the diisocyanate is changed from aliphatic to aromatic. In the PUs containing the aromatic diisocyanate MDI, grained texture is observed in all the compositions and in the PUs containing the aliphatic diisocyanates HMDI [17] and H_{12}MDI. The lower mesogen contents exhibit grained texture while higher mesogen contents exhibit threaded texture.

Stress-Strain Properties of the Polyetherurethanes

The stress-strain properties of the PUs prepared with PTMG 2000 and H_{12}MDI are listed in Table 6. It is observed from the table that as the mesogen content increased from 20–40 mol% (accompanied by an increase in hard segment), the tensile strength increased and the elongation at break decreased. Polymers prepared from PTMG ($M_n = 650$ and 1000) and H_{12}MDI and

TABLE 6 Stress-strain measurements of polyetherurethanes

Polymer code	*Tensile strength (MPa)*	*Elongation (%)*
PG-2-H_{12}-20	3.29	1138
PG-2-H_{12}-30	7.35	996
PG-2-H_{12}-40	12.19	125

the MDI series polymers formed brittle films and could not be subjected to stress-strain analysis. The poor stress-strain properties could be as a result of phase separation into polyol rich and the hard segment rich phase with the consequence that the covalent coupling between soft and hard segments remains incomplete and thereby poor mechanical properties are observed.

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