Macromol. Symp. **2003**, *199*, 277-292

Liquid Crystalline Properties of Unsegmented and Segmented Polyurethanes Synthesised from High Aspect Ratio Mesogenic Diols

Kalathur Sabdham Vangepuram Srinivasan, Tallury Padmavathy*

Polymer Division, Central Leather Research Institute, Adyar, Chennai 600 020, India
E-mail: srinivasan1@hotmail.com

Summary: A series of novel tetrad high aspect ratio mesogenic diol monomers 4-{[4-(n-hydroxyalkoxy)-phenylimino]-methyl}-benzoic acid 4-{[4-(n-hydroxyalkoxy)-phenylimino]-methyl}-phenyl ester were prepared with varying alkoxy spacer length (n=2,4,6,8,10) by reacting 4-formylbenzoic acid 4-formylphenyl ester and 4-(n-hydroxyalkoxy) anilines. Two series of thermotropic main chain liquid crystalline unsegmented polyurethanes (PUs) were obtained by the polyaddition of the mesogenic diols with hexamethylene diisocyanate (HMDI) and methylene bis(cyclohexylisocyanate) ($H_{12}MDI$) in dimethylformamide respectively. The effect of the incorporation of a third component namely polyol on the liquid crystalline properties of the polyurethanes was also studied. Linear segmented PUs were synthesised by a two-step block copolymerisation method. The PUs synthesised were based on six spacer mesogenic diol chain extender, soft segments poly(tetramethylene oxide)glycol (PTMG) (M_n= 650,1000,2000) and polycaprolactone diol (PCL) (M_n=530,1250,2000) of varying molecular weights and different diisocyanates including HMDI, $H_{12}MDI$ and methylene bis(phenylene isocyanate) (MDI). Structural elucidation was carried out by elemental analysis, fourier transform infra red (FT-IR), nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectroscopy. Inherent viscosity of the unsegmented polymers measured in methanesulphonic acid at 26°C was in the range of 0.13 - 0.65 dL/g while the molecular weights and molecular weight distribution of the segmented polyruethanes was determined using gel permeation chromatography (GPC). Mesomorphic properties were studied by differential scanning calorimetry (DSC) and hot stage polarising optical microscopy and the thermal stability was determined by thermogravimetric(TG)analysis. The monomeric diols and the polyurethanes exhibited nematic texture and good mesophase stability. It was observed that the partial replacement of the mesogenic diol by the polyol of varying molecular weights influenced the phase transitions and the occurrence of mesophase textures. The phase transition temperatures of the investigated polyurethanes showed dependence on the chain length of the soft segment and on the content of the mesogen moiety. A higher content of mesogenic moiety was needed to obtain

DOI: 10.1002/masy.200350924

liquid crystalline property when the soft segment length was increased as observed in the case of PTMG. Grained and threaded textures were observed depending on the molecular weight of the soft segment, the mesogen content and the diisocyanate. The stress-strain analyses showed that the polymers based on high molecular weight PTMG soft segment have elastomeric property while the PCL based PUs displayed no elastomeric property.

Keywords: chain extender, high aspect ratio mesogenic unit, liquid crystalline polymers, polyurethane

Introduction

Polyurethanes constitute one of the most versatile classes of polymeric materials known today. Thermoplastic liquid crystalline polyurethanes (TLCPUs) are being investigated with much interest owing to their application potential.[1-3] 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 (i) inserting flexible spacers into the mesogenic units,[4] (ii) introducing substituted mesogenic segments[5] or (iii) using secondary amines reacted with dichloroformates.[6]Among these methods, the introduction of long flexible spacers such as PTMG-1000 and 2000 into the polymer main chains was effective in decreasing the phase transition temperature, increasing solubility, reducing hydrogen bonding[7] and showing elastic properties. However, the use of long flexible spacers as modifying agents 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 the elastic nature of the polyurethane. Also it is important to investigate as to what extent a modifying agent would decrease the phase transition temperatures without destroying the liquid crystalline properties.

Experimental Part

Materials

4-Hydrxoybenzaldehyde, 4-formylbenzoic acid (Spectrochem, India), 4-hydroxyacetanilide, 6-chloro-1-hexanol (Fluka, Switzerland), PTMG (M_n=650, 1000 and 2000) and PCL (M_n= 530, 1250, 2000) was purchased from Aldrich, USA. The polyol was dried and degassed at

90-100°C under vacuum for 6-7 hours before use. 4-formyl benzoic acid, 4-hydroxy benzaldehyde, HMDI, H_{12}MDI and MDI (Aldrich), dibutyl tin 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 Techniques

Elemental analysis was done in a Heraues CHN RAPID, CHN analyzer. The FTIR spectra of the polymers were recorded using NICOLET Impact 400 by casting film in KBr disks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL 300P, 300 MHz NMR spectrometer. Visual observation of liquid crystal transitions were studied by using OLYMPUS BX 50 polarizing microscope equipped with a LINKAM THMS 600 heating stage. Thermogravimetry was performed on a Seiko model SSC 5200H system attached to a TG/DTA 220 module at a heating rate of 10°C/min in nitrogen atmosphere. A Seiko model SSC 5200H attached to a 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. The molecular weight determination was carried out using GPC with polystyrene standard in tetrahydrofuran solvent using an ultrastyragel column (Waters). 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 3.5x2.5x0.16mm.

Synthesis of Mesogenic Diols 4-{[4-(n-hydroxy alkoxy)-phenylimino]-methyl}-benzoic acid 4-{[4-(n-hydroxy alkoxy)-phenylimino]-methyl}-phenyl ester (3a-e)

0.01 mol (**1**) and 0.02 mol of the corresponding 4-(n-hydroxyalkoxy) aniline (n=2,4,6,8,10) (**2**) was refluxed in 20 ml ethanol for 1 hour with a catalytic amount of acetic acid. The precipitated product (**3**) was filtered and dried. All the compounds were recrystallised from DMF/methanol solvent mixture. Thus, 2.54g (0.01 mol) of 4-formyl benzoic acid-4-formyl phenyl ester and 4.18g (0.02 mol) of 4-(6-hydroxyhexyloxy) aniline were refluxed in 20 ml of ethanol for 1hour. The precipitated product **3c** was filtered, dried and recrystallised from DMF/methanol. Yield = 80%.

^{1}H NMR($CDCl_3$+Trifluoroacetic acid): δ 8.98 (s, 1H, C$\underline{H}$=N), 8.84 (s, 1H, C$\underline{H}$=N), 8.47 (d, 2H, Ar-$\underline{H}$), 8.28 (d, 2H, Ar-$\underline{H}$), 8.23 (d, 2H, Ar-$\underline{H}$), 7.61 (d, 2H, Ar-$\underline{H}$), 7.64-7.69 (m, 4H, Ar-$\underline{H}$), 7.1-7.27 (m, 4H, Ar-$\underline{H}$), 4.43 (t, 2H,-C$\underline{H}_2$), 4.08 (m, 4H, -C$\underline{H}_2$OH), 3.85 (t, 2H, -OC$\underline{H}_2$), 1.40-1.60 (m, 8H, -C$\underline{H}_2$), 1.52 (p, 4H, -C$\underline{H}_2$CH_2OH), 1.71 (p, 4H, -ArOCH_2C$\underline{H}_2$); FT-IR (KBr): 3306 (OH), 1736 (C=O of ester), 1623 (C=N), 1248 cm^{-1}(C-O).

Synthesis of Unsegmented Polyurethanes from HMDI (4a-e) and H_{12}MDI (5a-e)

Unsegmented polyurethanes (**4a-e**) and (**5a-e**) were synthesized by adding 0.0052 mol of the diisocyanate to a stirred solution of 0.005 mol of **3a-e** in 50 ml DMF at 60°C in nitrogen atmosphere. The reaction mixture was then stirred at 90°C. The progress of the reaction was followed by the disappearance of the NCO peak at 2260 cm^{-1} by FT-IR. Pouring the reaction mixture into methanol, the polyurethane was precipitated, filtered, and dried in vacuum. Phase separation was observed in the reactions with HMDI. The polyurethanes obtained were pale green solids.

Synthesis of Segmented Liquid Crystalline Polyurethanes

The polyurethanes were synthesised by the polyaddition reaction of HMDI with the dihydroxy compound at a molar ratio of 1:1. The mesogenic diol / PTMG ratio was changed according to the compositions as described in Table 1. A typical procedure for the synthesis of PU is as follows: PTMG 1000 (0.0005 M) was reacted with HMDI (0.001 M) at 80°C in inert atmosphere to prepare the prepolymer with end capped NCO group. When the theoretical NCO content was reached (confirmed by dibutylamine titration), the prepolymer was chain extended

Table 1. Composition of segmented polyurethanes.

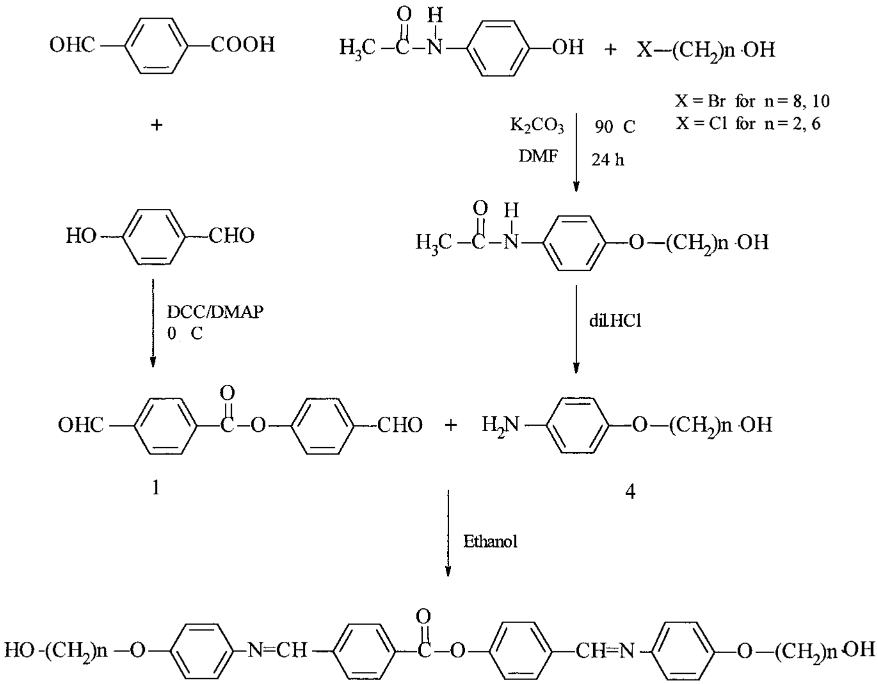
Mesogenic Diol	Polyol	Diisocyanate
0.5	0.5	1
0.4	0.6	1
0.3	0.7	1
02	0.8	1

with the mesogenic diol (0.0005 M) in DMF with a catalytic amount of DBTDL at 70 °C for 12 h. The polymer solution was then poured into a mold and films were cast.

Results and Discussion

Mesogenic Diols

The synthesis of the mesogenic diols is outlined in Scheme 1. The high aspect ratio tetrad mesogenic diols (**3a-e**) containing four phenyl rings para linked by ester and azomethine linkages and terminal spacers were synthesized by condensing 4-formylbenzoic acid-4-formyl phenyl ester with 4-(n-hydroxyalkoxy) anilines of varying spacer length (n=2,4,6,8,10).



3a-e

	3a	3b	3c	3d	3e
n	2	4	6	8	10

Scheme 1. Synthesis of mesogenic diols.

The yields and elemental analysis results are summarized in Table 2. The ester and azomethine linkages contribute to the linearity and the overall polarisability while the terminal spacers induce flexibility to the molecule. The diols were insoluble in all common solvents at room temperature but were soluble in aprotic solvents such as dimethylsulphoxide and DMF at elevated temperatures. FT-IR and ^1H NMR spectroscopy confirmed the chemical structure of the mesogenic diols.

DSC of the diols shows two endotherms corresponding to melting and isotropization transition, respectively. The transition temperatures of the mesogenic diols are summarized in Table 2. Though all the diols exhibited liquid crystalline phases in the first heating, no transition could be detected in the DSC cooling cycle, which could be due to the partial decomposition of the diols near their clearing temperatures. The transition temperatures decrease as the number of methylene spacers increase. All the diols exhibit nematic mesophase.

Table 2. Properties of mesogenic diols.

Diol	Yield (%)	Elemental Analysis (%)						LC phase$^{\#}$ °C	Transition Temperature§		
		C	H	N	C	H	N		T_m °C	T_i °C	ΔT °C
		Calculated			Found						
3a	77	70.97	5.38	5.34	70.75	5.31	5.22	228 - 310	228.4	312.9	84.5
3b	82	72.39	6.25	4.86	72.18	6.17	4.91	222 - 300	225.0	303.0	78.0
3c	80	73.56	6.97	4.40	73.52	6.84	4.33	202 - 269	196.7	270.3	73.6
3d	74	74.54	7.56	4.04	74.31	7.38	4.12	190 - 235	186.1	243.7	57.6
3e	76	80.12	2.29	3.97	79.86	2.23	3.94	180 - 230	180.2	226.9	46.7

$\Delta T = T_i - T_m$

[#] As observed under the polarising microscope

[§] From DSC, first heating, 10 °C /min heating rate

Figure 1a shows the first heating DSC thermogram of the diol **3c**. A sharp endotherm at 196.7°C and a weak endotherm at 270.3°C was observed corresponding to the melting and the isotropization transitions respectively. At these temperatures, the mesophase was observed to be nematic schlieren texture. Figure 2 represents a typical polarized microphotograph of the diol **3c** on heating at 212 °C.

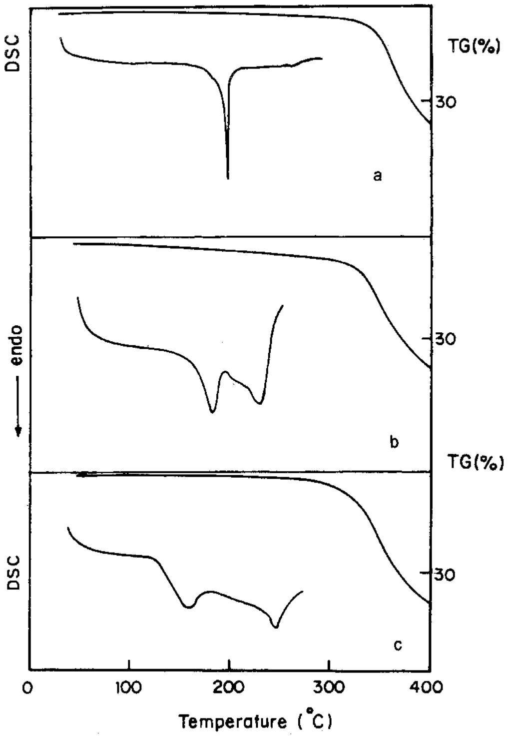


Fig. 1. Overlapped TG/DSC thermograms of mesogenic diol a) **3c**, polyurethanes b) **4c** and c) **5c.**

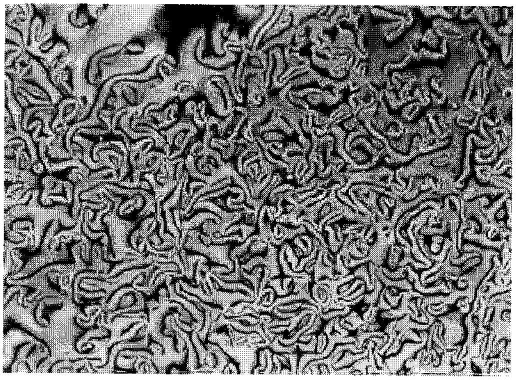


Fig. 2. Optical photomicrograph of mesogenic diol **3c** at 212° C.

Unsegmented Liquid Crystalline Polyurethanes

Polyurethanes (**4a-e, 5a-e**) were synthesized by the polyaddition of the tetrad mesogenic diol (**3a-e**) with HMDI and $H_{12}MDI$ respectively. Progress of the reaction was monitored by FT-IR. Phase separation was noticed in the polyurethanes prepared from HMDI. The polyurethanes were insoluble in common solvents at room temperature. Due to their insoluble nature, structural characterization of the polyurethane was restricted to FT-IR spectroscopy alone. The inherent viscosity of the polymers was measured in methanesulphonic acid at 26°C as a function of time and is shown in Table 2. Decomposition of the polyurethanes occurred when they were dissolved in methanesulphonic acid. It is documented in the literature that schiff-bases undergo extensive degradation in the presence of protonic acids due to the hydrolysis of -CH=N- linkages.[8,9] The relationship between inherent viscosity (η_{inh}) and time is shown in Figure 3. As the time is increased, η_{inh} of **5c** decreased from 0.652 dL/g to 0.014 dL/g in 60h. As shown in Table 2, **4a-e** polyurethanes have low inherent viscosity in the range 0.18 - 0.2 dL/g while **5a-e** polyurethanes have higher viscosity in the range 0.42 – 0.65 dL/g. than the HMDI based polyurethanes, which precipitated during the course of the reaction.

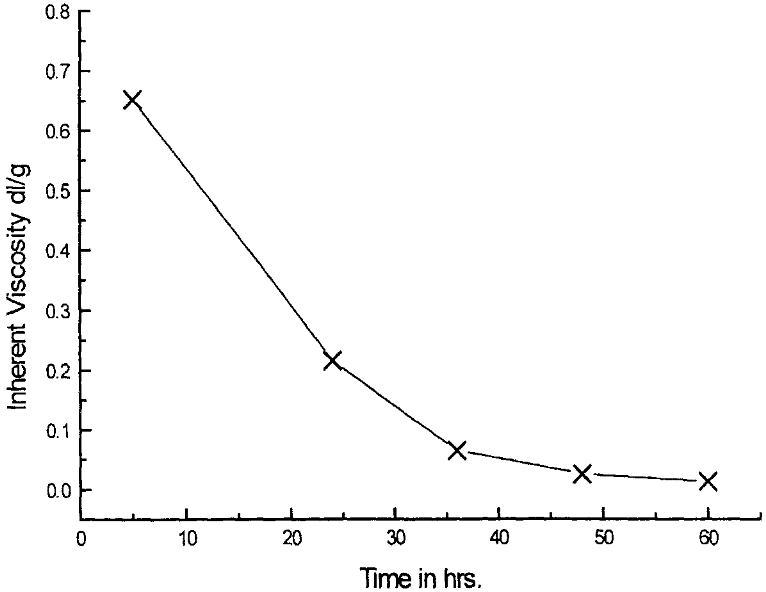


Fig. 3. Relationship between inherent viscosity and time of polyurethane **5c**.

The difference in the viscosity values could be attributed to the structure of the polyurethanes, which probably influences their solubility characteristics. The $H_{12}MDI$ used in this present study is a mixture of isomers (trans–trans, cis-cis, cis-trans). As a result of these isomers, the solubility of $H_{12}MDI$ based polyurethanes could have been enhanced and therefore these polymers have higher values of inherent viscosity.

Table 3. Properties of unsegmented Polyurethanes.

Polymer	Yield (%)	η_{inh}*(dL/g)	LC phase[#] °C	Transition Temperature[§]			5% Decomp Temp.
				T_m °C	T_i °C	ΔT °C	°C
4a (n=2)	78	0.184	232 - 270	231.2	274.2	43.0	310
4b(n=4)	79	0.163	230 - 251	224.0	245.5	21.5	308
4c(n=6)	75	0.139	175 - 258	185.4	231.6	46.2	312
4d(n=8)	72	0.168	185 - 231	186.2	223.5	37.3	323
4e(n=10)	70	0.202	175 - 228	180.2	226.9	46.7	320
5a(n=2)	77	0.426	226 - 263	220.1	252.7	32.6	316
5b(n=4)	76	0.473	214 - 255	212.3	249.0	36.7	314
5c(n=6)	80	0.652	191-269	162.2	246.2	84.0	319
5d(n=8)	73	0.546	175-250	155.3	245.5	90.2	322
5e(n=10)	71	0.482	145- 228	137	220.3	83.3	312

$\Delta T = T_i - T_m$

*Measured at a concentration of 0.5 dL/g in methanesulphonic acid at 26 °C.

[#] As observed under the polarising microscope

[§] From DSC, first heating, 10 °C /min heating rate

The thermal stability was determined by thermogravimetry and the thermotropic liquid crystalline property was evaluated by DSC and polarizing microscopy. The results are summarized in Table 3. DSC traces show two endothermic transitions corresponding to melting and isotropisation. In both the homologous series of the polyurethanes, the transition temperatures decrease as the length of the flexible spacers is increased. These polymers have good mesophase stability, which is attributed to the high length to breadth ratio of the mesogen.[10] On cooling, no transition was detected in both the polyurethane series, which could be due to the partial decomposition of the polymers. Figures 1b and 1c show the DSC heating thermograms of the polyurethanes **4c** and **5c** respectively.

As shown in Table 3, the phase transition temperatures of the polyurethanes measured by DSC were confirmed by observation with a polarised microscope. Both the series of polyurethanes based on HMDI and H_{12}MDI showed a nematic texture

Segmented Liquid Crystalline Polyurethanes

The thermotropic LCPUs were synthesised by the polyaddition of the diisocyanate with polyol of various molecular weights and chain extended with the mesogenic diol in the presence 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 namely PTMG (M_n 650, 1000, 2000) and PCL (M_n 530, 1200, 2000) were used. The mesogen content was also varied by 20-50 mol % in order to study the influence of the hard segment on the thermal and physical properties. The structure of the polyurethanes synthesised was characterized by FT-IR spectroscopy.

Table 4. Molecular weights and molecular weight distribution of polyurethanes.

Polymer code	M_n	M_w	M_w/M_n
PG-6-H-50	15000	25800	1.72
PG-1-H-50	20400	37800	1.61
PG-2-H-20	81000	14000	1.87
PG-1- H_{12}-40	40300	67200	1.66
PC-5-H-50	-	-	-
PC-1-H-50	-	-	-
PC-2-H-50	-	-	-
PC-5-H_{12}-50	10600	17700	1.67
PC-1-M-30	29000	54000	1.85

[PG=PTMG, PC=PCL,1=M_n 1000, 5 = M_n 530, 6 = M_n 650, 2 = M_n 2000, H=HMDI, H_{12}=H_{12}MDI, M = MDI, the numbers 20, 30, 40 and 50 stand for mesogen content in mol%].

The molecular weight of the polymers was determined by gel permeation chromatography. The number average molecular weight of the segmented polyurethanes is in the region of 10,000 – 80,000. Table 4 shows the molecular weight and molecular distribution of segmented polyurethanes. This is in contrast to unsegmented polyurethanes wherein the molecular weight data could not be obtained due to the insoluble nature of the polymers. Thus it is evident that the incorporation of soft segment improves the solubility characteristics of the polymers. Polyurethanes prepared from PCL M_n530 with HMDI and MDI were insoluble in tetrahydrofuran and the 50 mol % composition as in the case of PCL 1250 and PCL 2000 with HMDI were also insoluble.

The DSC heating cycle showed phase transition temperatures for the polyurethanes, but in the cooling cycle no transitions were observed which could be due to the partial decomposition of the polymers but the polarizing optical microscope showed the formation of a mesophase on cooling. Representative DSC thermograms of PG-1-H-50 and PG-6-H-40 are shown in Figures 4a and 4b.

PG-1-H-50 exhibited a transition at 14.7°C corresponding to the glass transition temperature of the PTMG soft segment and another transition at 104.5°C corresponding to the glass transition of the hard segments which is derived from isocyanate and mesogenic units. The thermogram shows four endotherms positioned at 133.6, 151.7, 169.3 and 190°C .The endotherm appearing at the lower temperature might be associated with a crystal-crystal transition since the polarizing microscope did not reveal any crystal-mesophase transition in this region. A similar observation was made by Lee *et al.*[11] The endotherms at 151.7 and 169.3°C were the result of crystal- mesophase transition temperature and isotropisation temperature respectively as confirmed by polarizing optical microscope.

The higher temperature melting endotherm at 190°C is a result of melting of microcrystalline hard segments, which is commonly observed in materials having longer aromatic urethane segments. The polymers prepared from HMDI containing 30, 40 and 50 mol% mesogen exhibited the crystal–crystal transition in the range 133-139 °C. 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 in DSC and were determined by optical polarizing microscope. In all the thermograms, the most prominent transition is that of the hard segment melting.

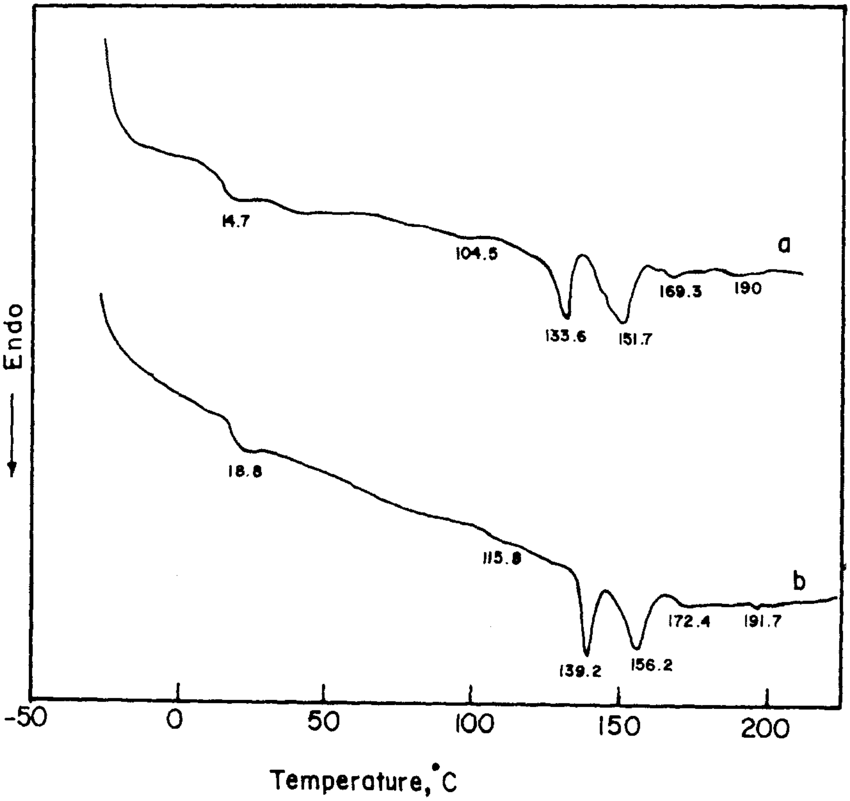


Fig. 4. DSC thermograms of a) PG-1-H-50 and b) PG-6-H-40.

Effect of Soft Segment

The phase transition temperatures of the segmented polyurethanes shift to lower values as a result of the variation in the flexible soft segment. Figure 5 shows the representative DSC thermograms of PCL 530, 1250 and 2000 with HMDI containing 50 mol % mesogen content. An increase in the molecular weight of the PCL soft segment from 530 to 2000 results in the lowering of glass transition, melting and isotropisation temperatures.

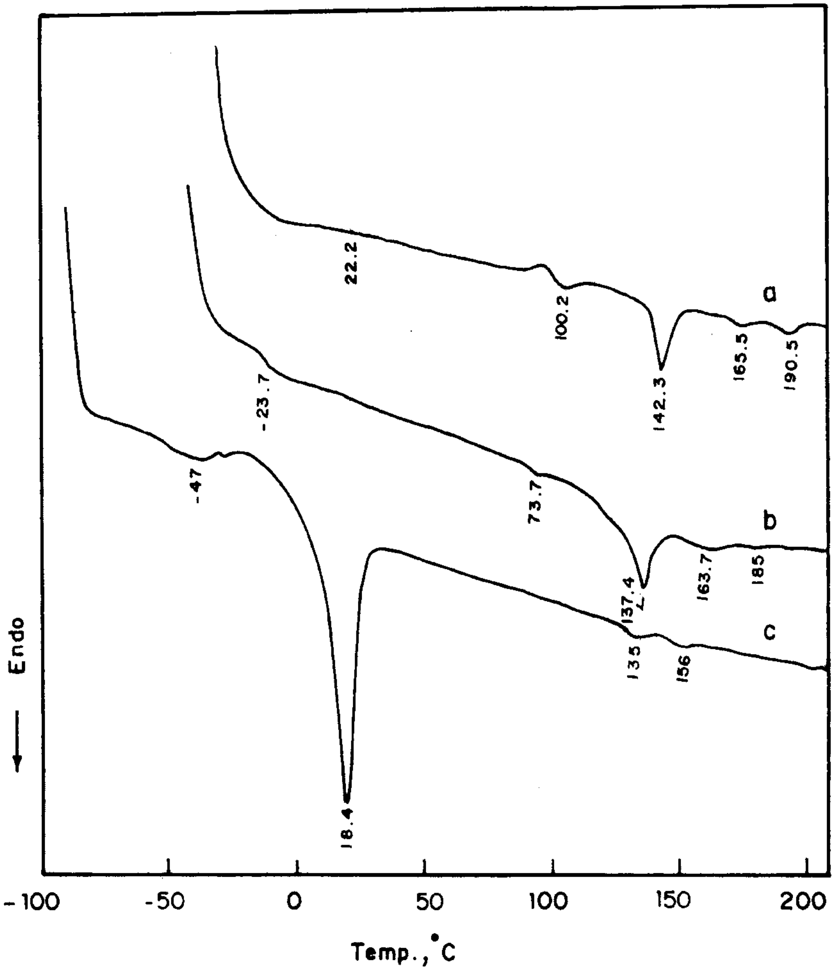


Fig. 5. DSC thermograms of a) PC-5-H-50 b) PC-1-H-50 and c) PC-2-H-50.

Effect of Diisocyanate

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.*[12] The PUs based on MDI have wider LC transition region than the polymer based on 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 and H_{12}MDI, the lower mesogen contents exhibit grained texture while higher mesogen contents exhibit threaded texture.

Effect of Mesogen

The effect of partial replacement of the mesogenic diol by the polyols resulted in the increase of transition temperatures increase with increasing mesogen content. Visual observation of mesophase transitions in optical microscope revealed that the minimum amount of mesogen content required to impart LC varies with PTMG soft segment molecular weight while a minimum amount of 20 mol % mesogen to impart LC property for the PCL containing polyurethanes.

Table 5. Appearance of LC Phase in polyetherurethanes.

Diisocyanate	Polyol M.W	Minimum of Mesogen Content to impart LC (mol%)
HMDI	650	20%
	1000	30%
	2000	40%
H_{12}MDI & MDI	650	20%
	1000	20%
	2000	40%

Apart from the transition temperatures, the mesophase texture of the polymers also varied with mesogen content. Lower mesogen contents displayed grained texture and thread like texture was observed as the mesogen content was raised in the case of HMDI and H_{12} MDI while only grained texture for MDI based Polyurethanes.

Table 6.Variation in Mesophase Texture of polyetherurethanes.

Diisocyanate	Mesogen Content	Mesophase Texture
HMDI	Low	Grain
	High	Thread
H_{12} MDI	Low	Grain
	High	Thread
MDI	All Compositions	Grain

Table 7. Variation in Mesophase Texture of polyesterurethanes.

Diisocyanate	Mesogen Content	Mesophase Texture
HMDI	Low	Grain
(M.W 530)	High	Thread
(M.W.1250)	All Compositions	Grain
(M.W. 2000)	All Compositions	Grain
H_{12} MDI	Low	Grain
	High	Thread
MDI	All Compositions	Grain

Stress-strain Properties of the Polyurethanes

Polymers prepared from PTMG 650 and PTMG 1000 formed very brittle films and could not be subjected to stress-strain analysis while those prepared from PTMG 2000 exhibited elastomeric property. In the polyetherurethanes, as the mesogen content increased from 20 – 40 mol %, the tensile strength increased and the elongation at break decreased. In contrast to the polyetherurethanes, the polyesterurethanes did not exhibit elastomeric property. This could be due to the presence of a number of aromatic rings (in the hard segment domains) that stiffens the polymer chains coupled with the crystalline nature of the polyol leading to enhanced rigidity and brittleness. On the other hand, the presence of flexible bonds in the ether polyol imparts elasticity to PU chains, which is lacking in the case of polyesterurethanes.

Conclusion

High aspect ratio tetrad mesogenic diols containing four phenyl rings para linked by ester and azomethine linkages and terminal spacers varying from 2-10 were synthesized. These mesogenic diols were reacted with HMDI and $H_{12}MDI$ resulting in thermotropic liquid crystalline main chain unsegmented polyurethanes. All monomeric diols and polyurethanes showed liquid crystalline behaviour. The diols and the unsegmented polyurethanes exhibited nematic mesophase. The mesogenic diol was partially replaced by polyol of varying molecular weights, which influenced the phase transitions and the occurrence of mesophase textures. The phase transition temperatures of the polyurethanes showed dependence on the chain length of the soft segment and on the content of the mesogen moiety. A higher content of mesogenic moiety was needed to obtain liquid crystalline property when the soft segment length was increased as observed in the case of PTMG. Grained and threaded textures were observed depending on the molecular weight of the soft segment, the mesogen content and the diisocyanate. The stress-strain analyses showed that the polymers based on high molecular weight PTMG soft segment have elastomeric property.

Acknowledgement

One of the authors, T.P., thanks the Council for Scientific and Industrial Research (CSIR), New Delhi, India for the award of Senior Research Fellowship.

[1]G. Smyth, E.M. Valles, S.K. Pollack, J. Grembowicz, P.J. Stenhouse, S.L. Hsu, W.J. Macknight, *Macromolecules* **1989**, *22*,1467.
[2] T.Padmavathy, K.S.V.Srinivasan, *J. Macromol. Sci. Polym. Rev.*, **2003**, 43 (1) (to appear)
[3] T.Padmavathy, S.Sudhakar, K.S.V.Srinivasan, *Liquid Crystals*, **2001**, *28*, 1475.
[4] P.J.Stenhouse, E.M. Valles, S.W. Kantor ,W.J. MacKnight, *Macromolecules*, **1989**, 22, 1467
[5] K. Imura, N. Koida, H. Tanabe, M. Takeda, *Makromol. Chem.* **1981**, *182*, 2569.
[6] H.R. Kricheldorf, J. Awe, *Makromol Chem.* **1989**, *190*, 2579.
[7] F. Higeshi, F, K. Nakajima, M. Watabiki, W.X. Zang, *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2929.
[8] C.J. Yang and S.A. Jenekhe, *Chem. Mater.*, **1991**, *3*, 878.
[9] S. Banerjee, P.K. Gutch ,C. Saxena, *J. Polym. Sci, Polym. Chem.*, **1995**, *33*, 1719.
[10]G.W.Gray, "*Molecular structure and the properties of liquid crystals,*" Academic Press, New York 1962, p. 158.
[11] T.J. Lee, D.J. Lee, J., H.D.Kim, *J. Appl. Polym. Sci.*, **2000**, *77*, 577.
[12] X. Jia, X. He, X. Yu, *J. Appl. Polym. Sci.* **1996**, *62*, 465.