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Studies on thermotropic main chain liquid crystalline segmented polyurethanes
I. Synthesis and properties of polyurethanes from high aspect ratio mesogenic diol as chain extender

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Thermotropic main chain liquid crystalline polyurethanes were prepared from 4-{[4-(6-hydroxyhexyloxy)phenylimino]methyl}benzoic acid 4-{[4-(6-hydroxyhexyloxy)phenylimino]methyl}-phenyl ester (mesogenic diol) and 1,6-hexamethylene di-isocyanate. The effects of partial replacement of the mesogenic diol by 20–50 mol % of poly(tetramethylene oxide)glycol (PTMG) of varying molecular mass ($M_n = 650, 1000, 2000$) on the liquid crystalline properties were studied. Structural characterization was carried out by FTIR spectroscopy and the molecular mass distribution was determined by GPC. Differential scanning calorimetry and hot stage polarizing optical microscopy were used to study the mesomorphic properties. It was observed that the partial replacement of the mesogenic diol by PTMG of varying molecular masses influenced the phase transitions and the occurrence of mesophase textures. When the molecular mass of PTMG was enhanced, a higher content of mesogenic agent was needed to obtain liquid crystalline properties.

1. Introduction

In recent years there has been world wide interest in main chain thermotropic liquid crystalline (TLC) polymers in which the mesogenic moieties occupy positions in the backbones, because these polymers exhibit unique mechanical properties, forming high strength fibres and exhibiting rheological properties in the melt. Thermotropic main chain liquid crystalline polyurethanes (TLCPUs) are currently being investigated with particular reference to their application potential. Due to the strong intermolecular interactions arising from hydrogen bonding of the urethane linkages, the synthesis of the TLCPUs appears to be more difficult than the synthesis of 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 [1], (ii) introducing substituted mesogenic segments [2] or (iii) using secondary amines reacted with dichloroformates [3]. Among these methods, the introduction of long flexible spacers such as those in poly(tetramethylene oxide)glycol (PTMG-1000 and PTMG-2000) into the polymer main chains was effective in decreasing the phase transition temperatures, increasing solubility, reducing hydrogen bonding [4] and generating elastic properties. However, the use of long flexible spacers could result in partial or complete loss of the liquid crystalline properties. Hence, we envisaged that the incorporation of a high axial ratio mesogenic unit into the polymer backbone could help to balance the mesogenic properties and the 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(hydroxyalkoxy)biphenyl [5–12], 4,4′-bis(ω-hydroxyalkoxy)-α-methylstilbene [13], 4,4′-bis(hydroxyhexyloxy)azobenzene [14] and there are a very few reports on the triad mesogenic diol benzene-1,4-di(4-iminophenoxy-*n*-hexanol) [15, 16] as chain extenders. Sun *et al.* [16] in their study reported that polyurethane elastomers with a low axial ratio mesogenic unit and long soft diol segment do not easily exhibit mesophases, and suggested that the axial ratio of the mesogenic unit must be increased to obtain a liquid crystal polymer with long flexible spacers.

Systematic studies on the design, synthesis and characterization of new high aspect ratio tetrad (four-ring) and pentad (five-ring) mesogenic model compounds, diols and liquid crystalline polyurethanes have been reported from our laboratory [17–21]. In continuation of this

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work, this paper reports the synthesis and properties of segmented polyurethanes from PTMG of different molecular masses ($M_n = 650$, 1000, 2000), aliphatic diisocyanate HMDI and high aspect ratio tetrad mesogenic diol 4-{[4-(6-hydroxyhexyloxy)phenylimino]methyl}-benzoic acid 4-{[4-(6-hydroxyhexyloxy)phenylimino]-methyl}phenyl ester as the chain extender. The effect of partial replacement of the mesogenic diol by PTMG and the effect of the chain length of the PTMG on the liquid crystalline properties are reported.

2. Experimental

2.1. *Materials*

Poly(tetramethylene oxide)glycols (PTMG) of molecular masses 650, 1000 and 2000 were purchased from Aldrich, USA. The polyol was dried and degased at 90–100°C under vacuum for 6–7 h before use. 1,6-Hexamethylene diisocyanate (HMDI) (Aldrich), 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.

2.2. *Characterization methods*

The FTIR spectra of the polymers were recorded using a Nicolet Impact 400 spectrometer by casting films on KBr disks. Visual observations of liquid crystal transitions were made using an Olympus BX 50 polarizing microscope equipped with a Linkam THMS 600 heating stage. A Seiko model SSC 5200H 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^{-1} in a nitrogen atmosphere. The molecular mass determinations were carried out using GPC with polystyrene standards in THF solvent using an Ultrastyragel column (Waters). Stress–strain measurements of polyurethane films were made using an Instron Universal Testing Machine at a constant speed of 50 mm min^{-1}. The specimens were conditioned before testing and the measurements were performed at room temperature with dumb-bell shaped specimens of dimensions $3.5 \times 2.5 \times 0.16$ mm^3.

2.3. *Monomer synthesis*

The detailed synthetic procedure for and the properties of the mesogenic diol 4-{[4-(6-hydroxyalkoxy)phenylimino]methyl}benzoic acid 4-{[4-(6-hydroxyalkoxy)-phenylimino]methyl}phenyl ester are reported elsewhere [21]. 2.54 g (0.01 mol) of 4-formylbenzoic acid 4-formylphenyl ester and 4.18 g (0.02 mol) of 4-(6-hydroxyhexyloxy)-aniline were boiled in 20 ml of ethanol with a catalytic amount of acetic acid for 1 h. The precipitated monomeric diol was filtered off, dried and recrystallized 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$_2$OH), 1.71 (p, 4H, –ArOCH$_2$C$\underline{H}_2$). FTIR (KBr): 3306 (OH), 1736 (C=O of ester), 1623 (C=N), 1248 cm^{-1} (C–O). Elemental analysis: calc. for $C_{39}H_{44}O_6N_2$ C 73.56, H 6.97, N 4.40; found C 73.52, H 6.84, N 4.33%.

2.4. *Polymer synthesis*

The polyurethanes were synthesized 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 described in table 1.

A typical procedure for the synthesis of a PU is as follows: PTMG 1000 (0.0005M) was reacted with HMDI (0.001M) at 80°C in an inert atmosphere to prepare the prepolymer with end-capped NCO groups. When the theoretical NCO content was reached (confirmed by dibutylamine titration), the prepolymer was chain extended with the mesogenic diol (0.0005M) in DMF with a catalytic amount of DBTDL at 70°C for 12 h. The polymer solution was then poured into a mould and films were cast.

3. Results and discussion

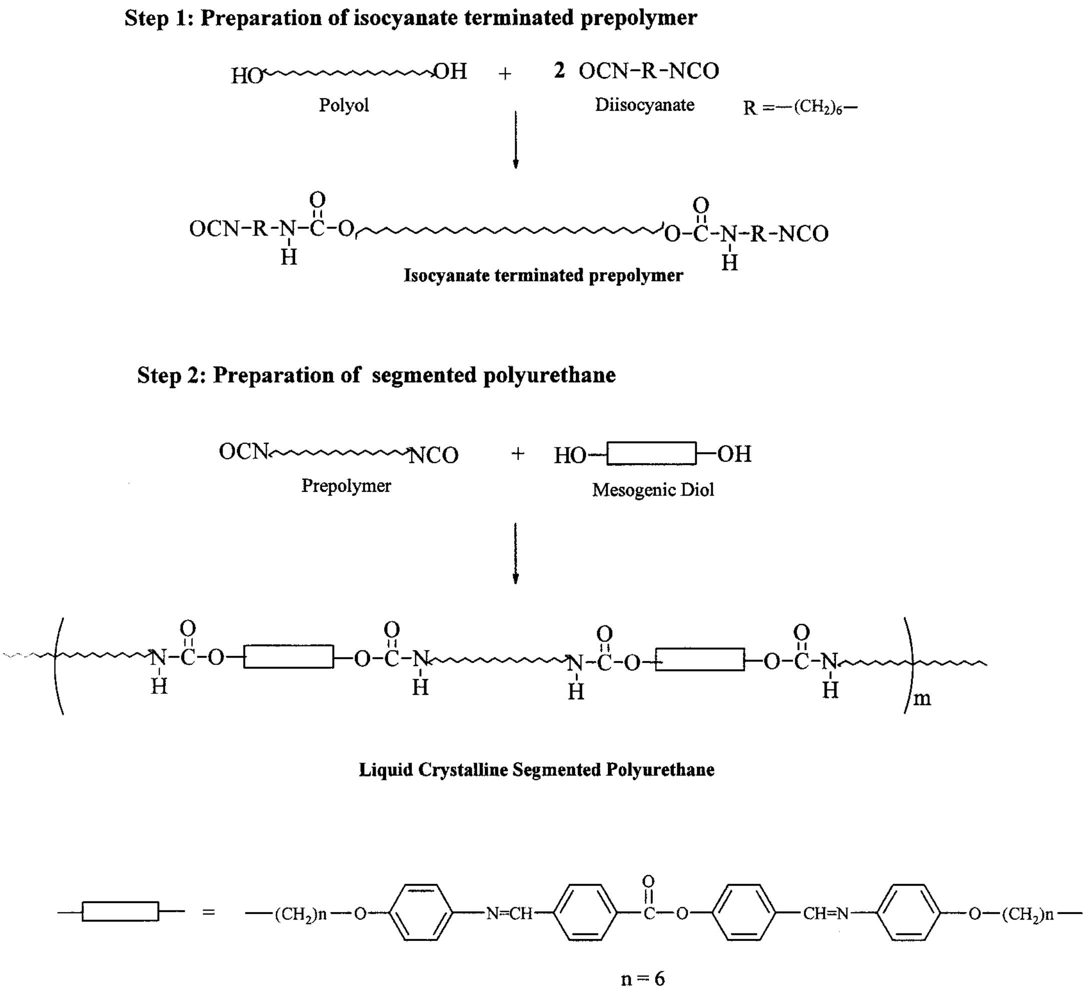
3.1. *Synthesis and characterization*

The general reaction route for the synthesis of all the polyurethanes in this study is shown in the scheme. The thermotropic LCPUs were synthesized by the polyaddition of HMDI with PTMG of various molecular masses 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 masses of the soft segment PTMG were chosen (M.W. 650, 1000, 2000). The mesogen content was also varied in order to study the influence of the hard segment on the thermal and physical properties. In contrast to the use of conventional chain extenders such as 1,2-ethylene glycol or 1,4-butane diol, the synthesized polyurethanes could exhibit mesophase transitions when using a high aspect ratio mesogenic diol as chain extender.

The structure of the polyurethanes synthesized was characterized by FTIR spectroscopy. The representative IR spectrum (figure 1) shows the characteristic absorption of the carbonyl band of the urethane group at

Table 1. Starting compositions of the polyurethanes (mol).

		PTMG Molecular mass			
Polymer code	Mesogenic diol	650	1000	2000	HMDI
LCP 0.50/650	0.50	0.50	—	—	1
LCP 0.50/1000	0.50	—	0.50	—	1
LCP 0.50/2000	0.50	—	—	0.50	1
LCP 0.40/650	0.40	0.60	—	—	1
LCP 0.40/1000	0.40	—	0.60	—	1
LCP 0.40/2000	0.40	—	—	0.60	1
LCP 0.30/650	0.30	0.70	—	—	1
LCP 0.30/1000	0.30	—	0.70	—	1
LCP 0.30/2000	0.30	—	—	0.70	1
LCP 0.20/650	0.20	0.80	—	—	1
LCP 0.20/1000	0.20	—	0.80	—	1
LCP 0.20/2000	0.20	—	—	0.80	1



Scheme Synthesis of segmented liquid crystalline polyurethanes.

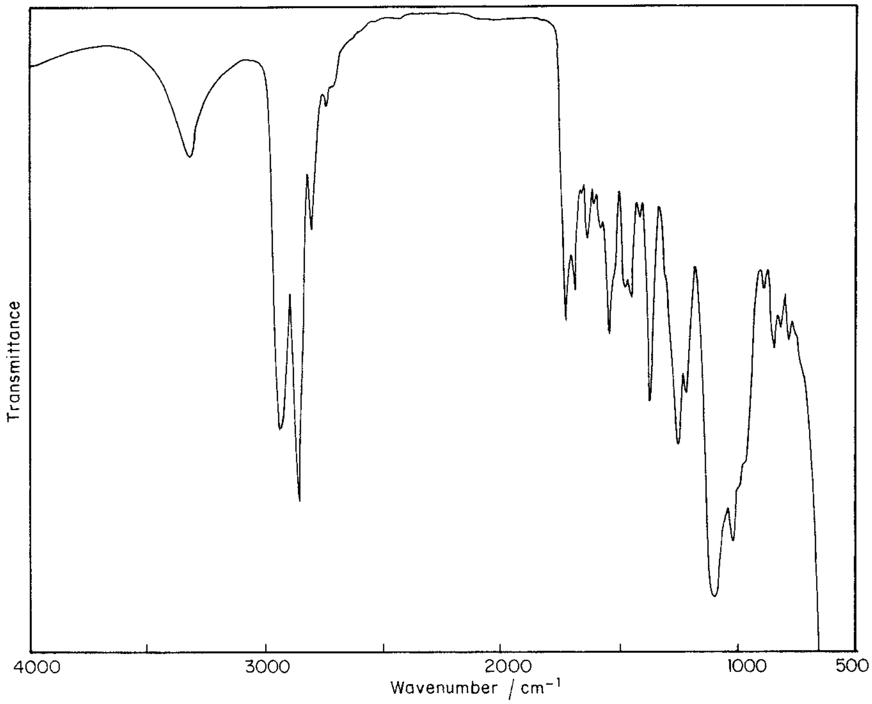


Figure 1. FTIR spectrum of polyurethane LCP 0.20/1000.

1725 cm^{-1}, –NH stretching of the urethane group at 3336 cm^{-1}, $-CH_2-$ stretching at 2925 and 2852 cm^{-1}, and the absorption of the azomethine group (–CH=N–) at 1692 cm^{-1}.

The molecular masses of the polymers were determined by gel permeation chromatography and the results are presented in table 2. The number average molecular mass of most of the segmented polyurethanes is in the region of 20 000–80 000. This is in contrast to our earlier report on unsegmented polyurethanes wherein molecular mass data could not be obtained due to the insoluble nature of the polymers [18, 21]. Thus it is evident that the incorporation of soft segments improves the solubility characteristics of the polymers.

Table 2. Molecular mass distribution of the polyurethanes.

Polymer code	M_n	M_w	Polydispersity
LCP 0.50/650	15020	25834	1.72
LCP 0.50/1000	23434	37824	1.61
LCP 0.50/2000	36409	61896	1.70
LCP 0.40/650	15901	26713	1.68
LCP 0.40/1000	20440	36921	1.80
LCP 0.40/2000	57728	99822	1.70
LCP 0.30/650	21576	41210	1.91
LCP 0.30/1000	45051	83675	1.85
LCP 0.30/2000	81215	141399	1.74
LCP 0.20/650	30468	54233	1.78
LCP 0.20/1000	30739	58591	1.90
LCP 0.20/2000	60335	112737	1.61

3.2. *Thermal and optical properties*

The thermal transitions of the PUs were determined by DSC measurements at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. The second heating scans are reported and the mesophase textures were observed by polarizing optical microscopy. The results are summarized in table 3.

The DSC traces of the PUs displayed glass transitions T_g, crystal–crystal transitions T_c, melting temperatures T_m, isotropization temperatures T_i and hard segment melting T_{hm}. Representative DSC traces of LCP 0.50/1000 and LCP 0.40/650 are shown in figure 2. The DSC trace of LCP 0.50/1000 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 derived from the 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 microscopy did not reveal any crystal–mesophase transition in this region. A similar observation has been made by Kim *et al.* [22]. The endotherms at 151.7 and 169.3°C indicated the crystal–mesophase transition temperature and isotropization temperature, respectively as confirmed by polarizing optical microscopy. The higher temperature melting endotherm at 191°C is a result of the melting of microcrystalline hard segments and this behaviour is observed in materials having longer aromatic

Table 3. Thermal properties of the polyurethanes, temperatures in °C.

Polymer code	Hard segment content/%	DSC[a]							Microscope	
		T_{sg}	T_{sm}	T_{hg}	T_c	T_m	T_i	T_{hm}	T_m	T_i
LCP 0.50/650	60	32.4	—	115.4	—	158.0	174.0	193.7	157	178
LCP 0.50/1000	49	14.7	—	104.5	133.6	151.7	169.3	190.0	152	173
LCP 0.50/2000	32	−34.2	23.3	95.0	—	143.6	163.0	188.0	140	164
LCP 0.40/650	52	18.8	—	115.8	139.2	156.2	172.4	191.7	153	168
LCP 0.40/1000	41	8.9	—	102.7	134.0	143.0	165.0	—	145	169
LCP 0.40/2000	26	−33.4	24.4	92.0	133.6	141.0	162.0	187.5	139	163
LCP 0.30/650	44	−21.0	43.4	111.7	136.4	154.7	167.5	190.0	148	168
LCP 0.30/1000	34	−28.5	23.4	90.3	133.0	141.2	162.0	186.2	138	165
LCP 0.30/2000	20	−33.4	24.4	87.0	—	—	—	188.0	—	—
LCP 0.20/650	36	−18.0	41.0	—	—	—	—	189.7	130	160
LCP 0.20/1000	27	−23.3	21.5	—	—	—	—	—	—	—
LCP 0.20/2000	16	−34.6	20.3	—	—	—	—	—	—	—

[a] 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 = isotropization temperature, T_{hm} = hard segment melting.

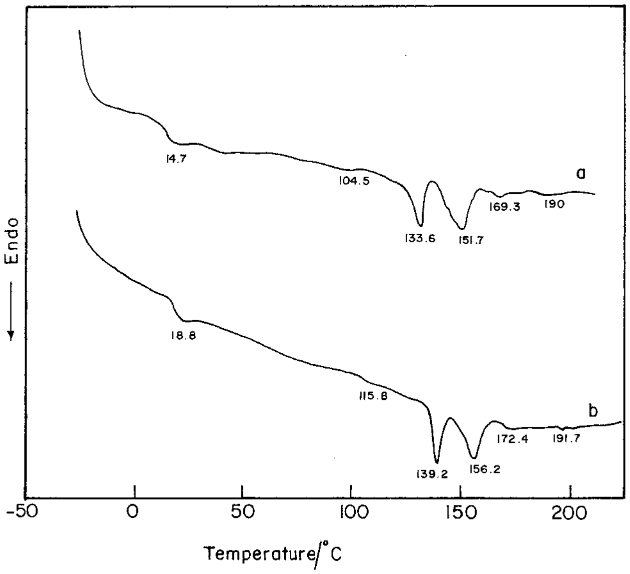


Figure 2. DSC traces of polyurethanes (*a*) LCP 0.50/1000 and (*b*) LCP 0.40/650.

urethane segments. Similarly, the DSC trace of LCP 0.40/650 exhibited a soft segment glass transition temperature at 18.8°C and a hard segment glass transition at 115.8°C. The endotherms at 139.2, 156.2, 172.4 and 191.7°C correspond to the crystal–crystal, crystal–mesophase, isotropization and hard segment melting temperatures, respectively.

The polymers containing 30, 40 and 50 mol % of mesogen unit exhibited the crystal–crystal transition in the range 133–139°C as observed in the DSC traces.

Visual observation of the mesophase transitions by optical microscopy revealed that only the PTMG 650 based PUs with 20 mol % mesogen content exhibited liquid crystallinity. When the mesogen content was raised to 30 mol %, polyurethanes prepared from PTMG 650 and PTMG 1000 showed liquid crystalline behaviour, while those from PTMG 2000 did not. When the mesogenic content was further raised to 40 and 50 mol %, liquid crystalline behaviour was seen in all the polymers. This suggests that the liquid crystalline properties of the polymers depend on the molecular mass of the soft segment, as well as on the content of the mesogenic unit. Increasing the PTMG diol spacer length requires higher contents of the mesogenic component to impart LC properties to the polyurethane.

The PUs prepared from PTMG 650, with 20 mol % mesogen content showed a grained texture, while with 50 mol % they showed a nematic-like texture. A similar observation was made for the PUs prepared from PTMG 2000 where a 40 mol % mesogen content showed a grained texture and an increase in the mesogen content gave a nematic-like texture. The texture therefore varies with mesogen content and such observations were also made by Szczepaniak *et al.* [7]. The optical micrograph of the polyurethane LCP 0.50/1000 obtained on cooling from the melt is shown in figure 3.

It can be seen from the data given in table 3 that the phase transition temperatures of the segmented polyurethanes shift to lower temperatures in comparison with the unsegmented polyurethanes [21] as a result of the flexible soft segment PTMG. An increase in the molecular mass of the soft segment from 650 to 2000 results in lower T_g, T_m and T_i. Comparing the PUs with the same soft segment and different mesogen contents, one can observe that the transition temperatures increase with increasing mesogen content. Although there is a trend, the variation in the transition temperatures is not

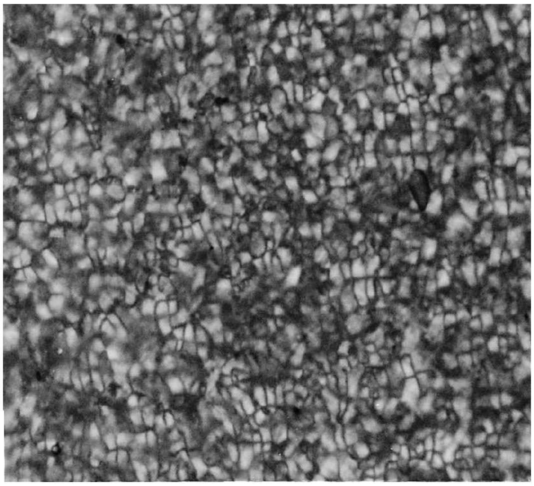


Figure 3. Optical photomicrograph of LCP 0.50/1000 on cooling from the melt.

great. This may be attributed to a high degree of phase segregation between the hard and soft segment domains and also due to less variation in the hard segment content of the polymers. In these polymers, the enhanced phase segregation may be due to (i) the presence of four aromatic rings in the hard segments contributed by the tetrad mesogenic diol and (ii) the ester and azomethine linkages in the mesogenic diol that impart additional hydrogen bonding. These factors could result in a greater degree of phase separation between the hard and soft segments. This seems to be more pronounced in the polymers prepared with PTMG 2000, as the phase transition temperatures, as well as the T_{sg} and T_{sm}, of all the compositions are very close.

3.3. *Mechanical properties*

The stress–strain properties of the PUs prepared with PTMG 2000 are listed in table 4. It is observed from the table that as the mesogen content increased from 20–40 mol % (accompanied by an increase in hard segment from 15 to 26%), the tensile strength increased and the elongation at break decreased. The stress–strain curves (figure 4) reveal that all the compositions have elastomeric behaviour and the modulus increases with an increase in the mesogen content. Polymers prepared from PTMG 650 and PTMG 1000 formed very brittle films and could not be subjected to stress–strain analysis.

Table 4. Mechanical properties of the polyurethanes.

Polymer code	Hard segment content/%	Tensile strength/MPa	Elongation /%
LCP 0.20/2000	15	3.9	1155
LCP 0.30/2000	20	13.2	1023
LCP 0.40/2000	26	15.2	104

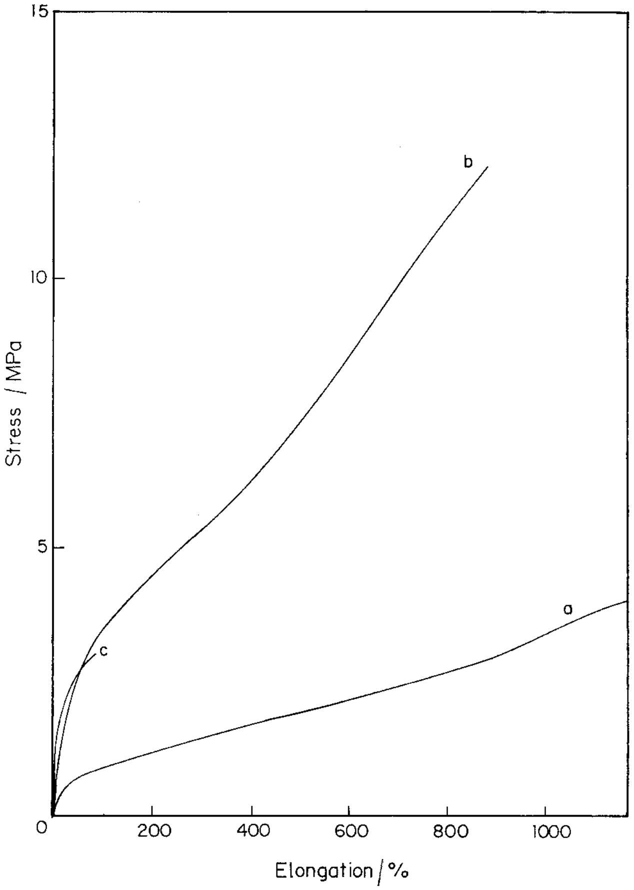


Figure 4. Stress–strain curves of (*a*) LCP 0.20/2000, (*b*) LCP 0.30/2000, (*c*) LCP 0.40/2000.

The rubber-like behaviour exhibited by PTMG 2000 based polymers is due to the higher degree of phase segregation between the hard and soft segments when compared with polymers prepared with PTMG 650 and PTMG 1000.

4. Conclusion

The phase transition temperatures of the polyurethanes investigated depend on the chain length of the flexible spacer and on the content of the mesogenic moiety. If the flexible spacer is longer, a higher content of mesogenic agent is needed to obtain LC properties. Depending on the flexible spacer length and the mesogenic content, grained and nematic textures were obtained. The polymers from PTMG 2000 with mesogen content 20–40 mol % showed elastomeric behaviour.

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