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PRELIMINARY COMMUNICATIONS

Synthesis and characterization of novel liquid-crystalline polyurethanes

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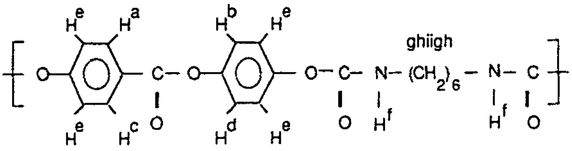
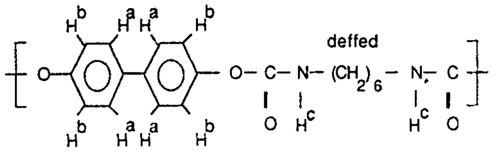
Novel polyurethanes have been synthesized by the condensation of two rigid diols, biphenyl-4,4′-diol (BPH(4,4′)D) and 4-hydroxyphenyl-4-hydroxybenzoate (4HPH4′HB), with the flexible hexamethylene diisocyanate (HDI). Their phase diagrams were established by means of differential scanning calorimetry, nuclear magnetic resonance and polarizing optical microscopy. Poly(4HPH4′HB/HDI) was found to display a nematic phase between 140 and 199°C; poly (BPH(4,4′)D/HDI) also exhibits a mesomorphic phase, but so far the nature of this phase has not been established.

Liquid-crystalline polymers, (mainly those of the nematic type), are exciting a great deal of scientific and industrial interest due to the wide range and importance of their applications, namely ultra-high modulus, high strength fibres and high performance thermoplastics. Most of the literature in main chain liquid crystal polymers refer to aromatic polyamides or polyesters. Polyurethanes are a distinct class of materials with industrial importance and it is interesting to develop new polymers of this kind capable of exhibiting liquid-crystalline phases [1–10]. The published work in this domain is scarce and very recent. In this preliminary communication we present results of the synthesis and characterization of two novel linear polyurethanes with a semi-flexible chain, which exhibit liquid-crystalline phases. The molecular structure of these polymers is:



PU1



PU2

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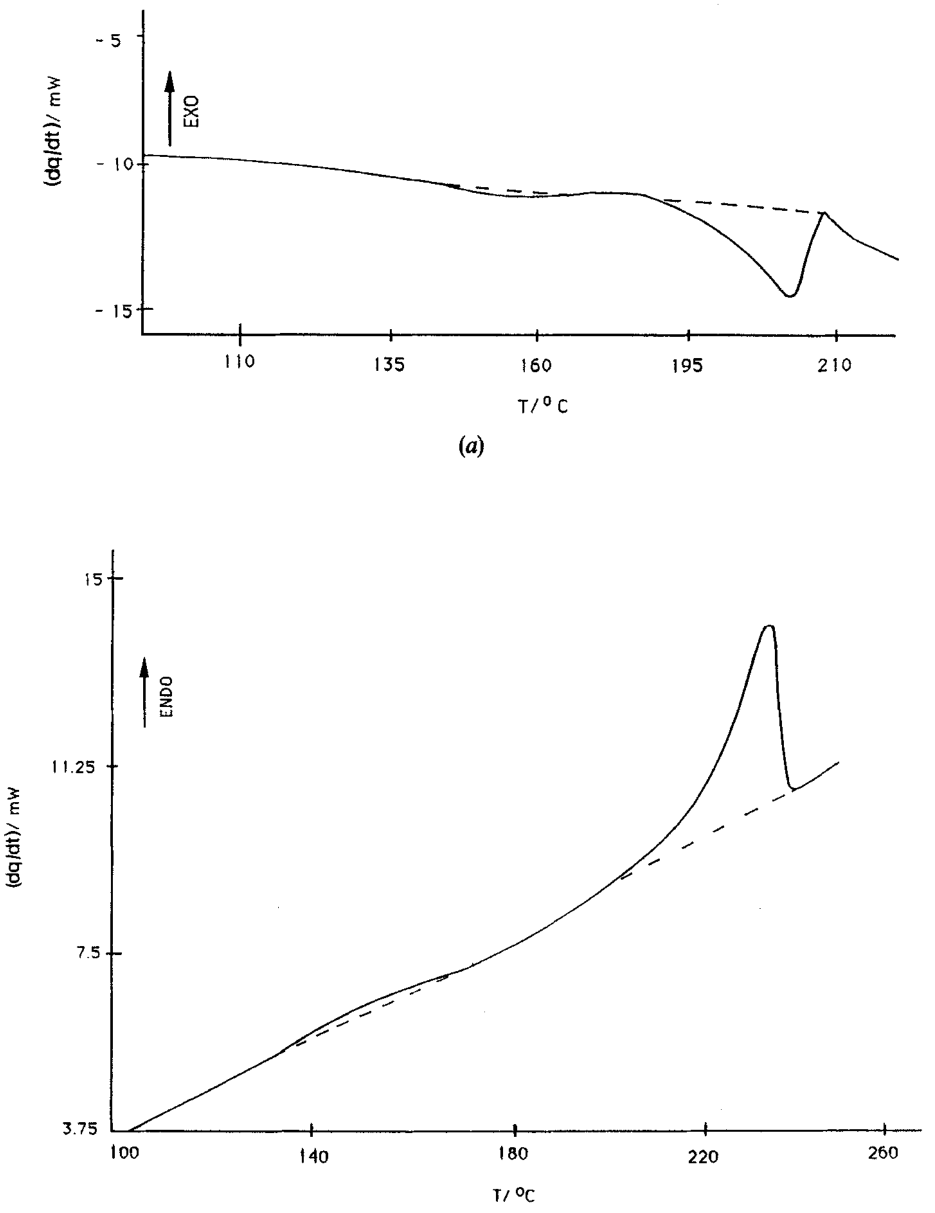
The starting materials for the synthesis were biphenyl-4,4′-diol (BPH(4,4′)D) and hexamethylene diisocyanate (HDI) which were used as received, and 4-hydroxyphenyl-4′-hydroxybenzoate (4HPH4′HB) which was prepared according to the method described by Kangas *et al.* [11], by direct esterification of hydroquinone with *p*-hydroxybenzoic acid using petroleum benzene as a solvent. The synthesis was carried out by condensation of 4HPH4′HB and BPH(4,4′)D with HDI, yielding polymers hereafter referred to as PU1 and PU2, respectively. Two batches (PU2a, PU2b) of the latter polymer were prepared. The reaction took place in methylethylketone (MEK), at 63°C, in a three necked flask reactor fitted with a condenser, a mechanical stirrer, a thermometer, a dropping funnel and a nitrogen inlet. Nitrogen was kept flowing continuously through the system during the synthesis. The diol (amounts used: 0·036, 0·052 and 0·100 mol for PU1, PU2a and PU2b, respectively) was added dropwise to the diisocyanate (amounts used: 0·036, 0·053 and 0·101 mol for PU1, PU2a and PU2b, respectively) and the mixture stirred for a few hours (3·5, 4 and 5 h for PU1, PU2a and PU2b, respectively). The catalyst (stannous octoate diluted 1 : 10 in acetone for PU1 and pure stannous octoate for PU2a) was added 10 min before stopping the stirring (for PU2b no catalyst was used). The solvent was removed in a rotary evaporator, immediately after reaction for PU2b, and the next day for PU1 and PU2a. When necessary the products thus obtained were washed with isopropanol to destroy any NCO group not reacted. For purification, the polymers PU1 and PU2a were dissolved in N-methylpyrrolidone, poured into distilled water, filtered and dried under vacuum at 80°C. For PU2b a fractionation of the washed product was achieved by dissolution in methanol, to the maximum extent. The insoluble material (with greater molecular weight) was filtered and dried under moderate vacuum at ambient temperature for several hours. The polymer PU2b as described later corresponds to this higher molecular weight fraction. The molecular structures of these polymers were confirmed by NMR and IR measurements. NMR spectra of the polymer solutions in deuteriated dimethylformamide (DMF-d_7) were recorded in a Bruker CXP spectrometer operating at 300 MHz and IR spectra were recorded in a Perkin–Elmer 157G. The data obtained are as follows: PU1 [^{1}H NMR, δ 9·67 (2H^{c}); 6·89 < δ < 8·19 (8H^{a,b,c,d,e}); δ 3·22 (4H^{g}); δ 1·43 (8H^{h,i}). IR (KBr): 3330 cm^{-1} (–NH); 1715 cm^{-1} (–C=O)]; PU2a [^{1}H NMR, δ 9·83 (2H^{c}); δ 7·57 (4H^{b}); δ 7·16 (4H^{a}); δ 3·19 (4H^{d}); δ 1·43 (8H^{e,f}). IR (KBr): 3340 cm^{-1} (–NH); 1710 cm^{-1} (–C=O)]; PU2b [^{1}H NMR, δ 9·49 (2H^{c}); δ 7·41 (4H^{b}); δ 6·88 (4H^{a}); δ 3·20 (4H^{d}); δ 1·43 (8H^{e,f}). IR (KBr): 3340 cm^{-1} (–NH); 1720 cm^{-1} (–C=O)]. Molecular weights relative to polystyrene standards were determined in DMF as eluent, at ambient temperature ($\simeq$ 18°C), in a 60 cm long TSK G2500 H8 column. Data from gel permeation chromatography are listed in the table.

The thermal properties of the polymers were studied by DSC, using a Perkin–Elmer DSC 7 and Setaram DSC111 differential scanning calorimeters calibrated with indium

Characterization of synthesized polyurethanes.

Polymer	M_n	M_w	*Dp*†	$T_{\mathrm{i,\,onset/top}}$/°C	$T_{\mathrm{m,\,onset/top}}$/°C	ΔH_{m}/J mru^{-1}	ΔH_{i}/J mru^{-1}
PU1	6626	10222	1·64	140/152	186/199	0·06	3·13
PU2a	3606	4834	1·34	125/153	222/236	0·64	5·45
PU2b	2374	3367	1·42	94/117	137/167	1·17	1·91

† Polydispersity.



(a)

(b)

Figure 1. DSC traces of (*a*) PU1 (data obtained with Setaram DSC111, heating rate = 2°C min^{-1}) and (*b*) PU2a (data obtained with Perkin–Elmer DSC7, heating rate = 5°C min).

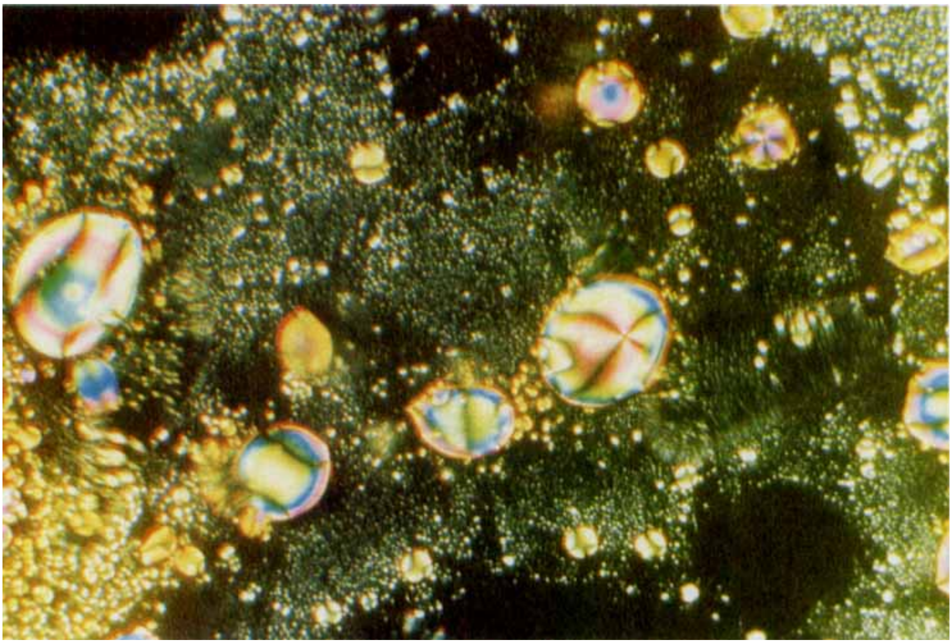


Figure 2. Optical photomicrograph of PU1 at 172°C (crossed polarizers, ×270).

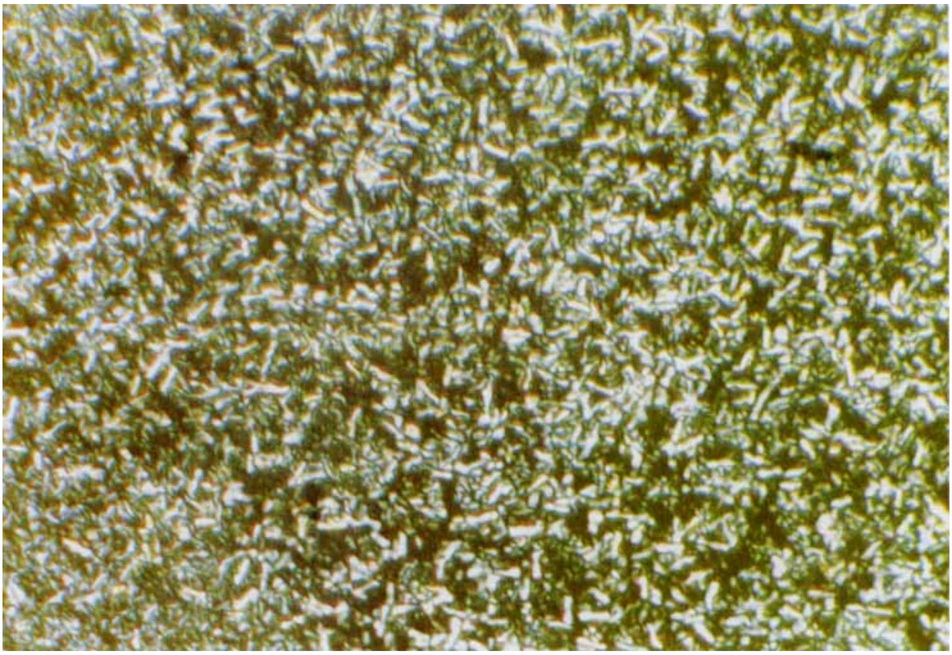


Figure 3. Optical photomicrograph of PU2a at 150°C (crossed polarizers, ×670).

and aluminium standards, polarizing optical microscopy, using an Olympus BHA polarizing optical microscope equipped with a Mettler FP 52 hot stage and a camera, and NMR, using a Bruker SXP4/100 spectrometer operating at 60 MHz. All of the polymers were found to exhibit mesomorphic properties. For PU1 it was possible to identify the observed mesomorphic texture as belonging to a nematic phase. The polymers appear to be rather stable, as no thermal degradation was observed on forming the isotropic phase and after several heating and cooling cycles.

The DSC traces of PU1 and PU2a exhibit two peaks, as shown in figures 1 (*a*) and (*b*), respectively. The smooth peak at the lower temperature corresponds to the melting transition and the sharp peak at the higher temperature, corresponds to the transition to the isotropic phase. The enthalpy change at the second transition (ΔH_i) is, in both cases, much greater than at the first, (ΔH_m). The same behaviour was observed in PU2b and is characteristic of many liquid crystal polymers. Two different values for each transition temperature are reported in the table: $T_{i,\mathrm{onset}}$, corresponding to the onset of the DSC peak, and $T_{i,\mathrm{top}}$, corresponding to the peak maximum. These data refer to the first heating of the virgin powder. DSC was not performed on cooling, but observations with the polarizing optical microscope revealed the same phases, although the phase transitions were found in this case to be shifted towards lower temperatures, with supercooling that could reach a few tens of degrees.

Thin homogeneous layers of the polymers were prepared for polarizing optical microscopy observations. A mesomorphic phase was evidenced for all samples but only in the case of PU1 was it possible, with sufficiently thin preparations, to observe textures characteristic of the nematic phase (see figure 2). The mesophase type exhibited by PU2 could not be identified unambiguously from the observed texture (see figure 3).

Proton NMR absorption and dispersion spectra were recorded as a function of temperature. The observed lineshapes and linewidths suggest that the sample structure is a powder of anisotropic (nematic) fluid domains. The linewidths of the absorption spectra at half height, $2\Delta_{1/2}$, recorded for increasing temperature for PU1 an PU2a are shown in figure 4, for PU2b the same kind of curve was obtained. These results show clearly the fusion of the materials and the temperatures at which the onset of the mesophase occurs (i.e. flattening of the values of $2\Delta_{1/2}(T)$ after their sudden fall). These data are in good agreement with the values of $T_{m,\mathrm{onset}}$ found by DSC. The limitations of the NMR equipment used did not allow for a more detailed study of the mesophases. It was not possible to reach the transition temperature to the isotropic phase, and the strength of the magnetic field 1·41 T, was not enough to align the polymers. The characteristic dipolar splitting of the aligned nematic phases (see, for example, [12])

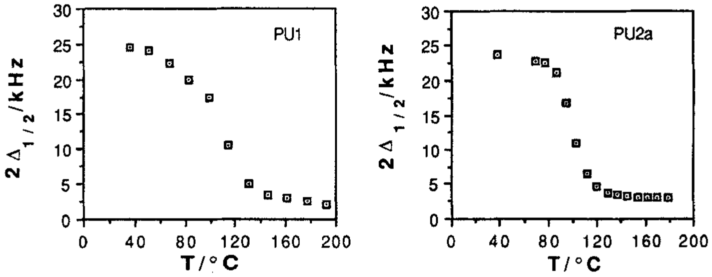


Figure 4. Linewidths at half height of the NMR absorption spectra, $2\Delta_{1/2}$, as a function of temperature for PU1 and PU2a.

was, therefore, not observed. This difficulty in aligning the polymers by the magnetic field is a consequence of their high viscosity.

In conclusion the results of the NMR measurements definitely show a solid–mesophase transition, where the DSC data are less confident. The existence of the two phase transitions is clearly established by the combination of these two techniques. This fact, in conjunction with the birefringence and the fluid character of the intermediate phase (mesophase), corroborated by its observation under the polarizing microscope, ensures the liquid-crystalline nature of this intermediate phase for the three polymers considered. In the case of PU1, as explained, the mesophase is nematic. The thermodynamic characterization of the polymers is summarized in the table.

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