ChemComm
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Synthesis of new thermotropic liquid crystalline polyurethanes containing biphenyl mesogens using a novel AB-type self-polycondensation†

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Received (in Cambridge, UK) 14th October 2003, Accepted 6th November 2003
First published as an Advance Article on the web 24th November 2003

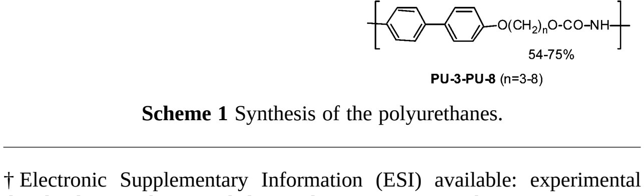
A series of thermotropic main chain liquid crystalline polyurethanes containing biphenyl mesogens and flexible methylene spacers were synthesized using the novel AB-type self-polycondensation approach for the first time.

Thermotropic liquid crystalline polyurethanes are an important class of polymers because of their widespread commercial applications, *e.g.* in high-strength fibers, thermoplastics, displays and optical storage devices. Main chain liquid crystalline polyurethanes prepared by the condensation of biphenol containing built-in methylene spacers with *meta*- or *para*- aromatic diisocyanates have been studied extensively.[1] The *para* linkage was shown to increase the melting temperatures and contribute to liquid crystallinity in these cases. Interestingly, only the A–A + B–B type polycondensation route for the synthesis of main chain thermotropic liquid crystalline polyurethanes has so far been reported. These methods also make use of kinks in the polymer backbone, in the form of methyl groups, to reduce the symmetry of the mesogen. Self-polycondensation of an AB type monomer, apart from the advantage of built-in stoichiometric control for attaining high molecular weight, also permits the generation of novel types of main chain thermotropic liquid crystalline polymers with better control over molecular structural features, such as configurational isomers,[2] well-defined placement of lateral substituents,[3] and the controlled introduction of branching.[4] The reason that the AB type route has not been explored for the synthesis of main chain thermotropic liquid crystalline polyurethanes is the incompatibility of isocyanate and hydroxy groups which makes the synthesis and purification of an AB type monomer difficult. Recently, carbonyl azide groups have been used successfully for the protection of isocyanate functionality in the synthesis of hyperbranched polyurethanes and polyureas.[5] Thermal decomposition of the carbonyl azide groups generated *in-situ* the corresponding isocyanates, which were then reacted with hydroxy groups for the synthesis of polyurethanes. In principle this approach can be extended to the design of AB monomers containing rigid groups and flexible spacers for the synthesis of main chain thermotropic liquid crystalline polyurethanes. In this paper, we report, for the first time, the synthesis and characterization of these liquid crystalline polyurethanes using an AB type self-polycondensation route.

The polyurethanes containing biphenyl mesogens and different methylene spacers were synthesized as depicted in Scheme 1. The monomers for the AB approach should essentially contain both isocyanate (protected in the form of an azide) and hydroxy groups on the same molecule with built-in flexible spacers. So the flexible aliphatic spacers were incorporated into 4-methoxycarbonyl-4′-hydroxybiphenyl and then the ester groups were hydrolyzed to give the corresponding ω-hydroxycarboxylic acids.[6] The mixed anhydride method was used to convert the carboxylic acid to the carbonyl azide group to obtain the final monomers.[7] The FT-IR and ^{1}H NMR spectra of the monomers confirmed the structure of the carbonyl azides. The IR spectra of the monomers showed the characteristic peak of the azide groups at 2135 cm^{-1}. The carbonyl azide monomers were dried thoroughly under high vacuum before polymerisation in a minimum amount of anhydrous NMP. The solution was slowly heated to 110 °C (the thermal decomposition of the aromatic carbonyl azides has been reported[5] to occur at 107 °C). Rapid evolution of nitrogen was observed during the initial stages of the reaction, after which the solution was maintained at 110 °C for 10 h. The polyurethanes **PU-3–8** thus obtained were purified by reprecipitation of the hot NMP solutions of the polymers in methanol. The solid obtained was centrifuged, washed with methanol and dried in a vacuum oven to give the pure polymers. The polymerization yields were in the range 54–75%. The polymers were soluble in hot DMSO, NMP, DMF, phenol and 1,1,2,2-tetrachloroethane (TCE). The viscosities were measured at 50 °C in an Ubbelohde viscometer with phenol as the solvent and the values for the intrinsic viscosity (η) are given in Table 1. The intrinsic viscosities were found to be in the range of 0.3–0.69 dL g^{-1} indicating that the polymers have reasonably high molecular weights.

The FT-IR spectra of the polymers indicated the absence of any residual azide (no absorption at 2135 cm^{-1}) or isocyanate (no absorption at 2270 cm^{-1}) and showed strong absorptions at 1700 and 3320 cm^{-1} indicating the formation of the urethane linkage. The peak at 1700 cm^{-1} is due to the hydrogen bonded carbonyl stretching and the one at 3320 cm^{-1} is due to the N–H stretching of the urethane linkage. In the ^{1}H NMR spectra, methylene protons attached to the urethane linkage showed a triplet at 4.2 ppm and another triplet assigned to methylene protons adjacent to the oxygen connected to the biphenyl was observed at 4.0 ppm.

The thermal stability of the polyurethanes was analyzed by TGA studies, which indicated that 10% decomposition of polyurethanes occurs in the region of 350–380 °C. All the polyurethanes exhibited two endothermic peaks in the DSC heating thermogram and two exothermic peaks in the cooling thermogram. The peaks are designated as T_m and T_i in the order of increasing temperature. T_m



Scheme 1 Synthesis of the polyurethanes.

Table 1 DSC results of polyurethanes **PU-*n***

n	Yield (%)	η_{int}/ dL g^{-1}	T_m/°C	T_i/°C	ΔH_m/ kJ mol^{-1}	ΔH_i/ kJ mol^{-1}
3	75	0.34	—	—	—	—
4	57	0.33	—	—	—	—
5	54	0.30	286(270)	292(279)	4.13	1.24
6	73	0.42	275	282(265)	7.37	9.17
7	55	0.40	182(162)	233(227)	1.23	2.05
8	56	0.69	228(216)	241(223)	0.80	1.61

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† Electronic Supplementary Information (ESI) available: experimental details along with spectral data and DSC traces. See http://www.rsc.org/suppdata/cc/b3/b312826a/

DOI: 10.1039/b312826a

indicates the transition from the crystal to liquid crystal phase (melting temperature) and T_i denotes the transition from the liquid crystalline state to the isotropic liquid state (isotropic temperature). The enthalpy changes associated with these transitions are represented as ΔH_m and ΔH_i, respectively, and are given in units of kJ mol^{-1}, where 'mol' refers to a mole of the repeating unit. The transition temperatures obtained in the heating scan and their corresponding enthalpy changes are tabulated in Table 1. The transition temperatures observed in the cooling scan are given in parentheses. The lower members of the series, **PU-3** and **PU-4**, did not show any peak in the DSC studies and thermal decomposition of the polymers occurs before melting. This can be attributed to the high rigidity of these systems because of the presence of shorter spacers. The observation for **PU-5–8** of two endothermic peaks in the heating scan and two exothermic peaks in the cooling scan (except for polyurethane **PU-6**, which showed only one peak during cooling) indicates the enantiotropic nature of the mesophase. The larger enthalpy found for the second curve compared with the first is indicative of a smectic type of mesophase. The isotropization temperature decreased monotonically as the length of the spacer increased. The melting temperature of these polyurethanes also showed a similar trend. This is due to the decrease in the polarity and rigidity of the system as the spacer length is increased. One interesting aspect observed is that polymers of a similar structure with an ester linkage instead of urethane showed an odd–even effect in the transition temperature and type of mesophase.[6] The odd–even oscillation is mainly governed by the conformations of the flexible spacers in the case of polyesters. However, in the case of the polyurethanes, hydrogen bonding dominates over the conformational constraints of the flexible spacers in determining the packing of the mesogens and hence no odd–even oscillation is observed.

The transition temperatures obtained from the DSC studies were confirmed by optical polarized microscopy. When the polymer samples were viewed under a polarized optical microscope a mesomorphic state with birefringence was observed in the temperature range between the two endothermic peaks (observed in DSC). One exception was the case of **PU-8** which showed a glass transition at 168 °C and two endothermic peaks at 228 and 241 °C in the DSC heating scan; the birefringence was observed in the region between 175 and 215 °C. On cooling the polymer melt a batonnet-like texture appeared which is characteristic of the Smectic A mesophase (Fig. 1). In some cases, when the polymer melt was kept for 2–3 h at the mesophase temperature, the texture changed to a fan-like texture with focal conics.

In conclusion, a series of thermotropic main chain liquid crystalline polyurethanes containing biphenyl mesogens and flexible methylene spacers were synthesized for the first time using the novel AB-type self-polycondensation approach. The polymers with spacer lengths shorter than 5 methylene units were found to decompose before melting and hence did not exhibit liquid crystalline behavior. However, the polyurethanes containing spacers longer than 5 methylene units exhibited smectic mesophases with focal conic structures (Smectic A). The melting and isotropization temperatures were found to decrease as the spacer length increased. Variable temperature FT-IR spectroscopic and XRD studies are in progress at present to gain further insight into the mesophasic characteristics. The structural modifications required to reduce the transition temperatures of the polyurethanes are also in progress.

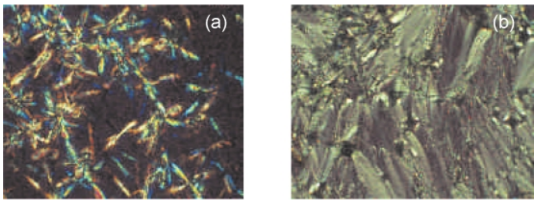

Fig. 1 Polarized optical micrographs of the polyurethanes: (a) **PU-6** at 262.6 °C and (b) **PU-7** at 190 °C.

We would like to thank the CSIR, India for financial help and the RSIC, Bombay for instrumental facilities. T. R. thanks the CSIR, India for a Senior Research Fellowship.

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