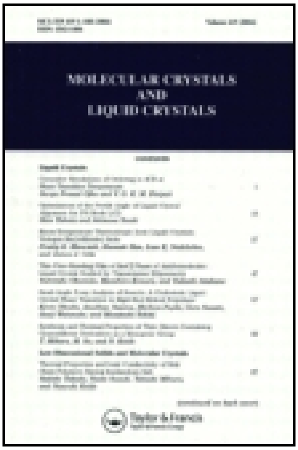

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Synthesis and Liquid Crystalline Properties of New Thermotropic Polyurethanes

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Synthesis and Liquid Crystalline Properties of New Thermotropic Polyurethanes

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The synthesis and liquid crystal behavior of new thermotropic polyurethanes derived from different mesogenic diols, alkylene di[4-(ω-hydroxyalkyloxy-4-oxybenzoyl)oxybenzoate]s, and 2,4-toluenediisocyanate are reported. Depending upon the chemical structure of the repeat unit, the polyurethanes formed either one or two mesophases extending over a fairly broad (>60 K) and accessible range of temperature ($T_i < 430$ K). A cybotactic nematic mesophase was identified in each polyurethane sample.

Keywords: liquid crystal polymer, thermotropic polyurethane, nematic mesophase, cybotactic nematic

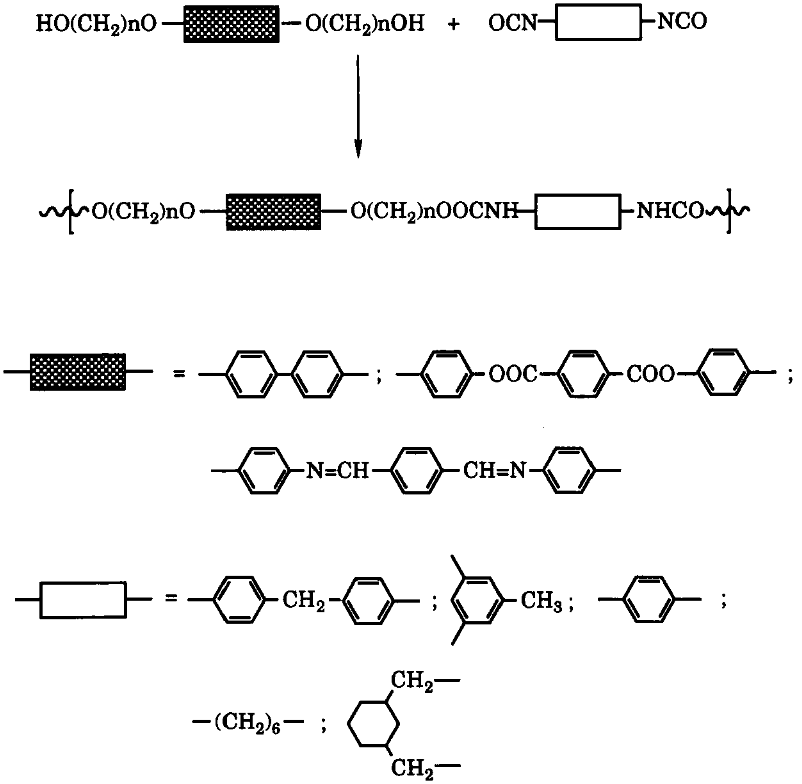
INTRODUCTION

The synthesis of liquid crystal (LC) main-chain polymers has greatly evolved over the last few years to include thermotropic polymers with a variety of structural features and linking groups.[1] Successful applications of these synthetic efforts have led to the commercialization of thermotropic polyesters, in addition to the already established lyotropic aramides. This has generated further stimulus for development of a new engineering with mesomorphic polymeric materials, which encompasses structural application, processing, blends and self-reinforcing composites of LC polymers.[2]

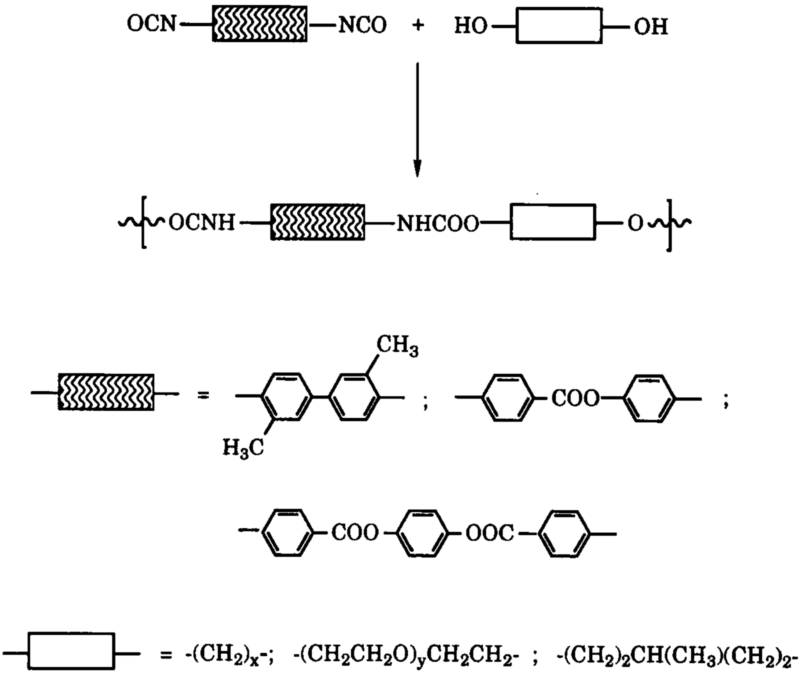
From a more fundamental standpoint, recent research activity has concentrated on both improving the understanding of structure-property relationships and assessing specific aspects of the physical character of LC polymers. Most of the attention has focused on a variety of thermotropic polyesters, including functional polymers such as poly(amino-esters),[3] poly(sulfide-esters),[4] or poly(ester-amides).[5] Less frequent examples of other thermotropic main-chain polymers consist of polyethers,[6] polyamides,[7] polyazomethines,[8] and comparatively little information is available on structurally analogous polyurethanes.

Limiting factors to a larger development of this last class of LC polymeric materials should be associated to more demanding conditions for their synthesis from somewhat unstable and hazardous intermediates and monomers, and their general relatively low thermal and chemical stability at elevated temperatures and in hostile environments. Occasional investigations on LC polyurethanes had started in the early eighties,[9] but only very recently was a more systematic approach to the synthesis of tailormade polyurethanes initiated by a few research groups.[10–25]

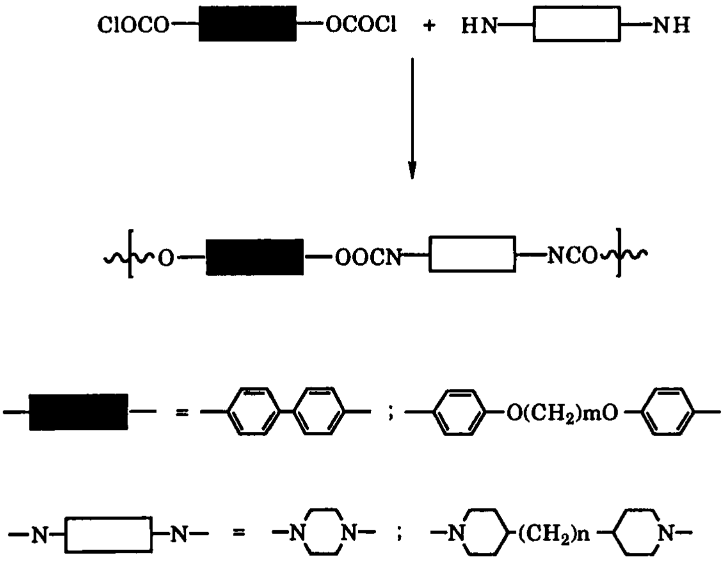
The preparation of thermotropic LC polyurethanes is performed essentially according to two synthetic pathways involving the stepwise polyaddition reaction of i) a mesogenic diol with an aliphatic or aromatic diisocyanate (Scheme 1), or



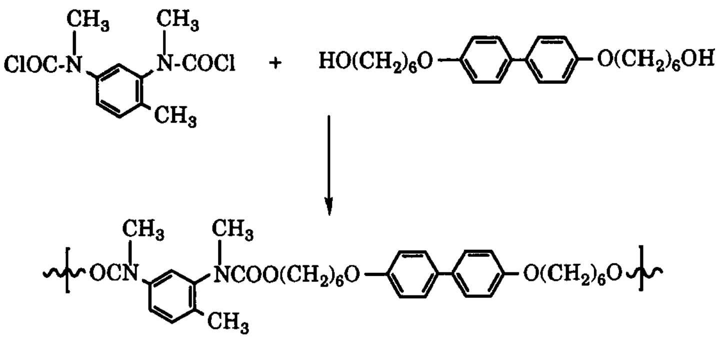
SCHEME 1 Synthesis of example LC polyurethanes from mesogenic diols and diisocyanates (from References 10–16, 18 and 25).



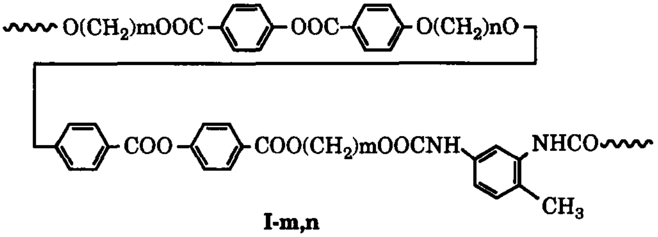
SCHEME 2 Synthesis of example LC polyurethanes from mesogenic diisocyanates and diols (from References 19–22).



SCHEME 3 Synthesis of example LC polyurethanes from diamines and dichloroformates (from References 23 and 24).



SCHEME 4 Synthesis of LC polyurethanes from a carbamoyl dichloride and a diol (from References 17 and 25).



I-m,n

m = 2, 4, 5, 6
n = 4, 6, 8, 10

CHART I

alternatively of ii) a mesogenic diisocyanate with typically an aliphatic diol (Scheme 2). A somewhat peculiar position is held by polyurethanes formally derived from N-carboxylic acids of secondary diamines that can be prepared by reaction of aromatic dichloroformates with cycloaliphatic diamines (Scheme 3), or more rarely, by reaction of an aromatic carbamoyl dichloride with a mesogen-containing diol (Scheme 4). Generally, these different polyurethane compositions were found to have rather high melting temperatures, especially due to intermolecular hydrogen bonding of the urethane moiety, which consequently determined a poor thermal stability and formation of mesophases over narrow ranges of temperatures below the decomposition point. Substitution at the urethane nitrogen atom, for instance *N*-methyl substitution in the example of Scheme 4, usually resulted in a depressed melting temperature with, however, a concomitant decrease in the isotropization temperature relative to corresponding unsubstituted polyurethanes.

We have started to investigate the synthesis and LC properties of new polyurethanes **I-m,n** derived from various mesogenic alkylene di[4-(ω-hydroxyalkyloxy-4-oxybenzoyl)oxybenzoate]s and 2,4-toluenediisocyanate. Structural design of these polymers was directed to reduce the melting temperature, while still retaining their LC behavior over a broad range of temperatures, by both introducing flexible segments of mismatching lengths along the polymer main-chain and creating structural irregularities which should prevent polymers from crystallizing.

The systematic study of these polymer systems can help address the fundamental question about the role of the urethane (—OCONH—) moiety in affecting the character and structure of LC polymers. It is pertinent, in fact, to speculate whether hydrogen bonding will enhance, or otherwise depress the propensity of LC polymers to give rise to stable mesophases, and how mesophase transition and ordering will be driven by the formation/destruction of such intermolecular interactions in condensed states.[26] On the other hand, it is also possible to envisage that thermotropic LC polyurethanes might find new applications, ranging from surface coating to formulation of polymer blends and self-reinforcing composites with, e.g., commercial aromatic and aliphatic polyamides and polyesters.

EXPERIMENTAL PART

Synthesis of Intermediates and Monomers

Commercially available 2,4-toluenediisocyanate was distilled under nitrogen atmosphere prior to use.

Full details of the synthesis and liquid crystalline properties of the mesogenic diols (**m,n**) will be described in detail elsewhere. As a typical example, the synthesis of 1,6-hexamethylene di[4-(6-hydroxyhexyloxy-4-oxybenzoyl)oxybenzoate] (**6,6**) is reported here.

6-Hydroxyhexyl 4-hydroxybenzoate. A mixture of 16.6 g (0.12 mol) of 4-hydroxybenzoic acid, 12.0 g (0.12 mol) of dry potassium bicarbonate and 13.7 g (0.10 mol) of 1-chloro-6-hydroxyhexane in 70 ml of dry dimethylsulfoxide was heated at 80°C for 5 h. It was then poured into 200 ml of cold, sodium chloride saturated water and kept at 5°C overnight. The crude product was then filtered, washed with cold water, dried, and crystallized from chloroform (yield 75%): mp 100°C.

^{1}H NMR (DMSO-d_6): δ (ppm from TMS) = 7.9 (dd, aromatic); 4.2 (*t*, $COOCH_2$); 3.6 (*t*, CH_2OH); 3.4 (bs, OH); 1.9–1.4 (m, $(CH_2)_4$).

4,4'-Hexanedioxydibenzoic acid. A solution of 9.80 g (0.040 mol) of 1,6-dibromohexane in 75 ml of dimethylsulfoxide was added dropwise with vigorous stirring to a solution of 12.4 (0.090 mol) of 4-hydroxybenzoic acid in 40 ml of 5 M sodium hydroxide at 90°C. After 5 h, the reaction mixture was poured into 200 ml of water at 60°C. The solution was then acidified with hydrochloric acid. The precipitate was isolated, washed with water, dried and purified by two crystallizations from ethylene glycol monomethylether (yield 56%): mp > 300°C (with decomposition).

1,6-Hexamethylene di[4-(6-hydroxyhexyloxy-4-oxybenzoyl)oxybenzoate] (**6,6**). A solution of 3.0 g (0.0084 mol) of 4,4'-hexanedioxydibenzoic acid, 2.0 ml (0.027 mol) of thionyl chloride and a catalytic amount of dimethylformamide in 50 ml of 1,2-dichloroethane was refluxed for 2 h. The solvent and excess thionyl chloride were then removed by azeotropic distillation with benzene. The solid residue was dissolved in 50 ml of anhydrous 1,2-dichloroethane and the solution was added to a solution containing 4.4 g (0.0168 mol) of 6-hydroxyhexyl 4-hydroxybenzoate and 1.0 g (0.0028) mol of benzyltributylammonium bromide in 50 ml of 1 M sodium hydroxide. The mixture was vigorously stirred for 15 min and then poured into 200 ml of methanol. The solid product obtained was washed with methanol, dried and crystallized from chloroform (yield 89%): mp 126°C.

^{1}H NMR (DMSO-d_6): δ = 8.1 (m, aromatic); 7.4 (dd, aromatic); 7.1 (dd, aromatic); 4.3 (*t*, $COOCH_2$); 4.1 (*t*, $ArOCH_2$); 3.7 (bs, OH); 3.4 (*t*, $\underline{CH_2}OH$); 1.9–1.3 (m, aliphatic).

Synthesis of Polyurethanes

In order to find the best experimental conditions, the polymerization reaction between 1,6-hexamethylene di[4-(6-hydroxyhexyloxy-4-oxybenzoyl)oxybenzoate] (**6,6**) and 2,4-toluenediisocyanate monomers was performed in dimethylsulphoxide, dimethylformamide, or chloroform, in the presence or not of the 1,4-diazabicyclo[2.2.2]octane catalyst, at different temperatures. The main results of these exploratory experiments are collected in Table I. Once the reaction conditions had been optimized, all polyurethanes were synthesized according to the experimental procedure that is here reported in detail for **I-6,6** sample.

1.00 g (1.25 mmol) of diol (**6,6**) and 0.22 g (1.25 mmol) of 2,4-toluenediisocyanate and 10 ml of chloroform freshly distilled over calcium hydride were introduced into a dry Schlenk tube. The polymerization mixture was heated to 90°C under a nitrogen atmosphere for 48 h. It was then diluted with 20 ml of chloroform, filtered and poured into 100 ml of methanol. The precipitated polymer was washed with methanol and purified by several precipitations from chloroform solution into methanol (yield 90%).

TABLE I

Polymerization of diol (**6,6**) and 2,4-toluenediisocyanate[a] under different experimental conditions: polymer yields and average molecular weights

Run	Solvent	[Catalyst][b] (mol l^{-1})	Temperature (°C)	Duration[c] (h)	Yield (%)	M_n[d] (g mol^{-1})
1	DMSO	-	120	24	84	3200
2	DMSO	-	120	24	84	1300
3	DMSO	-	120	24	84	8700
4	DMSO	0.05	120	1	72	1700
5	DMF	-	120	24	80	4300
6	DMF	-	120	24	80	7300
7	DMF	-	120	24	80	15800
8	DMF	0.05	120	1	65	1300
9	CHCl3	-	90	48	90	19500
10	CHCl3	-	90	48	90	20500
11	CHCl3	-	90	48	90	19000
12	CHCl3	0.05	90	1	65	1300

[a] Concentration of each monomer = 0.125 mol l^{-1}

[b] 1,4-diazabicyclo[2.2.2]octane (Dabco)

[c] The reaction was stopped when the infrared signal of the isocyanate group at 2375 cm^{-1} disappeared.

[d] By SEC, in chloroform at 30°C.

^{1}H NMR ($CDCl_3$): δ = 8.2 (m, aromatic); 7.3 (dd, aromatic); 7.0 (dd, aromatic); 4.3 (*t*, $ArCOOCH_2$); 4.1 (*t*, $ArOCH_2$); 3.7 (*t*, $NHCOOCH_2$); 2.0–1.3 (m, aliphatic).

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer with TMS as an internal reference. Infrared absorption spectra were recorded with a Perkin Elmer 1600 FT-IR spectrophotometer on KBr pellets or on thin films between KBr plates.

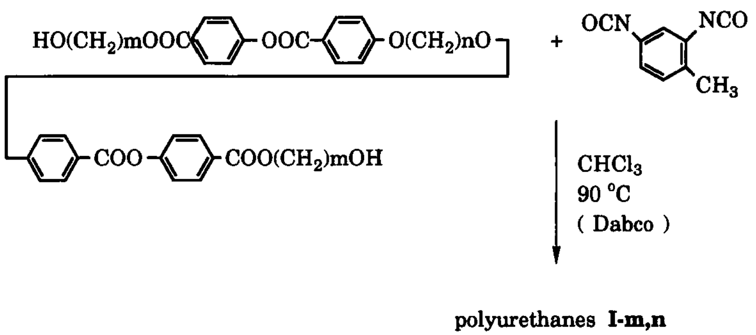
Average molecular weights were determined by size exclusion chromatography (SEC) of chloroform solutions with a 590 Waters chromatograph equipped with a Shodex KF-804 column. Polystyrene standard samples were used for the universal calibration method.

Differential scanning calorimetry (DSC) analyses were carried out under dry nitrogen flow with a Perkin Elmer DSC 7 apparatus. Samples of 5–10 g were employed. The temperature scale was calibrated against the melting temperature of indium. For the determination of the transition enthalpy, indium was used as a standard material. The transition temperatures were taken from the DSC traces of samples annealed by cooling from the isotropic melt, as corresponding to the maximum of the enthalpic peaks, at an heating rate of 10 K min^{-1}. Thermogravimetry analysis (TGA) was performed with a Mettler TG50 thermobalance at a scanning rate of 10°C min^{-1} from room temperature up to 500°C under dry nitrogen flow using alumina crucibles.

Optical microscopy observations were performed on polymer films between glass slides by means of a Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage at a scanning rate of 10 K min^{-1}. X-ray measurements were performed by using a Rigaku DENKI RV300 rotating anode generator equipped with a pin-hole flat camera. Diffraction diagrams were recorded, using Ni-filtered $CuK_{\alpha I}$ (λ = 1.54 Å) radiation, on powder specimens from room temperature up to the isotropization point. Fibers were oriented by pulling up with tweezers the viscous liquid crystal melt at different temperatures throughout the entire mesophase range, or the isotropic melt at 440 K. Their diffraction patterns were recorded at room temperature.

RESULTS AND DISCUSSION

Polyurethanes **I-m,n** were obtained by a stepwise polyaddition reaction of commercial 2,4-toluenediisocyanate with mesogenic diols (**m,n**) consisting of two *p*-oxybenzoyl diads interconnected by a polymethylene segment containing *n* (*n* = 4, 6, 8, or 10) methylene groups and flanked by two linear ω-hydroxyalkyl segments containing *m* (*m* = 2, 4, 5, or 6) methylene groups (Scheme 5). To optimize the polymerization reaction, several orienting experiments were performed by reacting 1,6-hexamethylene di[4-(6-hydroxyhexyloxy-4-oxybenzoyl)oxybenzoate] (**6,6**) and 2,4-toluenediisocyanate in various conditions. The results are collected in Table I. When the polymerization reactions were carried out in DMSO or DMF at 120°C for 24 h without any added catalyst, a substantial irreproducibility of the molecular



SCHEME 5 Synthesis of LC polyurethanes **I-m,n** from 2,4-toluenediisocyanate and alkylene di[4-(ω-hydroxyalkyloxy-4-oxybenzoyl)oxybenzoate]s.

characteristics of the polymers was observed in successive preparations and sometimes an induction period was detected. These effects are probably due to the presence of adventitious water in these solvents, which is able to react with the diisocyanate monomer leading to reactive and unreactive by-products. The addition of catalytic quantities of 1,4-diazabicyclo[2.2.2]octane (Dabco) considerably increased the reaction rate, but only oligomeric products were obtained. Polymeric products with reproducible high molecular weights were obtained by running the reactions at 90°C in dry chloroform in a nitrogen atmosphere (Runs 9–11 in Table I). Accordingly, all polymers **I-m,n** were prepared under the above experimental conditions and purified by repeated precipitations from chloroform solution into methanol. All the prepared polymers have good solubilities in chlorinated organic solvents, such as chloroform and 1,2-dichloroethane, as well as in hot 1,4-dioxane and are characterized by average number molecular weight (M_n) values ranging from 9000 to 32000 gmol^{-1} and polydispersity indexes (M_w/M_n) in the range 1.6–2.5 as determined by SEC.

Polyurethanes **I-m,n** are rather thermally stable as estimated by thermogravimetry under nitrogen atmosphere. The onset of thermal degradation occurs in each case at temperatures above 260–270°C, a 10% decomposition being reached at 320–340°C (heating rate of 10°C min^{-1}). Their thermal and LC behavior is rather complex (Table II). At room temperature, all of the **I-m,n** samples are amorphous and do not crystallize even after prolonged annealing treatments at temperatures above the glass transition. Accordingly, their LC behavior extends between the glass transition (T_g) and the transition to the isotropic melt (T_i). The DSC heating curves of **I-6,4**, **I-6,10** and **I-2,6** show a step due to the glass transition and an endothermic peak attributed to the transition to the isotropic melt. Both transitions are reversible on cooling. A supercooling degree of 8–10 K is observed for the mesophase transition. X-ray diffraction patterns of powder samples obtained from room temperature up to the isotropization point are only constituted by an outer broad halo corresponding to an intermolecular distance $D \approx 4.4$ Å, typical of the nematic mesophase.

Samples **I-6,8**, **I-6,6**, **I-5,6** and **I-4,6** show similar thermal behavior which is illustrated for **I-6,8** in Figure 1, as a typical example. On heating, the glass transition at 322 K and two endothermic peaks at 390 K and 395 K are observed. Both

TABLE II

Liquid-crystalline properties of polyurethanes **I-m,n**

Sample	M_n[a] (g mol^{-1})	M_w/M_n[a]	T_g (K)	T_{LC}[b] (K)	T_i (K)	ΔS_i (Jmol^{-1}K^{-1})	ΔS_{LC}[b] (Jmol^{-1}K^{-1})
I-6,4	16000	1.9	337	-	431	25.5	-
I-6,6	24000	2.0	333	412	415	15.9	10.7
I-6,8	9000	2.0	322	390	395	15.7	6.4
I-6,10	18000	2.2	328	-	394	36.0	-
I-2,6	32000	2.5	362	-	424	8.7	-
I-4,6	9000	1.6	337	398	418	13.5	2.9
I-5,6	11000	2.0	334	411	418	16.0	10.7

[a] By SEC, in chloroform at 30°C.

[b] Intermediate mesophase transition.

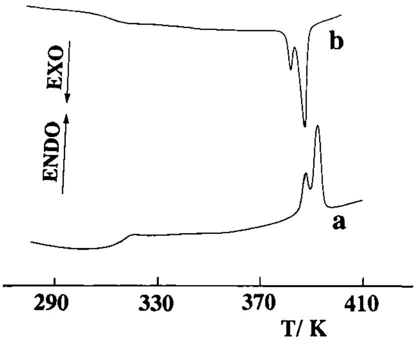


FIGURE 1 DSC second heating (a) and cooling (b) curves (10 K min^{-1}) of polyurethane **I-6,8**.

transitions are reversible on cooling with supercooling degrees of 5–8 K. The x-ray diffraction spectra on unoriented samples, recorded at temperatures within the existence range of the higher temperature mesophase are constituted by an outer broad halo only, thus indicating the presence of a nematic mesophase for these polymers too. However, the x-ray diffraction spectra do not change at temperatures within the range of existence of the lower temperature nematic mesophase. To gain more structural information, an x-ray study was performed for all the polymers **I-m,n** on oriented fibers pulled out of the mesophases at different temperatures and rapidly quenched to room temperature. The x-ray patterns of the oriented mesophases of **I-6,4**, **I-6,10** and **I-2,6** are very similar to each other and characterized by a rather complex pattern (Figures 2(a)–(c)). The anisotropy shown in the x-ray pattern clearly demonstrates that a high degree of molecular orientation can be achieved by drawing fibers from the mesophase. The diffraction pattern consists of two symmetrically placed equatorial wide angle crescents corresponding to $D \approx 4.3$ Å and four diffuse small angle spots roughly equidistant from the origin and forming pairs on a straight line making an angle $\beta \approx 41°$ with respect to the equator

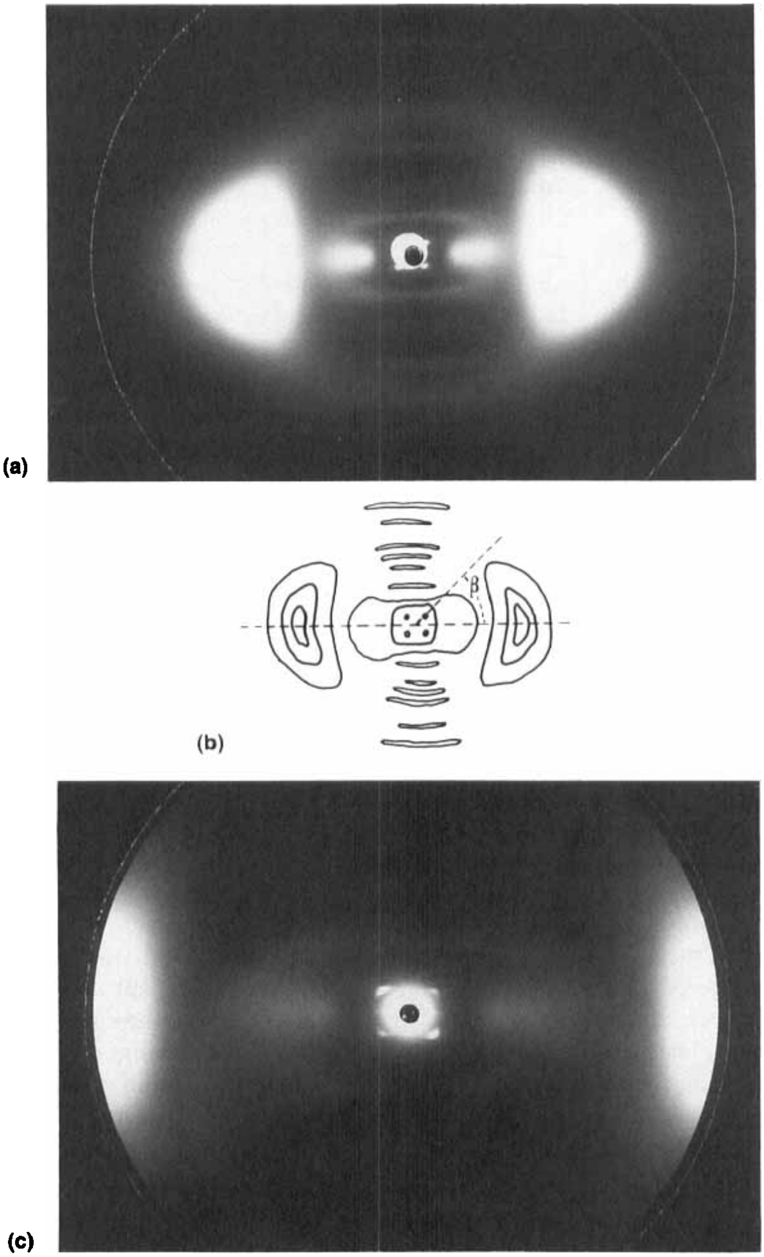


FIGURE 2 Fiber x-ray diffraction pattern (vertical fiber axis) at room temperature of the cybotactic nematic phase of polyurethane **I-6,4** (a) (sample to detector distance = 75 mm) and (b) schematic of its intensity contour map; (c) same as in (a) (sample to detector distance = 144 mm).

(Figure 2(b), (c)). These spots suggest the existence of smectic C fluctuations in the nematic mesophase.[27–29] Similar x-ray patterns have been observed in other main-chain LC polymers, including polyesters[30] and polyurethanes[17] and are indicative of a cybotactic nematic array involving a skewing of the mesogenic groups between polymer chains presumably driven by hydrogen bonding interactions. In addition, a small portion of the diffraction signals is localized on diffuse lines perpendicular to the fiber axis (Figure 2(a)). These diffuse lines result from the linear correlation of the polymer repeat units along the chain director and the short range correlations between polymer chains normal to the director.[31] According to the DeVries structural model of cybotactic micellar clusters,[27] from the values of the tilt angle $\beta \approx 41°$ and of the spacing of the innermost off-meridional reflection $d = 36.4$ Å we calculate for polyurethane **I-6,4** the length $l = 55.5$ Å of the repeat unit in the cybotactic micelle.[30] This value is in agreement with the length $L \approx 56$ Å of the repeat unit in the fully extended all-*trans* conformation of both spacer segments calculated using Dreiding stereomodels.

The x-ray patterns of the oriented mesophases of samples **I-6,8**, **I-6,6**, **I-5,6** and **I-4,6** produced by drawing fibers at temperatures inside the lower temperature

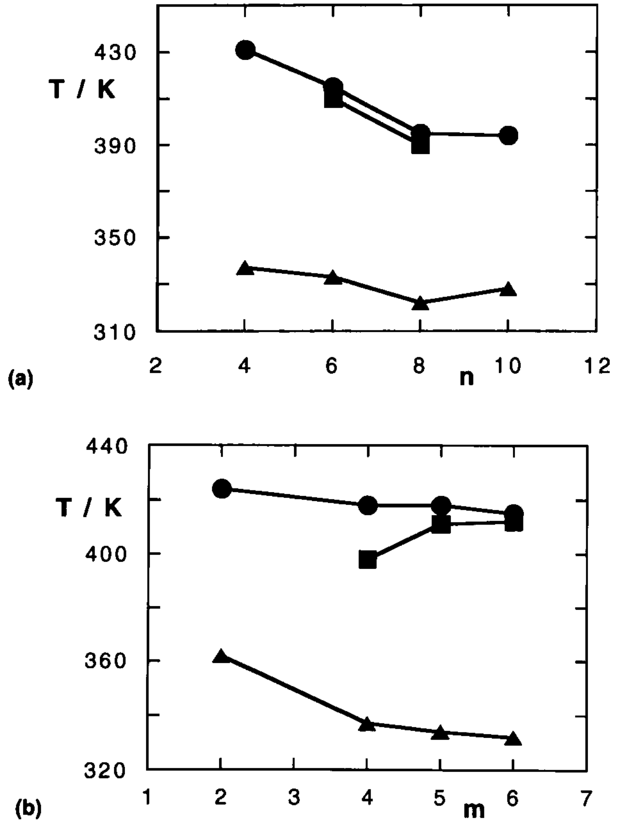


FIGURE 3 Trends of the glass (▲), isotropization (●), and intermediate mesophase transition (■) temperatures for polyurethanes **I-m,n** as a function of the number *n* ($m = 6$) (a) and *m* ($n = 6$) (b) of methylene units in the alkylene segments.

mesophase region are characteristic of a cybotactic nematic mesophase as for the above polymers. The x-ray diagrams of fibers oriented from the higher temperature mesophase are also typical of a cybotactic nematic phase and do not change with annealing the fibers at different temperatures within the whole mesophase range. Therefore, the collected x-ray diffraction data of both powder and fiber samples strongly point toward the formation of two sequential nematic phases differing in their fine structure or degree of order possibly promoted by hydrogen bonding between urethane groups. The precise nature of the higher temperature mesophase of these polymers remains to be further elucidated and the complete analysis of the x-ray diffraction spectra of the oriented mesophases of polymers **I-m,n** will be the subject of a forthcoming paper. Figure 3(a), (b) illustrates the dependence of the transition temperatures of polymers **I-m,n** on the number n and m of methylene units in the alkylene segments. The nematic to isotropic and glass transition temperatures regularly decrease with increasing numbers n (keeping m constant, m = 6) or m (keeping n constant, n = 6) of methylene units, whereas the transition temperatures relevant to the lower temperature mesophase (T_{LC}) vary in a somewhat irregular fashion.

CONCLUSION

Several new liquid crystalline polyurethanes forming a cybotactic nematic mesophase were prepared. Incorporation of mixed spacer segments and bulky 2,4-toluenediyl residues introduces sufficient structural irregularities along the polymer chain, including the random placement of the methyl group, thus preventing polyurethanes from crystallizing. In addition, we suggest that their ability to form (intermolecular) hydrogen bonding can play a role in enhancing the lateral packing strength between adjacent chains thus stabilizing the cybotactic nematic mesophase. This conclusion should be further supported by temperature dependent FT-IR investigations of the polyurethanes and their *N*-substituted analogs.

The independent variations of the numbers n and m of methylene units in the flexible spacers and of the nature of the diisocyanate residues will allow a large variety of polyurethanes with extremely differentiated thermal and physical properties to be obtained.

Acknowledgment

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