

Liquid crystal copolyethers with mixed mesogenic units and flexible spacers

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SUMMARY

Liquid crystalline copolyethers were prepared from monomer pairs selected from biphenol (BP), dihydroxy- α -methylstilbene (DHMS), and 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene (DMAz) which were copolymerized with either dibromononane or dibromodecane spacers by phase transfer catalysis. Nematic LC mesophases were observed for most copolymers, but some exhibited dual mesophases. Smectic to nematic transitions were found in polymers with intermediate ratios of DMAz and DHMS with the nonamethylene spacer. These polymers showed excellent solubility in THF and CHCl_3 . The longest mesophase range which consisted of two mesophases was found in a polymer composed of a 4:1 ratio of DHMS to BP and a nonane spacer.

INTRODUCTION

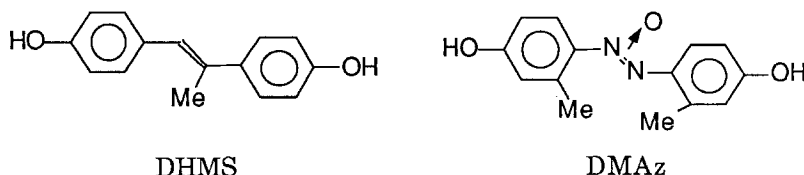
Thermotropic polymers have recently achieved commercialization and at the same time continue to attract interest in the basic research community. While many papers and reviews have been published concerning the combination of both mesogenic and non-mesogenic units in copolyesters (1-4) and copolyethers (5), studies of mixed mesogenic cores in liquid crystal polymers have been virtually restricted to aromatic liquid crystalline (LC) copolyesters. Little research has been performed on linear polymers with mixed mesogenic groups of well-defined structure.

Yoo and Kim (6) have introduced mixed mesogenic units to produce polyesters with two mesophases by reacting selected bisphenols with terephthaloyl chloride. It should be noted that while the authors reported that these copolymers contained only two mesogenic groups, their polymers in fact contained three mesogenic structures due to the manner of copolymerization used. It is interesting that despite the irregularities in their structures these copolymers should possess a smectic to nematic transition.

Several recent studies have demonstrated the rapidity with which such LC polyesters can rearrange in the melt state due to transesterification (7). This property is of special concern with LC polyesters where transesterification can lead to inconclusive measurements caused by exchange between labelled and unlabelled chains (8). Liquid crystalline polymers which resist rearrangement in the melt are therefore of significant interest as model systems. Recently a great deal of research, particularly on the part of Percec and coworkers, has concentrated on the synthesis of new, readily soluble LC polyethers - polymers which are not subject to such rearrangement (9,10).

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The goals of the research reported here were to synthesize structurally stable LC copolyethers with mixed mesogenic groups and to determine the composition of mesogenic cores which afford both liquid crystallinity and good solubility. An additional objective of this research was to explore the effects of mixed mesogenic groups on the types and numbers of mesophases found in these copolymers. Mesogenic comonomer pairs were selected from 4,4'-biphenol (BP), dihydroxy- α -methylstilbene (DHMS), and 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene (DMAz) and copolymerized with either dibromononane or dibromodecane spacers by phase transfer catalysis. Biphenol has been observed to produce smectic polyethers (11) whereas DHMS and DMAz produce nematic polyethers (10, 12). By combining both types of mesogenic groups it was hoped to produce soluble copolyethers which exhibit a smectic to nematic transition.



EXPERIMENTAL

1. Synthesis of Monomers The procedure used to prepare dihydroxy- α -methylstilbene (DHMS) was similar to that reported earlier by Percec and coworkers (10,11). The synthesis of 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene (DMAz) was made from the appropriate nitrosophenol (13) using a newer procedure (14) which afforded higher yields in the synthesis of nitroso-*m*-cresol. Dry reaction conditions in the synthesis of DMAz improved yield by an additional 17%.

To a mixture of 12.17 g (112.5 mmol) *m*-cresol in 85 ml of 95% ethanol under nitrogen at 0°C, 85 ml of concentrated HCl was added slowly dropwise, and then 14.51 g (170.4 mmol) potassium nitrite was added every five minutes in one gram aliquots. The mixture was poured into 1.5 liters of cold water, resulting in a yellow precipitate. The product was filtered, washed with 250 ml cold water, and dried *in vacuo*. TLC in 50% EtOAc/petroleum ether showed one spot, and the yield was 12.37 g (80.2%) yellow powder.

For the preparation of DMAz, tosyl chloride was used as obtained (Aldrich 99+%); pyridine was refluxed under nitrogen with barium oxide for two hours, then distilled and dried over 3Å molecular sieves. Under nitrogen, 100 ml pyridine was added dropwise by double-ended needle to separate flasks containing 12.3 g (89.7 mmol) of nitroso-*m*-cresol and 13.15 g (68.9 mmol) tosyl chloride. The tosylate solution was transferred dropwise while cooling in an ice-water bath. Stirring under nitrogen was maintained for 15 hours, and the ice bath was allowed to reach room temperature. The reaction mixture was then heated to 100°C until an exothermic reaction occurred. A dark, red-black mixture was cooled to room temperature, placed in an ice water bath, and slowly neutralized dropwise with 150 ml of 25 volume-% sulfuric acid. This mixture was divided into three parts, extracted three times with equal amounts of anhydrous diethyl ether, dried over magnesium sulfate, filtered, and the solvent evaporated. The black viscous mass remaining in the reaction flask was also extracted with ether. The yellow-orange crude product was recrystallized from 25% EtOH/water. Product was then stirred in chloroform

overnight, filtered, and recrystallized, yielding 4.47 g (38%) orange-yellow powder.

2. Synthesis of Polymers Nitrobenzene was used as obtained (Aldrich 99+%), as was biphenol (BP) and tetrabutylammonium hydrogen sulfate (TBAH). A typical synthesis of a mixed mesogen copolyether is as follows. Under nitrogen, 0.22 g (0.97 mmol) DHMS, 0.25 g (0.97 mmol) DMAz, and 0.12 g (0.34 mmol) TBAH were added to a room temperature 25 ml solution of 50% by wt. sodium hydroxide in a flask equipped with a mechanical stirrer. A solution of 0.55 g (1.94 mmol) 1,9-dibromononane in 30 ml nitrobenzene was then added to the above mixture and stirring maintained 15 hours at 85-95°C. The reaction was allowed to cool, and the aqueous layer was neutralized with 5N HCl and decanted off. The organic layer was precipitated in methanol, and the polymer washed with methanol and water. Polymer was precipitated by dissolving into a minimal amount of chloroform and pouring into methanol.

3. Characterization Thermal transition temperatures were obtained on a Perkin Elmer DSC-2C at heating and cooling rates of 20°C/min. Liquid crystal mesophases were examined by Leitz polarizing optical microscope at 200X magnification equipped with a Mettler FP-52 hot stage and a Canon AE-1 35 mm camera. Compositions of the monomers and polymers were determined by Varian XL-200 ¹H NMR on eight polymers soluble in chloroform-d₆. Inherent viscosities were measured in a 1:1 mixture of phenol/*o*-dichlorobenzene. Number and weight average molecular weights were determined for THF soluble polymers by GPC using RI and UV detectors with Ultrastyrigel™ columns of 500, 10³, 10⁴, and 10⁶ Å pore sizes calibrated with monodisperse polystyrene standards.

RESULTS AND DISCUSSION

Liquid crystalline polyethers are a relatively recent addition to the growing number of polymers which exhibit liquid crystallinity. In our work, a series of LC copolyethers combining pairs of these mesogenic groups were synthesized and the properties of these polymers are described below.

DHMS, DMAz and BP have been used extensively in LC polyesters and polycarbonates (1). In the case of polyethers, copolymerizations have been performed with DHMS using mixed spacers to produce nematic polymers with very broad liquid crystalline phases, and good solubilities (5, 15, 16). DHMS-nonane and DHMS-decane homopolymers synthesized in our laboratory possessed nematic mesophases and only partial solubility in THF. Biphenol has been employed in copolyethers with mixed spacers, and reportedly produced smectic polymers with limited solubility (17) in agreement with our results. Interestingly, neither the BP-decane nor the DHMS-decane homopolymers produced for this study have to the best of our knowledge been previously reported.

Polyethers of DMAz and aliphatic spacers were soluble in 1:1 tetrachloroethane/*m*-cresol and have been found to be nematic (12). Monotropic nematic LC phases were found for lower molecular weight samples. Homopolyethers with nonane and decane were reported to be soluble only in a mixture of *m*-cresol and tetrachloroethane (12). We have found that these nematic polymers also have solubility in THF.

1. Copolyethers of BP and DHMS Table 1 lists the properties of the LC polymers synthesized using biphenol and dihydroxy- α -methyl stilbene. One of the polymers of this series (described below) showed a dual mesophase. In contrast, polymers with 84 mol-% biphenol showed little solubility and either were not liquid crystalline (BH9d) or possessed a very short mesophase (BH10e).

Table 1 - Properties of Copolyethers of BP and DHMS

<u>Sample</u>	<u>% BP</u>	<u>T_m</u> (°C)	<u>T_i</u> (°C)	<u>[η]</u> (dl/g)	<u>Solubility</u>
*	0	130	148	--	--
BH9a	10	119	139	0.37	phenol/dcb
BH9b‡	16	107	180	0.45	phenol/dcb
BH9c	50	167	187	0.90	phenol/dcb
BH9d	84	--	197	--	insoluble
*	100	190	205	--	--
BH10a	0	178	230	--	phenol/dcb
BH10b	10	173	183	0.24	phenol/dcb
BH10c	16	173	188	0.29	phenol/dcb
BH10d	50	--	194	--	insoluble
BH10e	84	208	216	--	insoluble
BH10f	100	270	305	--	insoluble

* Data from Reference (18); ‡ Evidence of s \rightarrow n transition at 116°C; dcb = o-dichlorobenzene

Polymers with increased DHMS concentration varied considerably in mesophase behavior. A 1:1 ratio of DHMS:BP (BH9c) showed reproducible heating and cooling curves with both colorful "oil-streak" textures, and stir opalescence. The polymer with the same mesogenic group composition and decane spacer (BH10d) showed reproducible heating and cooling curves. The sample was very viscous and difficult to characterize by microscopy; however, the cooling curve revealed several other transitions that may have been associated with a several mesophases.

Polymers with 16 mol-% BP showed nematic textures near clearing. The polymer with nonane spacer (BH9b) exhibited reproducible melting and clearing transitions at 107°C and 180°C by microscopy, and the DSC trace showed a peak corresponding to an additional transition at 118°C. Confirmation of the second mesophase for this polymer was observed by microscopy, where at 118°C the melt changed from thread-like to "hazy" in appearance. The polymer with the decane spacer (BH10c) showed no second mesophase.

Polymers with 10 mol-% BP possessed obvious nematic mesophases immediately prior to crystallization. The polymer with the nonane spacer (BH9a) possessed a longer mesophase and lower melting transitions than the polymer with the decane spacer (BH10b), which is in qualitative agreement with a presumed odd-even effect.

The relationship between thermal transitions on heating and polymer compositions is summarized in Figure 1. For polymers with either spacer length, thermal transitions increased with higher concentrations of biphenol,

and a monotropic mesophase was obtained for one polymer of each series. The range of the mesophase was largest for polymers containing 84 mol-% DHMS and decreased with higher concentrations of this mesogenic group. The data on the homopolymer of DHMS and dibromononane was previously reported by Percec and coworkers (18).

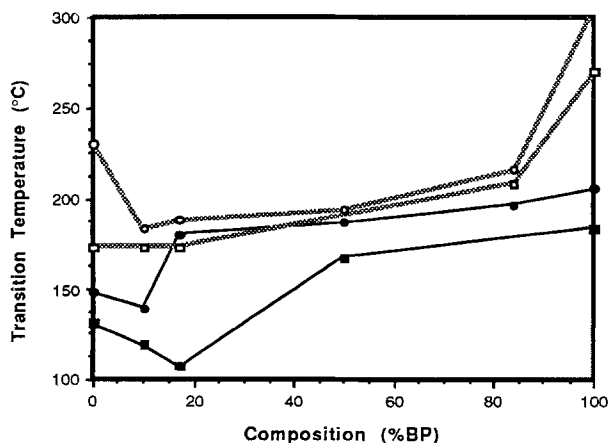
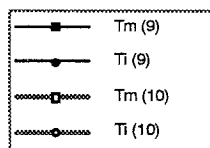


Figure 1. Plot of Composition versus Transition Temperature for BP-DHMS Copolymers



2. Copolymers of DMAz and BP The properties of copolyethers of 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene and biphenol are listed in Table 2. Only one of the copolymers in this series showed a dual enantiotropic mesophase (BM10d). Copolymers with 20 mol-% BP showed nematic textures. The polymer with the decamethylene spacer, BM10b, possessed wider mesophases with higher melting transitions. Polymers with a 1:1 ratio of mesogenic groups had reproducible monotropic nematic LC phases. The DSC cooling trace of BM10c showed the presence of a monotropic intermediate transition between clearing and melting indicating the possibility of a second mesophase.

Table 2 - Properties of Copolymers of DMAz and BP

Sample	% BP	T_m (°C)	T_i (°C)	M_n	Solubility
BM9a	0	102	113	12 200	THF or CHCl_3
BM9b	20	92	122	3 400*	THF or CHCl_3
BM9c	50	--	153	9 000	THF or CHCl_3
BM9d	80	173	183	8 800	THF or CHCl_3
BM10a	0	133	146	5 000*	THF or CHCl_3
BM10b	20	117	153	14 400	THF or CHCl_3
BM10c	50	--	140	5 700*	THF or CHCl_3
BM10d‡	80	159	208	--	insoluble

* M_n of THF soluble fraction; ‡ Evidence of s \rightarrow n transition at 195°C

Polymers with a composition of 80 mol-% BP showed complex mesophase behavior with no stir opalescence. Three distinct peaks were obtained by DSC for the polymer with the decamethylene spacer (BM10d). Similar multiphase behavior has been reported for DSC response of biphenol homopolymers with

aliphatic spacers (11). The thermal transitions of both polymers were in agreement with a presumed odd-even effect.

The relationship between thermal transitions on heating and copolymer composition is summarized in Figure 2. Transitions increased with higher compositions of biphenol, and a monotropic mesophase resulted in polymers with a 1:1 ratio of the mesogenic groups in each series. The temperature range of the mesophase reached a maximum with concentrations of 20 mol-% BP and decreased with higher amounts of this mesogenic group. Narrow mesophases were obtained with compositions of greater than 50 mol-% BP. An almost linear relationship between T_i and composition was found for polymers containing the nonane spacer.

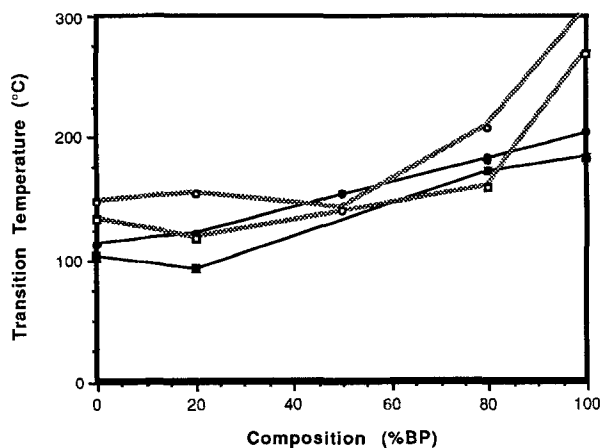
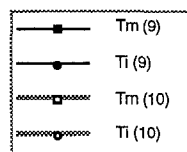


Figure 2. Plot of Composition versus Transition Temperature for DMAz-BP Copolymers



3. Copolymers of DMAz and DHMS The most interesting polymers investigated in this study were copolymers of dihydroxy- α -methyl stilbene and 2,2'-dimethyl-4,4'-dihydroxyazoxybenzene, the properties of which are listed in Table 3. The melts of both polymers with compositions of 80 mol-% DHMS possessed nematic textures. However, MH10c had the shorter mesophase and higher thermal transitions. MH9c had an additional reproducible mesophase on both heating and cooling where the melt became hazy and viscous as shown in Fig. 3.

Table 3 - Properties of Copolymers of DMAz and DHMS

Sample	% DHMS	T _m (°C)	T _{s→n} (°C)	T _i (°C)	M _n	Solubility
MH9a	20	94	120	166	26 400	THF or CHCl ₃
MH9b	50	58	86	153	28 400	THF or CHCl ₃
MH9c	80	94	--	133	14 800	THF or CHCl ₃
MH10a	20	103	--	155	13 500	THF or CHCl ₃
MH10b	50	130	--	158	15 200	THF or CHCl ₃
MH10c	80	160	--	177	--	phenol/dcb*

* dcb = o-dichlorobenzene

Polymers with a 1:1 ratio of mesogens, MH9b, and MH10b possessed

nematic textures and low viscosity melts near clearing. The polymer with the decamethylene spacer, MH10b, had higher and shorter thermal transitions. The polymer with the nonane spacer, MH9b, had no crystallization transition on cooling; however, this polymer showed another reproducible phase on heating and cooling where the melt exhibited a textural change which we believe is a smectic to nematic transition.

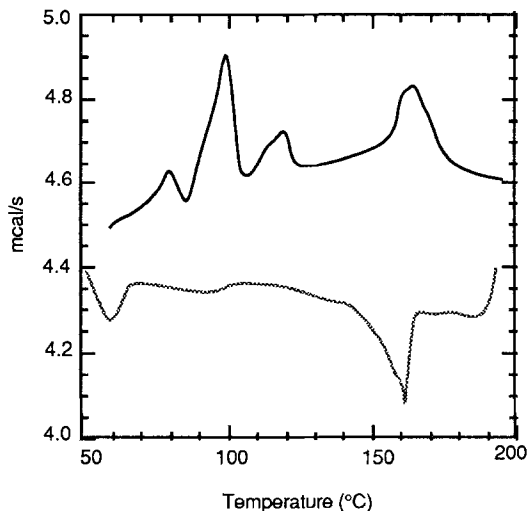


Figure 3 - DSC Trace for Polymer MH9c (heating and cooling)

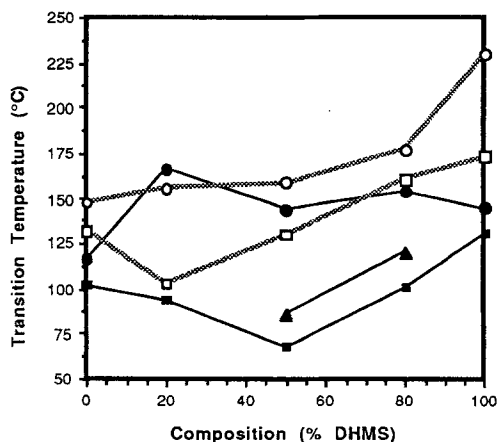


Figure 4. Plot of Composition versus Transition Temperature for DMAz-DHMS Copolymers

Both polymers with 20 mol-% DHMS possessed melts with nematic thread-like textures, and stir opalescence. However, neither polymer exhibited a second mesophase. Polymer MH10a had higher phase transitions, which was in agreement with the odd-even effect, but both polymers possessed similar mesophase temperature ranges.

The relationship between thermal transitions on heating and copolymer composition is summarized in Figure 4. For polymers with the nonane spacer, the range of the mesophase was greatest with a 1:1 ratio of mesogenic groups, and the second mesophase transition paralleled melting temperatures. For polymers with the decamethylene spacer, the largest mesophase range was obtained with a composition of 20 mol-% DHMS.

CONCLUSIONS

Incorporation of two mesogenic groups into liquid crystal polymers in some cases produced polymers with dual mesophase behavior. Most copolymers exhibited nematic mesophases, except for those copolymers with high biphenol contents. Both smectic and nematic transitions were obtained in certain copolymers. Excellent solubility in THF and chloroform was observed for most copolymers containing the DMAz mesogenic group. Variable temperature x-ray diffraction studies are underway to better understand the nature of the intermediate transitions observed in these copolymers.

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