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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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James V. Crivello^a; Margret Deptolla^b; Helmut Ringsdorf^b

^a General Electric Corporate Research and Development, Schenectady, New York, U.S.A. ^b Institut für Organische Chemie, Universität Mainz, Mainz, F.R. Germany

To cite this Article Crivello, James V. , Deptolla, Margret and Ringsdorf, Helmut(1988) 'The synthesis and characterization of side-chain liquid crystal polymers based on polystyrene and poly- α -methystyrene', *Liquid Crystals*, 3: 2, 235 – 247

To link to this Article: DOI: 10.1080/02678298808086370

URL: <http://dx.doi.org/10.1080/02678298808086370>

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The synthesis and characterization of side-chain liquid crystal polymers based on polystyrene and poly- α -methylstyrene

by JAMES V. CRIVELLO

General Electric Corporate Research and Development, P.O. Box 8, Schenectady,
New York 12301, U.S.A.

and MARGRET DEPTOLLA and HELMUT RINGSDORF

Institut für Organische Chemie, Universität Mainz, J.-J.-Becher-Weg 18-20,
D-6500 Mainz, F.R. Germany

(Received 30 June 1987; accepted 5 August 1987)

The polymer analogous synthesis of new liquid-crystalline side-chain polymers having polystyrene and poly- α -methylstyrene backbones bearing pendant azobenzene mesogenic groups is described. The effects of various spacer lengths on the mesophase types were examined. Several liquid-crystalline copolymers were also prepared and their mesophase types determined.

1. Introduction

One of the basic conditions for the synthesis of thermotropic liquid crystal side-chain polymers is that the main chain be in the liquid state to enable it to adopt a statistical chain conformation [1]. This allows the side-chain mesogens sufficient mobility to assume an anisotropic orientation without steric hindrance from the main chain. Accordingly, during the past decade, research in this field has centred on attaching mesogenic groups to the backbones of flexible polymers with low glass transition temperatures through the use of spacer groups. Thus, liquid crystal side-chain polymers based on acrylates [2-4], methacrylates [5, 6], itaconates [7] and polydimethylsiloxanes [8-10] have received much attention.

At the outset of the present work, there had been no report of side-chain liquid crystal polymers based on the relatively stiff polystyrene and poly- α -methylstyrene backbones with their high glass transitions. However, while this manuscript was in preparation, a paper appeared by Percec *et al.* [11] describing the preparation of liquid-crystalline poly(p-vinylbenzylether)s. To us, the possibility of preparing liquid-crystalline polystyrene and poly- α -methylstyrene polymers appeared promising since it has been observed that substituted polystyrenes and poly- α -methylstyrenes bearing 4-*n*-alkyl or 4-*n*-alkoxy groups display markedly lower glass transitions than their unsubstituted counterparts [12, 13]. This suggested that a plasticizing effect caused by the presence of such moieties in the spacer groups of the mesogens may lead to a corresponding decrease in the glass transition of the main chain, with resulting enhancement of their liquid-crystalline characteristics. In addition, it has been shown that even rigid-rod and semiflexible main chain polyesters with high glass transitions, bearing lateral mesogenic groups, form interesting classes of liquid crystal side-chain polymers [14].

In the light of these observations, it was decided to undertake the synthesis of polystyrene and poly- α -methylstyrene main chain polymers bearing lateral mesogenic

groups and to determine whether such polymers exhibit enantiotropic liquid crystal properties.

2. Experimental

2.1. Materials

Poly-4-hydroxystyrene was supplied by the Maruzen Oil Company (Japan) and had a \bar{M}_N of 27 000 g mol⁻¹. 4-Hydroxy-4'-cyanoazobenzene [15] and 4-acetoxystyrene [16] were prepared as described previously. Bisphenol-A, 4-hydroxyacetophenone, and α, ω -dibromoalkanes were purchased from the Aldrich Chemical Company.

2.2. Synthesis of 4(ω -bromoalkoxy)-4'-cyanoazobenzenes

Into a 500 ml single-neck, round-bottomed flask were placed 0.04 mol of 4-hydroxy-4'-cyanoazobenzene and 0.4 mol of α, ω -dibromoalkane, 0.29 mol (40 g) of powdered potassium carbonate and 160 ml of acetone. The reaction mixture was refluxed for 20 h and then cooled and filtered to remove potassium bromide and excess potassium carbonate. The acetone was partially removed using a rotary evaporator, and the reaction mixture was cooled to induce crystallization. The crystalline product was suction filtered and washed thoroughly with *n*-hexane. Thin layer chromatography using a 9 : 1 mixture of chloroform and methanol revealed the presence of only one azobenzene-containing product. Yields ranged from 40 to 77%. After recrystallization from absolute ethanol or a mixture of water and ethanol, the product was dried in a vacuum oven.

2.3. Preparation of poly-4-hydroxystyrene

To 3.24 g (0.02 mol) of 4-acetoxystyrene in a dry 25 ml two-necked flask fitted with rubber septa and a magnetic stirrer were added 0.3 g of 2,2'-azo-bis-isobutyronitrile (AIBN). The reaction mixture was purged thoroughly with nitrogen and then heated in an oil bath at 75–80°C for 3.5 h. The solid polymer was dissolved in 15 ml of methylene dichloride and precipitated into 200 ml of methanol. After filtering and washing with methanol, the polymer was dried in a vacuum oven to give 1.90 g (58.6% of the theoretical yield) of poly-4-acetoxystyrene.

To 1.134 g (0.007 mol) of this polymer dissolved in 100 ml dioxane, was added 6 ml (0.12 mol) of hydrazine hydrate. The mixture was stirred for 4 h at room temperature, and then the polymer was poured into 200 ml of water to precipitate the hydrolysed polymer. After vacuum drying, 0.78 g (94 per cent of the theoretical yield) of poly-4-hydroxystyrene was obtained which corresponded in all respects to that reported in the literature [17].

2.4. Preparation of poly-4-hydroxy- α -methylstyrene

Into a 250 ml round-bottomed flask fitted with a distillation head, air condenser and receiver were placed 50 g of bisphenol-A and 0.5 g of sodium hydroxide. The mixture was heated slowly to 250°C under nitrogen, and the products, a mixture of phenol and 4-isopropenylphenol (46 g) were collected. To this mixture in a 150 ml flask equipped with a magnetic stirrer and a reflux condenser were added 51 g (0.5 mol) of acetic anhydride and 0.25 ml of pyridine. The acetylation was carried out at 100°C for 3 h. After cooling, the mixture was poured into 500 ml of water and extracted with 100 ml of ether. The aqueous layer was discarded and the ether layer

was washed three times with 10% sodium carbonate and finally dried over sodium sulphate. Next, the ether was removed on a rotary evaporator and the reaction mixture fractionally distilled in a short column. The fraction boiling at 50–52°C/0.015 mm (20.15 g, 52.2 per cent) was collected and found, by ¹H N.M.R., to be pure 4-isopropenylphenyl acetate.

Into a carefully dried 250 ml two-necked flask fitted with a magnetic stirrer and rubber septa were placed 100 ml of dry distilled methylene dichloride and 13.5 g (0.077 mol) of 4-isopropenylphenyl acetate. The reaction mixture was thoroughly purged with nitrogen and cooled to –22°C. Then 0.0545 g (0.00038 mol) of distilled BF₃ · Et₂O was injected using a syringe. Polymerization was allowed to proceed for 3 h, after which the reaction was terminated by injecting 1 ml of methanol. The reaction mixture was diluted with methylene dichloride, and the polymer precipitated into 500 ml of methanol. After filtering the polymer and washing with fresh methanol, the recovered polymer was dried at 60°C *in vacuo*. 9.6 g (71% of the theoretical yield) of poly-4-acetoxy- α -methylstyrene was obtained. Its calculated analysis was 74.98 wt% C, 6.86 wt% H, while experimental analysis gave 74.90 wt% C, 6.76 wt% H.

To 4.95 g of poly-4-acetoxy- α -methylstyrene dissolved in 400 ml dioxane was added 24 ml (0.48 mol) of hydrazine hydrate. The reaction mixture was stirred at room temperature for 2.75 h, during which time the hydrolysed polymer was observed to precipitate from solution as an oil. The entire reaction mixture was poured into 2 l of water, and the solid polymer collected by suction filtration and washed with water. After drying, the yield of poly-4-hydroxy- α -methylstyrene was 3.55 g (94% of the theoretical yield). ¹H N.M.R. analysis of the hydrolysed polymer showed the loss of the absorption at 2.20 ppm due to the acetoxy methyl group in the precursor polymer, together with the appearance of a new peak at 3.55 ppm which was attributed to the phenolic OH.

2.5. Phase transfer catalysed synthesis of mesogenic polystyrenes and poly- α -methylstyrenes

To 0.005 mol of poly-4-hydroxystyrene or poly-4-hydroxy- α -methylstyrene were added 0.007 mol (0.28 g) of sodium hydroxide, 0.006 mol of the desired 4(ω -bromoalkoxy)-4'-cyanoazobenzene, 0.0005 mol (0.161 g) of tetra-*n*-butylammonium bromide, 5 ml of water and 20 ml of toluene. The reaction was carried out under reflux for 20 h. The resulting mixture was cooled and diluted with 50 ml of methylene dichloride, and the solution washed several times with water. The methylene dichloride was removed by rotary evaporation and the glassy solid again dissolved in a few millilitres of methylene dichloride and precipitated into methanol. After drying, the yields ranged from 81 to 93%. To remove completely the unattached mesogen it was usually necessary to extract the polymer with methanol for 24 h in a Soxhlet extractor. T.L.C. analysis was routinely employed to ensure that the polymers were free of unattached mesogen. Samples for analysis by elemental, microscopic, D.S.C. and X-ray analysis were prepared by dissolving the polymers in chloroform and filtering first through paper and then through a 10 μ m Millipore filter. Finally, the solvent was removed and the polymers were dried in a vacuum oven.

2.6. Copolymerization of styrene and 4-acetoxystyrene

Various molar ratios of freshly dried and distilled styrene and 4-acetoxystyrene were placed in polymer tubes fitted with rubber septa. 0.07 g of 2,2'-azobisisobutyronitrile

was added and the reaction mixture thoroughly purged with nitrogen gas. Polymerization was conducted at 75–82°C in an oil bath for 5 h. The copolymers were isolated by dissolving the solid polymers in methylene dichloride and precipitating them into methanol, followed by drying in a vacuum oven. After the copolymers were hydrolysed using the hydrazine method described for poly-4-acetoxy- α -methylstyrene, they were reacted in a polymer analogous reaction with 4(6-bromohexamethyleneoxy)-4'-cyanoazobenzene under the same phase transfer conditions to attach the mesogen. The resulting copolymers were isolated by precipitation into methanol and purified by Soxhlet extraction with methanol for 24 h.

2.7. Characterization methods

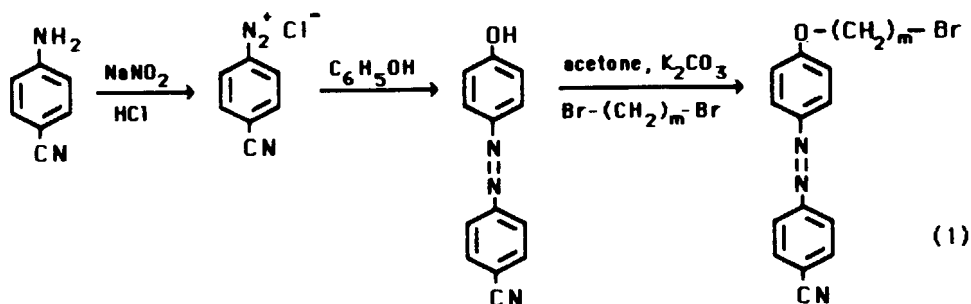
The structures of the 4(ω -bromoalkoxy)-4'-cyanoazobenzene mesogens and the polymers were determined by elemental analysis and ^1H N.M.R. spectroscopy using a Bruker WP60 60 Mz Spectrometer. Their thermal characteristics were examined by means of a Perkin-Elmer DSC-2C differential scanning calorimeter. The glass transition temperatures were measured at a scan rate 20 K min $^{-1}$, and the mesophase transitions were determined at a scan rate of 10 K min $^{-1}$. Peak maxima were taken as the transition temperatures. Characterization of the birefringent textures was performed on samples prepared between untreated glass slides with the aid of a Leitz POL/BK II polarizing microscope equipped with a Mettler FB 52 hot stage. Molecular weights were determined using polystyrene standards on a Waters model 440 GPC chromatograph equipped with a U.V. detector and PL Gel 10 3 –10 4 60 cm \times 7 mm columns. X-ray measurements were made on fibres drawn from the polymer melts and performed on a Siemens Kristalloflex diffractometer using nickel filtered Cu K $_{\alpha}$ radiation. The fibre patterns were recorded with a flat-plate camera.

3. Results and discussion

At the outset of this work we anticipated difficulties associated with the preparation, purification and stability of reactive mesogens containing styrenic and α -methylstyrenic monomers. In addition, the presence of polar and basic groups as well as groups which inhibit free radical polymerization within the diazobenzene mesogenic groups which we chose to use made the polymerization of such groups potentially problematical. For these reasons we elected to approach the synthesis of mesogenic polystyrenes and poly- α -methylstyrenes by first preparing suitably functionalized versions of the parent polymers, and then attaching the desired mesogens to the backbones using a polymer analogous reaction. Recently, Keller [4, 6, 7] successfully employed phase transfer methods for the synthesis of side-chain liquid crystal polymers. A variation of this method has been used in this laboratory for the preparation of the desired mesogenic polystyrenes and poly- α -methylstyrenes. In the present case, the 4-hydroxy substituted precursor main chain polymers were prepared, and cyanoazobenzene mesogens attached by a phase transfer catalysed etherification reaction.

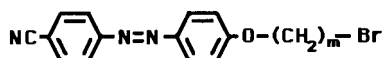
3.1. Precursor mesogens

The general reaction scheme used in the preparation of the required 4(ω -bromoalkoxy)4'-cyanoazobenzene compounds is



These syntheses were carried out, with good yields, by reacting 4-hydroxy-4'-cyanoazobenzene with an excess of the α, ω -dibromoalkane and potassium carbonate in acetone. The chemical analyses and mesomorphic characteristics of these low molar mass azo compounds are given in table 1. With the exception of the compound with the four-carbon alkyl spacer, all exhibit liquid-crystalline behaviour. It is interesting to note that while the compounds with six and ten carbon spacers have only a nematic mesophase, the compound with the eight-carbon spacer possesses an additional smectic mesophase.

Table 1. Properties of 4- ω -bromoalkoxy-4'-cyanoazobenzenes



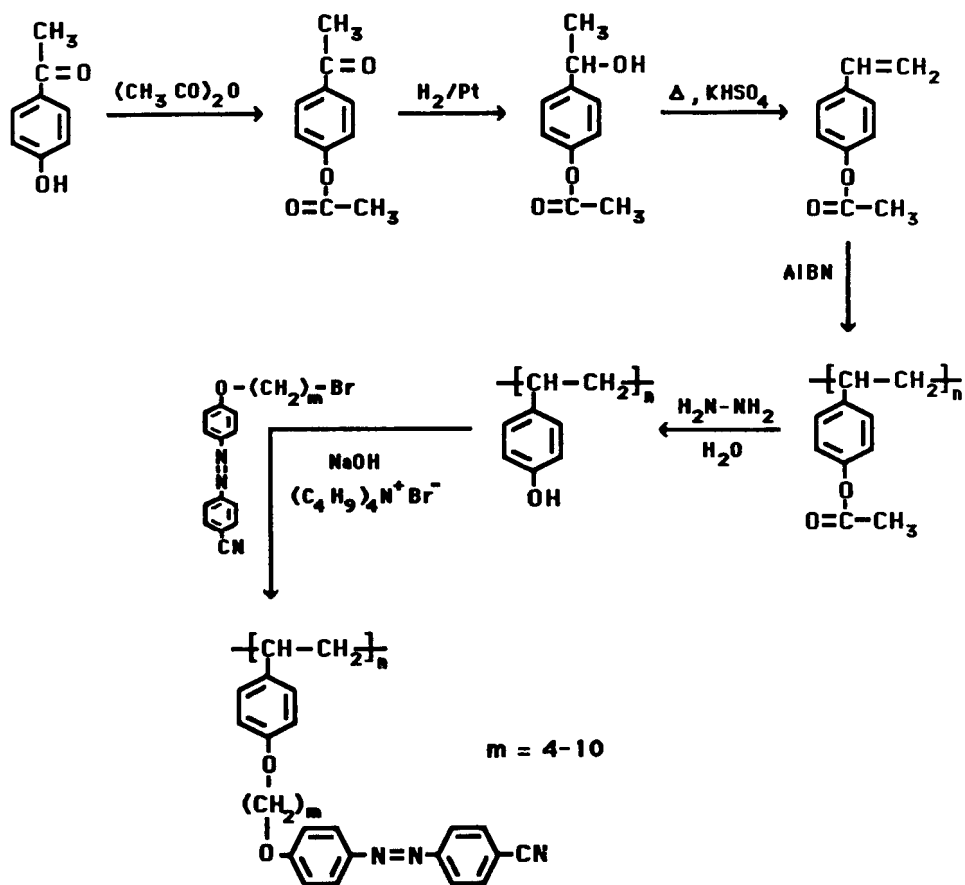
<i>m</i>	Phase transitions [†]	Chemical analyses/wt% [‡]			
		C	H	N	Br
4	C 124-4 I	56.99	4.50	11.73	22.21
		57.12	4.65	11.40	22.02
6	C 93 N 103-4 I	59.07	5.22	10.88	20.69
		59.03	5.20	10.38	19.44
8	C 84.4 S _A 98.3 N 102.8 I	60.87	5.84	10.14	19.29
		61.29	5.96	10.20	19.39
10	C 106 (N 94.7) I	62.44	6.33	9.52	18.10
		62.49	6.41	9.55	18.09

[†] Transition temperatures in °C; C = crystal, S_A = smectic A, N = nematic, I = isotropic.

[‡] The upper value of each pair is the calculated value, and lower value the experimentally determined one.

3.2. Mesogenic polystyrenes

The general method which was used for the preparation of mesogenic polystyrenes is shown in scheme 1. Poly-4-hydroxystyrene was obtained from commercial sources, as well as being prepared as depicted in Scheme 1 by the polymerization of poly-4-acetoxystyrene [16] followed by hydrolysis under very mild conditions with hydrazine hydrate according to the method of Arshady *et al.* [17]

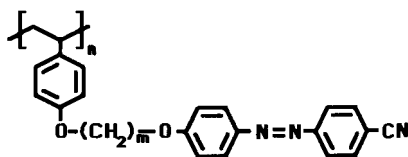


Scheme 1

The attachment of the mesogenic groups by this method gave rise in all cases to liquid-crystalline polystyrenes. Polymers prepared using poly-4-hydroxystyrene synthesized according to Scheme 1 or from commercial sources gave essentially identical results. The chemical analyses of the mesogenic polystyrene polymers given in table 2 indicate that the attachment of the mesogens using the phase transfer catalysed etherification reaction proceeds quantitatively in all cases. $^1\text{H N.M.R.}$ spectra of the polymers were in agreement with the structures shown in Scheme 1. Size exclusion chromatography on the polymers prepared using commercial poly-4-hydroxystyrene showed, in all cases, a broad peak with a shoulder at high molecular weight. The molecular weights of the mesogenic polystyrenes were all above $24\,000\text{ g mol}^{-1}$, which appears to be sufficiently high to preclude the influence of molecular weight effects on the phase behaviour.

The liquid-crystalline behaviour of the mesogenic polystyrenes was investigated using D.S.C., polarizing microscopy and X-ray analysis on fibres drawn from the melt. The D.S.C. heating curves were similar for all the polymers appearing in table 2 and consisted of a step corresponding to the glass transition at T_g , followed by a single endothermic peak. Figure 1 shows the heating and cooling curves for a typical member of this series of polymers. As predicted, there is a marked decrease in T_g for polystyrene ($T_g = 100^\circ\text{C}$ [18]) as a result of fixing the alkoxy substituted azobenzene

Table 2. Properties of mesomorphic polystyrenes



Polymer	m	$\bar{M}_N \dagger$	Phase transitions‡	$\Delta H_{NI}/\text{J g}^{-1}$	Chemical analysis/wt%§		
					C	H	N
I	4	27 400	g 87 N 177 I	2.7	75.47	5.78	10.69
					74.45	5.76	10.30
II	6	24 800	g 69 N 170 I	5.2	76.12	6.34	9.89
					75.67	6.24	9.70
III	8	37 900	g 66 N 169 I	6.4	76.72	6.83	9.39
					75.61	6.84	9.08
IV	10	41 200	g 68 N 158 I	6.8	77.31	7.32	8.73
					77.42	7.16	8.28

† Determined by size exclusion chromatography in chloroform using polystyrene standards.

‡ g = glass, N = nematic, I = isotropic.

§ The upper value of each pair is the calculated value, and the lower value is the experimentally determined one.

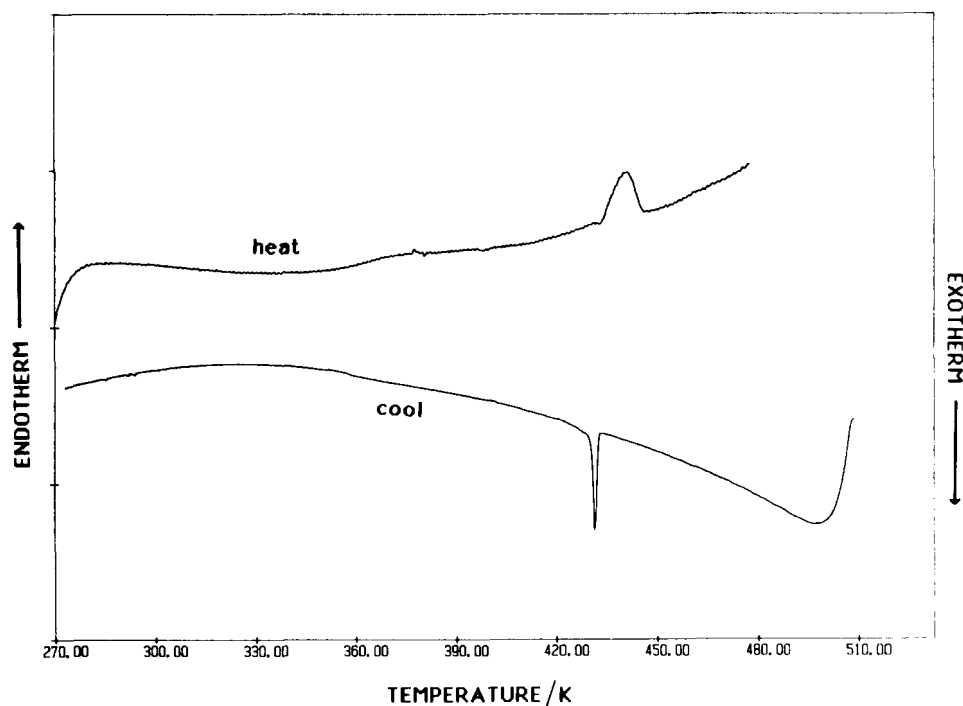


Figure 1. Heating and cooling curves measured at 10 K min^{-1} for a mesogenic polystyrene bearing a four-carbon spacer.

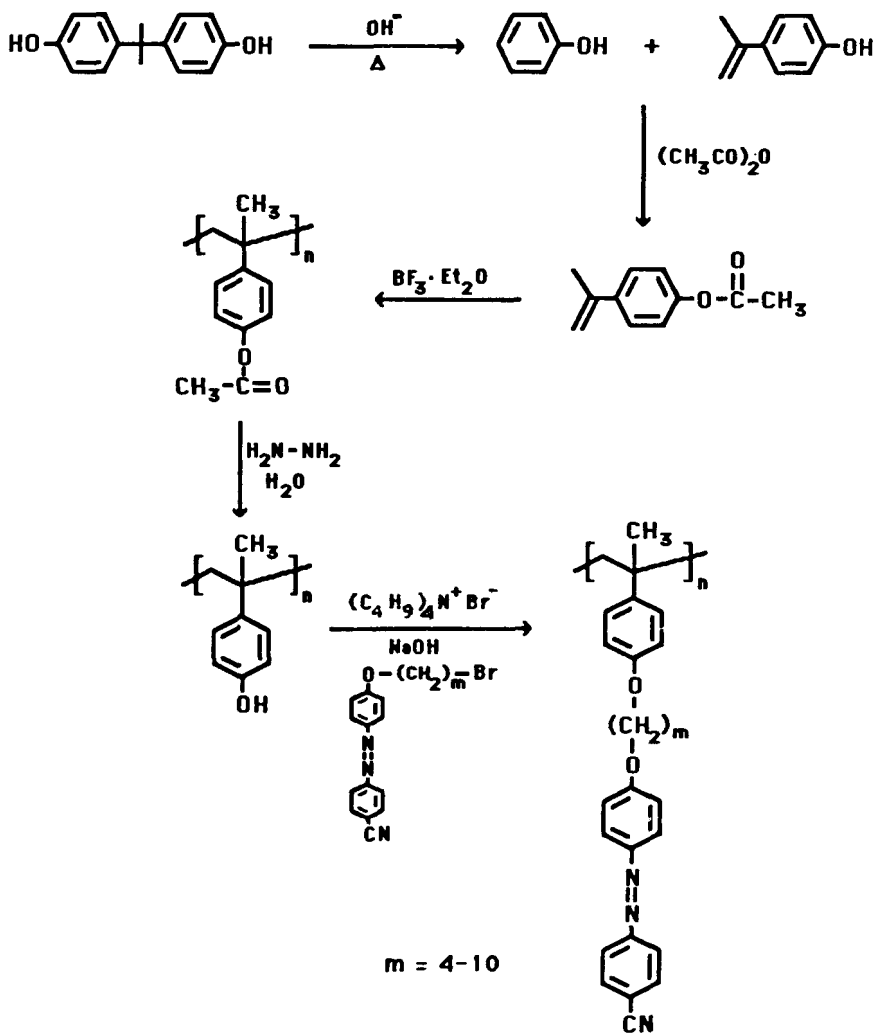
mesogen at the para position of the aromatic rings. On cooling at 10 K min^{-1} , the recrystallization exothermic peak is sharp and supercooled by only 3–7 K from the corresponding endotherm maximum. Observations with a polarizing microscope confirmed that the polymers form fluid, birefringent viscous melts which at the temperatures indicated by D.S.C. undergo a transition from the liquid-crystalline to the isotropic phase. As expected, the clearing temperature rises as the length of the spacer is shortened. Below the clearing temperature, the textures consisted of very small domains from which no definitive classification of the mesophases could be made. Even after annealing for several days, the textures showed no appreciable change. The assignments of the mesophases as nematic could be made, however, on the basis of the X-ray patterns obtained from fibres drawn from the melt of the polymers. These patterns consisted of a single broad halo reflection in the wide-angle region, with no reflections in the small-angle region. The rather low values $(2.7\text{--}6.8 \text{ J g}^{-1})$ obtained for the enthalpies of the mesophase–isotropic transitions for these polymers also suggests a low degree of order, consistent with their assignment as nematic. It may also be observed that the enthalpies of transition increase with length of the spacer chain, which indicates a corresponding increase in the order of the polymers, which may be due to a better decoupling of the mesogens from the main chain.

3.3. Mesogenic poly- α -methylstyrenes

Scheme 2 gives the reaction sequence which was employed for the synthesis of side-chain liquid-crystalline poly- α -methylstyrenes.

A mixture of phenol and 4-isopropenylphenol was obtained by the base catalysed thermolysis of bisphenol-A [19]. This mixture was acetylated and fractionally distilled to give pure 4-isopropenylphenylacetate, which was polymerized under cationic conditions using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the catalyst. Attempts here, as well with poly-4-acetoxystyrene, to displace the acetate directly with 4(bromoalkoxy)4-cyanoazobenzene led to only partial displacement. It was necessary, therefore, in both cases to prepare the corresponding hydroxy substituted polymeric derivatives. Poly-4-hydroxy- α -methylstyrene was obtained from the corresponding poly-4-acetoxy- α -methylstyrene by hydrolysis with hydrazine hydrate. Finally, the azobenzene mesogens were fixed to the polymer backbone by phase transfer catalysed etherification. Table 3 gives the phase transitions, molecular weights and chemical analyses of the four polymers prepared using this synthesis scheme. Again, the very good agreement between the calculated and observed chemical analyses confirms the nearly quantitative nature of the phase transfer etherification. Molecular weight determination by size exclusion chromatography showed that the polymers had high molecular weights, ranging from 38 000 to 48 000, with monomodal distributions.

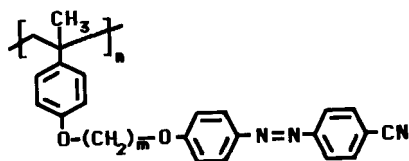
Surprisingly, the mesogenic poly- α -methylstyrenes show even greater depression of their glass transitions than do the corresponding mesogenic polystyrenes. Poly- α -methylstyrene homopolymer has $T_g = 168^\circ\text{C}$. Thus, the glass transitions have been depressed by between 90 and 100°C by the attachment of the mesogenic groups to the polymer backbone. D.S.C. analysis of the polymers shows in each case, in addition to the glass transition, the presence of an endothermic transition which is completely reversible and which does not change on repeated heating and cooling cycles. The enthalpies of transition for this are nearly the same for all the polymers ($10.4\text{--}10.7 \text{ J g}^{-1}$), and is independent of the length of the spacer. The higher values for these polymers suggest that they are more highly ordered than the corresponding mesogenic



Scheme 2

polystyrenes. For polymers having four and eight carbon spacers, polymers V and VII, there is an additional small irreversible endotherm at 172 and 136°C, respectively. These transitions may be attributed either to side chain or to main chain crystallization. Figure 2 shows the heating and cooling curves for the mesogenic poly- α -methylstyrene polymer bearing the four-carbon spacer group (polymer V).

All the polymers displayed very small grain-like textures when examined by polarizing microscopy. On long annealing (2 days), the polymers with six and eight carbon spacer groups developed clearly recognizable smectic batonnet textures. X-ray analyses of fibres drawn from the melt, as well as bulk samples of the polymers, showed in all cases the presence of weak first-order and sharp second-order small-angle reflections, as well as a broad wide-angle reflection indicative of a smectic ordering of the mesophases. The pattern is strongly suggestive of a smectic-A ordering, however, the possibility that the mesophases are smectic-C with a small tilt angle cannot be discounted. The Bragg inter- and intralayer spacings d determined from the

Table 3. Properties of mesomorphic poly- α -methylstyrenes

Polymer	m	\bar{M}_N^\dagger	Phase transitions ‡	$\Delta H_{SI}/\text{J g}^{-1}$	Chemical analysis/wt% §		
					C	H	N
V	4	37 800	g 69 S 207 I	10.4	75.89	6.12	10.21
					76.94	6.15	10.26
V	6	48 300	g 54 S 183 I	10.5	76.51	6.65	9.56
					74.24	6.66	9.53
VII	8	40 500	g 71 S 182 I	10.5	77.06	7.11	8.99
					77.01	7.09	9.20
VIII	10	41 600	g 72 S 172 I	10.7	77.58	7.47	8.48
					77.64	7.40	8.18

† Determined by size exclusion chromatography in chloroform using polystyrene standards.

‡ g = glass, S = smectic, I = isotropic.

§ The upper value of each pair is the calculated value, and the lower value is the experimentally determined one.

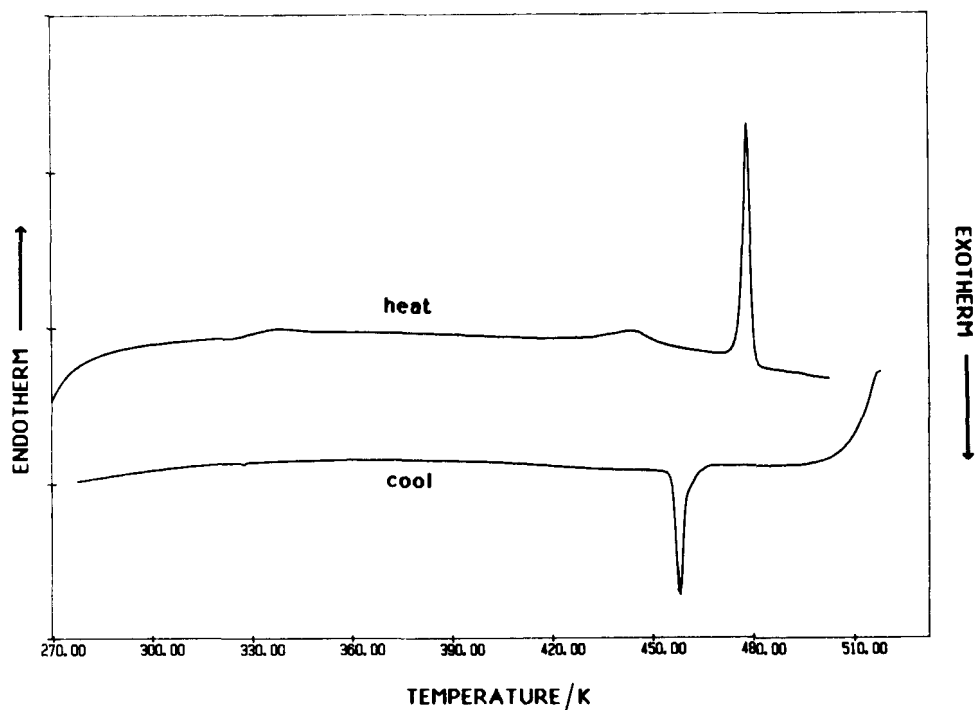


Figure 2. Heating and cooling curves measured at 20 K min^{-1} for a mesogenic poly- α -methylstyrene bearing a four-carbon spacer.

Table 4. X-ray diffraction data of mesomorphic poly- α -methylstyrenes.

Polymer	m	d spacings/Å		
		Interlayer		Intralayer
V	4	29	15.5	4.6
VI	6	33	16.7	4.3
VII	8	38.5	18.2	4.4
VIII	10	42	19.3	4.4

X-ray patterns are given in table 4. The first-order (interlayer) spacings are of the same order of magnitude as, but slightly larger than, the estimated lengths of the mesogens. As the spacer length increases in increments of two methylene units, an approximate 3–4 Å increase in the width of the interlayer spacing is observed. Since the small-angle reflections occur at positions orthogonal to both the beam and the fibre axis, it may be assumed that the director of the smectic layers lies in the same direction as the fibre axis.

3.4. Liquid-crystalline copolymers

It was of some interest to determine whether styrenic-copolymers having both non-mesogenic and mesogenic side-groups would also possess liquid-crystalline characteristics. Accordingly, styrene was copolymerized together with 4-acetoxystyrene at different molar ratios under free radical conditions. Subsequently, the copolymers were hydrolysed using hydrazine hydrate, and then the mesogen bearing the six-carbon spacer was attached to the polymer chain by methods directly analogous to that shown in Scheme 1. In this way, copolymers having 86, 73 and 51 per cent mesogenic segment units were prepared. The copolymers were all high polymers with molecular weights of 91 800, 124 500 and 145 000 g mol⁻¹, respectively. D.S.C. and polarizing microscopy observations showed that only the copolymer (polymer IX) having the highest content of mesogenic segments (86 per cent) was liquid crystalline. As shown in table 5, for this copolymer $T_g = 85^\circ\text{C}$, and it shows a nematic–isotropic transition at 128°C ($\Delta H = 4.7 \text{ J g}^{-1}$). The mesophase transition was completely reversible, and on cooling it occurs at 122°C . There is no evidence in the D.S.C. results for crystallinity in any of the copolymers. The texture of the mesogenic copolymer observed by polarizing microscopy consists of very small liquid-crystalline domains and closely resembles that of the corresponding homopolymeric mesogenic polystyrene. X-ray analysis of a fibre drawn from the melt shows the presence of a wide-angle reflection consisting of a broad halo corresponding to an average distance of 4.7 Å between the mesogens. These data, together with the rather low enthalpy of the clearing transition, are consistent with a nematic mesophase.

In addition to these polymers which contain a mixture of mesogenic and non-mesogenic groups, copolymers were also prepared containing a 50/50 molar mixture of mesogenic repeating units containing spacers of different lengths. These polymers were easily synthesized by the phase catalysed polymer analogous reaction using poly-4-hydroxystyrene and equimolar amounts of the 4(ω -bromoalkoxy)4'-cyanoazobenzene mesogens. Two copolymers were prepared; the first having 4 and 8 carbon spacers (polymer X) and the second 6 and 10 carbon spacers (polymer XI), respectively. As expected, both polymers were also shown to be nematic materials by the D.S.C. and X-ray data, which are shown in table 5.

Table 5. Characteristics of mesomorphic polystyrene copolymers

Copolymer	M_N †	Phase transitions‡	$\Delta H_{NI}/J g^{-1}$	Chemical analysis/wt%§		
				C	H	N
IX	91 800	g 85 N 128 I	4.7	74.69	6.22	8.50
				74.88	6.55	8.51
X	7 800	N 158 I	6.7	76.14	6.30	10.04
				74.56	6.31	9.75
XI	10 900	N 160 I	4.8	76.71	6.83	9.35
				75.19	6.97	9.54

† Determined by size exclusion chromatography in chloroform using polystyrene standards.

‡ g = glass, N = nematic, I = isotropic.

§ The upper value of each pair is the calculated value, and the lower value is the experimentally determined one.

4. Conclusions

The attachment of mesogenic 4-cyanoazobenzene moieties through spacer groups to polystyrene and poly- α -methylstyrene backbones using phase transfer catalysis provides a simple, quantitative and versatile route to the synthesis of liquid-crystalline side-chain polymers. Moreover, the polymers prepared in the present work have very broad mesophase ranges which, together with the inherent hydrolytic and thermal stability of both the main and side-chains, suggests potential applications in displays and in reversible optical recording devices. Interesting possibilities for future investigations in this area also present themselves. Among these are a study of the effects of a variation in the position of attachment of the mesogen on the aromatic groups of the backbone, and the use of alternative types of mesogenic groups in an attempt to prepare polymers with nematic, cholesteric, discotic and other types of mesophases. It would also be interesting to study the influence of the tacticity on the liquid-crystalline behaviour in the mesogenic poly- α -methylstyrenes.

The authors wish to express their appreciation to Dr. R. Zentel and to Mr. H. Kapitza for their help in obtaining and interpreting the X-ray data.

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