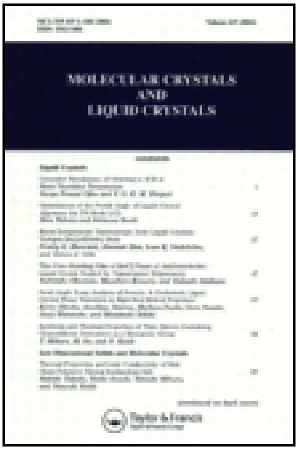

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Side-Group Liquid Crystal Copolymers Containing Nonmesogenic Units: Dependence of the Thermal Behaviour upon Composition

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The synthesis and properties of a new mesogenic/nonmesogenic copolymer system, namely the poly[6-(4'-methoxyazobenzene-4'-oxy)hexyl methacrylate]-co-poly[methyl methacrylate]s, are described. Copolymers containing 0.59 or greater mol fraction of the mesogenic side-groups exhibit nematic behaviour while those containing 0.39 or less mol fraction mesogen are amorphous. The glass transition temperatures exhibit a negative deviation from linear behaviour on varying the copolymer composition. In contrast, the nematic-isotropic transition temperatures decrease in an essentially linear fashion on increasing the nonmesogen content. This behaviour is compared with that of a smectogenic series and differences are accounted for in terms of a microphase separated smectic phase.

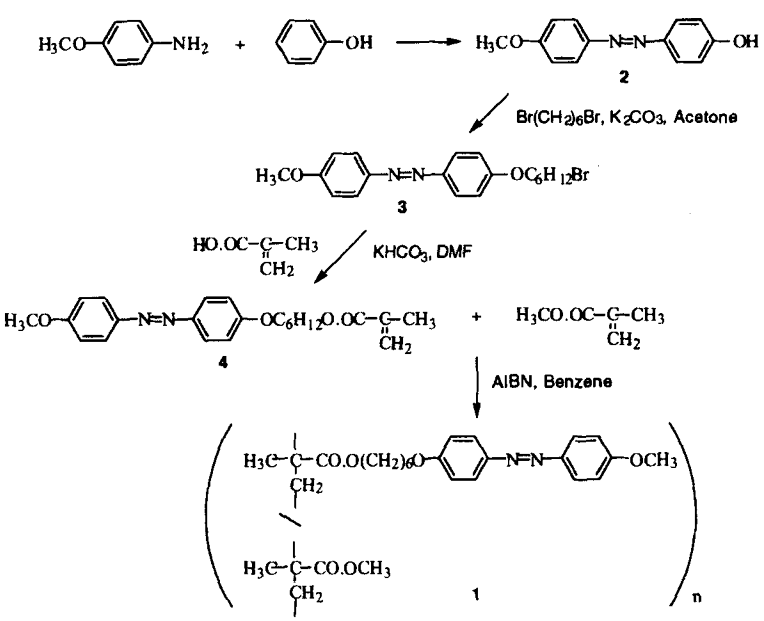
Keywords: liquid crystal side-group copolymers; nonmesogenic units; polymethacrylate derivatives; azobenzene

INTRODUCTION

Side-group liquid crystal polymers continue to be the focus of considerable research activity not only because of their considerable application potential in a range of advanced electro-optic technologies[1] but also because they provide a quite demanding challenge to our understanding of self-assembly in condensed matter[2]. A side-group liquid crystal polymer normally consists of three components: a polymer backbone, a flexible spacer and a mesogenic group. The properties of such a polymers may, however, be modified by copolymerisation of the mesogenic monomer with a nonmesogenic monomer[3]. By varying the ratio of the mesogenic to nonmesogenic units some control can be achieved, for example, over the transition temperatures and, to a lesser extent, the phase structures exhibited. If we are now to design new materials having targeted properties in a rational manner, however, we must first establish and understand the relationships between structure and properties for these copolymers. As part of a continuing programme of research probing the fundamental structure-property relationships in side-group liquid crystal polymers, we have synthesised and characterised a new mesogenic/nonmesogenic copolymer system, namely the poly[6-(4'-methoxyazobenzene-4'-oxy)hexyl methacrylate]-co-poly[methyl methacrylate]s (**1** in Scheme 1). The acronym we use to refer to these copolymers is $(MeOAzo)_x$ where MeOAzo refers to the mesogenic side-group and x is the mole fraction present in the copolymer.

EXPERIMENTAL

The copolymers were prepared using the synthetic route shown in Scheme 1. The preparation of 4-methoxy-4'-hydroxyazobenzene, **2**, 1-bromo-6-(4-methoxyazobenzene-4'-oxy)hexane, **3**, and 6-(4'-methoxyazobenzene-4'-oxy)hexyl methacrylate, **4**, have been described in detail elsewhere[4].



SCHEME 1 Synthesis of the (MeOAzo)$_x$ copolymer series.

Materials

Benzene was distilled over calcium hydride. AIBN was purified by recrystallisation from toluene, washed with petroleum spirits (80-100 °C) and dried under vacuum. Methyl methacrylate was purified by vacuum distillation.

Copolymerisation

Appropriate amounts of the mesogenic monomer **4** and methyl methacrylate were dissolved in benzene (10 mL) and 1 mol % AIBN added as initiator. The reaction mixture was flushed with argon for 20 min, then heated on a water bath at 60°C to initiate polymerisation and left overnight. The copolymer was precipitated into methanol and collected. The product was redissolved in chloroform and precipitated into methanol; this procedure was repeated until the copolymer was spectroscopically free of monomer.

$(MeOAzo)_{0.39}$: yield 0.29 g, 35 %. IR (KBr) υ / cm^{-1}: 1730 (C=O). ^{1}H NMR ($CDCl_3$) δ: 7.8 (m, 4H, aromatic), 6.9 (m, 4H, aromatic), 4.1-3.9 (m, 4H, OCH_2), 3.8 (s, 3H, $ArOCH_3$), 3.6 (s, 4.7H, $CO.OCH_3$), 2.1-0.8 (m, 24.8H, CH_2).

Characterisation

The proposed structures of all the compounds were verified using ^{1}H NMR and IR spectroscopy. The molecular weights of the polymers were measured by gel permeation chromatography (GPC): chloroform was used as the eluent and a calibration curve was obtained using polystyrene standards. Phase identification was performed by polarised light microscopy. The instrumentation used for these characterisation procedures has been described recently in the literature[4]. The thermal properties of the polymers were determined by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC 820 equipped with an intracooler and calibrated using an indium standard. Two samples were used for each polymer and the results averaged.

RESULTS AND DISCUSSION

The compositions and thermal properties of the copolymers are listed in Table 1. The compositions were assessed using ^{1}H-NMR spectroscopy and specifically, the sum of the integrals of the peaks arising from the aromatic protons (δ 6.9, 7.8 ppm) in the mesogenic unit was compared to the integral of the peak corresponding to the ester methyl protons (δ 3.6 ppm). The number average molecular weights of the copolymers were in all cases in excess of 11, 000 g mol^{-1} with associated degrees of polymerisation above 37. These high molecular weights ensure that the thermal properties of the copolymers all lie in the molecular weight independent regime[5]. Before we can discuss the dependence of the thermal properties on the structure of the copolymers, we must first consider the microstructure of the polymer chains. For copolymers prepared via a chain polymerisation, the chain microstructure is determined by the reactivity ratios of the monomers. We have recently shown that the reactivity ratios for a very similar mesogenic methacrylate / methyl methacrylate comonomer system were equal and approximately unity[6]. Thus, for that specific system the copolymerisation is azeotropic with the resulting copolymers possessing a random distribution sequence of the two monomers. Given the strong chemical similarity between the two systems, it would appear reasonable to assume that the copolymers prepared as part of this study will also possess a random distribution sequence of the two monomers.

TABLE 1 The compositions and thermal properties of the $(\mathrm{MeOAzo})_x$ copolymer series.

X	T_g/°C	T_{SmAN}/°C	T_{NI}/°C	$\Delta S_{NI}/R$
0	123			
0.09	97			
0.22	76			
0.32	70			
0.39	66			
0.59	55		88	0.35
0.63	69		100	0.32
0.74	71		106	0.36
0.76	73		110	0.39
0.80	80		119	0.40
0.90	85	89	128	0.46
1	80	95	135	0.33

The dependence of the transition temperatures on the copolymer composition is shown in Figure 1. The nematic phases were assigned on the basis of the observation of characteristic schlieren nematic textures on cooling from the isotropic phase. On cooling the nematic phases exhibited by $(\mathrm{MeOAzo})_{1.0}$, *i.e.* the mesogenic homopolymer, and $(\mathrm{MeOAzo})_{0.9}$ a well-defined focal conic fan texture was observed and this was assigned as a smectic

A phase. The transition temperatures of $(MeOAzo)_{1.0}$ are in excellent agreement with those reported in the literature[7].

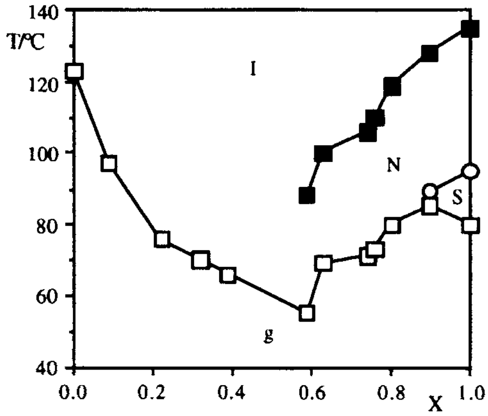


FIGURE 1 The dependence of the transition temperatures on the mol fraction of mesogenic side-groups for the $(MeOAzo)_x$ copolymer series. Glass transition temperatures (□), smectic A-nematic (○), nematic-isotropic (■).

The copolymers containing between 0 and 0.39 mol fraction mesogenic side-groups do not exhibit liquid crystallinity. By contrast the remaining members exhibited nematic behaviour and as we have seen, $(MeOAzo)_{1.0}$ and $(MeOAzo)_{0.9}$ also show a smectic A phase. The glass transition temperature, T_g, initially decreases with increasing mesogen content but after passing through a minimum, coincident with the observation of liquid crystallinity, further addition of mesogenic side-groups increases T_g, see Figure 1. The initial decrease in T_g presumably reflects the plasticization of the backbone by the side-groups. On increasing the mol fraction of mesogen, the copolymer becomes liquid crystalline, the free volume decreases compared with that of an amorphous polymer and hence, an increase in T_g is observed.

In contrast to the dependence of T_g on composition, the nematic-isotropic transition temperature, T_{NI}, decreases essentially in a linear fashion on increasing the nonmesogenic content. The smectic A phase is rapidly extinguished on increasing the nonmesogenic content because T_{SmAN} falls more rapidly than T_g. The dependence of the transition temperatures on composition for the $(MeOAzo)_x$ copolymer series is very similar to that exhibited by the two other methacrylate-based mesogen / nonmesogen copolymer series reported in the literature[6,8].The entropy changes associated with the clearing transition are in the range 0.31-0.46 supporting the assignment of a nematic-isotropic transition, see Table 1, but do not exhibit a simple dependence on composition.

The ability of mesogen/nonmesogen copolymers to exhibit liquid crystallinity with just 59% mesogenic side-groups present, and indeed this figure is considerably lower for more flexible backbones, has been rationalised for smectic materials in terms of a microphase separated morphology in which the backbones reside largely between the smectic layers[9,10]. As the mol fraction of mesogen is reduced the backbone can be compressed in the direction perpendicular to the director ensuring a sufficient packing density of mesogens is maintained for the observation of liquid crystallinity, see Figure 2. This distortion of the backbone inevitably produces an increased interfacial mixing between the backbone and mesogenic domains which becomes more pronounced as the mesogen content is reduced. It has been suggested that this mixing is responsible for the observed broadening of the clearing endotherm in the DSC trace on increasing the nonmesogen content[10-12].

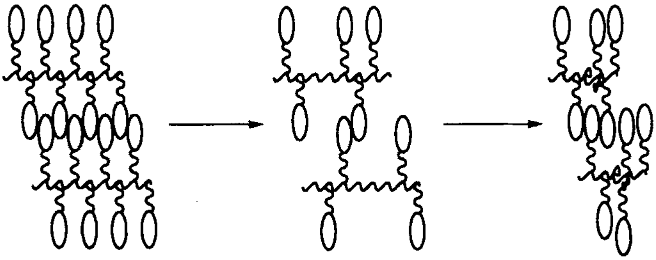


FIGURE 2 Sketch of the distortion of the backbone to accommodate nonmesogenic units in a smectic phase.

For a nematic copolymer, the distortion of the backbones required to accommodate the nonmesogenic groups while still preserving liquid crystallinity is a more facile process because this is not a microphase separated morphology[13]. In addition, increased interfacial mixing need not be invoked and hence, the width of the clearing endotherm in the DSC trace should be less sensitive to composition. The $(MeOAzo)_x$ copolymer series allows this suggestion to be tested and if we compare the width at half height of the clearing endotherms of the $(MeOAzo)_x$ copolymers with those of a chemically similar but smectogenic series[6] we do indeed find that for the smectic series the clearing endotherm broadens considerably on increasing nonmesogen content while the clearing endotherm exhibited by the nematogenic $(MeOAzo)_x$ copolymers is relatively insensitive to composition. This strongly supports the view that interfacial mixing between the backbone and smectic domains gives rise to the broadening of the clearing endotherm on increasing the nonmesogen content in smectogenic polymers.

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