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Synthesis and characterisation of side chain liquid crystal copolymers containing sulfonic acid groups

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ABSTRACT

A series of novel side chain liquid crystal copolymers, the poly[10-(4-methoxy-4′-oxy-azobenzene) decyl methacrylate]–co-poly[2-acrylamido-2-methyl-1-propanesulfonic acid]s (10-MeOAzB/AMPS-*x*/*y*) have been synthesised by free radical copolymerisation. The mol fraction of the sulfonic acid-based group, AMPS, has been varied over a broad range of composition in the copolymers, and these have been characterised using differential scanning calorimetry (DSC), polarised light microscopy (PLM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). The liquid crystal homopolymer and copolymers containing up to 0.54 mol fraction AMPS-based units, all exhibit a smectic A phase, while at higher mol fraction AMPS-based groups, liquid crystallinity is extinguished and the copolymers are amorphous. The local packing arrangements within the smectic A phase varies with composition attributed, in part, to phase separation between acid rich domains and liquid crystal regions. The dependence of the transitional properties on copolymer composition may be interpreted in terms of the packing efficiency of the mesogenic side chains and hydrogen bonding between the sulfonic acid groups, as a consequence of increasing the concentration of acid-based groups.

1. Introduction

The design and preparation of new polymers and copolymers for advanced membrane applications offers a wide range of possibilities to combine macromolecular behaviour and functionality, with mild processing conditions [1]. Current challenges in several chemical and engineering separation areas require a rational design of the chemical composition and the distribution of functional groups of new dissimilar materials. For example, in the case of ionomers and polyelectrolytes, it is the number and distribution of polar or charged groups which promote the observed phase separated structures [2–6]. The hydrophobic/hydrophilic balance determines the polymeric aggregation state (microstructure) and the resulting macromolecular transport properties of the materials, which are linked at a molecular level to, for example, domain size, interconnectivity, and interfacial regions [7–10]. In some applications, such as fuel cells or piezoelectric materials, the presence of solvents may disturb the polar/non-polar balance and spontaneous polymer aggregation can lead to structures for which the transport properties are not optimised [11–16]. In such cases, the use of liquid crystals (LC) offers an attractive mechanism to control the ultrastructure of new ionomeric membranes, through the formation of mesophases in certain temperature and composition ranges [17,18]. Liquid crystals containing ions (such as alkali, calcium and transition metal ions) and ionogens (carboxylic and sulfonic acid groups) combine the formation of orientated anisotropic LC structures with the functionality of ionomers [19]. The microstructure (and resulting physico-chemical and transport properties) of an ionic or acid-containing LC (also referred to as liquid crystal ionomers and ionogens) may then be controlled by external stimuli, such as, for example, UV light, electrical and magnetic fields, and shear forces.

An interesting route to new liquid crystalline membrane materials involves side chain liquid crystal polymers (SCLCP) and indeed, sulfonic acid groups have been incorporated into SCLCPs, usually with a view to preparing liquid crystal ionomers [19–23]. A SCLCP consists of three structural components: a polymer backbone, a flexible alkyl spacer and a mesogenic group [24]. The mesogenic unit is attached as a pendant group to the polymer backbone *via* the flexible spacer. The role of the flexible spacer is to decouple, to some extent, the relative tendencies of the mesogenic

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groups to self-assemble and form a liquid crystal phase, from those of the polymer backbone to adopt a random coil configuration, and hence, endows upon the polymer a unique duality of properties. Thus, a SCLCP exhibits macromolecular characteristics, such as mechanical integrity, coupled with, for example, the electro-optic properties of low molar mass liquid crystals, albeit on a much slower timescale. This combination of properties has led to the proposed use of SCLCPs in areas such as optical information storage and nonlinear optics [24]. The formation of a smectic phase by a SCLCP may be thought of in terms of a microphase separation in which the liquid crystal side chains constitute one domain and the polymer backbones another [25–29]. Thus, depending on the placement of the sulfonic acid groups in the structure of the polymer, they may, in principle, be located in either of these domains. In the majority of SCLCPs containing sulfonic acid groups, they are attached to a mesogenic moiety and hence reside in the smectic layer, although hydrogen bonding between them tends to disrupt the layering tendency [30–33]. Indeed, hydrogen bonding has been considered to be the driving force for the formation of phase separated structures in this class of materials such as one consisting of ionic clusters and nematic blocks [34] or a smectic phase in which layers are ether rich or poor in mesogenic groups containing the sulfonic acid group [35]. In structurally closely related side chain liquid crystal elastomers prepared using a crosslinking agent containing sulfonic acid groups, a phase separated smectic arrangement was observed consisting of alternating layers of liquid crystal groups or ionic units [36,37].

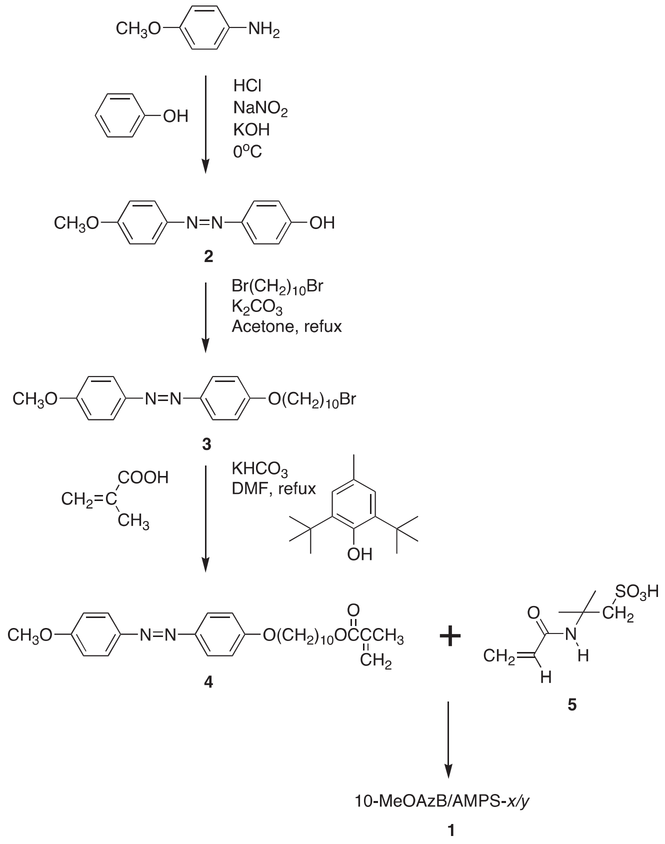
Here we extend this approach to the design of new SCLCPs by incorporating sulfonic acid groups into non-mesogenic units and close to the polymer backbone. Imrie, Ingram and co-workers have shown that ion transport properties in ionically conducting poly(ethylene oxide)-based SCLCPs are, to a large extent, determined by the interaction of the backbones and the liquid crystalline environment, and that this gives rise to appreciable ionic conductivities in solid-like films [38–44]. Here we explore the extent to which sulfonic acid groups may be incorporated into a liquid crystal environment ultimately to provide materials having enhanced anisotropic conductivities. This design approach combining liquid crystallinity and proton conducting units has proved successful in areas including obtaining membranes from liquid crystalline solutions of highly sulfonated forms of poly(p-phenylene terephthalamide) [45–47], and through the formation of conducting smectic [48] and columnar [49] phases and in lyotropic columnar phases [50] or polymer dispersed liquid crystals (PDLC) [51]. Thus, we have prepared and characterised side chain liquid crystal copolymers consisting of a liquid crystal monomer and a non-mesogenic unit containing sulfonic acid groups, the poly[10-(4-methoxy-azobenzene-4′-oxy)decyl methacrylate]-co-poly[2-acrylamido-2-methyl-1-propanesulfonic acid]s, **1**, over a broad range of composition of the co-monomers.

The acronym 10-MeOAzB/AMPS-*x*/*y* is used to refer to copolymers **1**, in which *x* denotes the mole fraction of mesogenic side chains, 10-MeOAzB, and *y* the mole fraction of the monomer, 2-acrylamido-2-methyl-1-propanesulfonic acid, AMPS, present in the copolymer. The mesogenic unit is azobenzene-based and such materials have attracted considerable research interest for their photoactive behaviour (see, for example [52,53],) although this is beyond the scope of the present work.

2. Experimental section

2.1. Synthesis and materials

The 10-MeOAzB/AMPS-*x*/*y* copolymer series was prepared using the synthetic route shown in Scheme 1. The syntheses of 4-hydroxy-4′-methoxy-azobenzene, **2**, 1-bromo-10-(4-methoxy-azobenzene-4’oxy) decane, **3**, and 10-(4-methoxy-4′-oxy-azobenzene) decyl methacrylate, **4**, have been described in detail elsewhere [54–56]. 2-Acrylamido-2-methyl-1-propanesulfonic acid (*AMPS*), **5**, was purchased from Sigma–Aldrich and used without further purification. All other reagents were used as received from Sigma–Aldrich.



Scheme 1. Synthetic route used to obtain the 10-MeOAzB/AMPS-*x*/*y* copolymers.

2.1.1. *Poly[10-(4-methoxy-4′-oxy-azobenzene)decyl methacrylate]*

The free radical polymerisation of **4** was performed using a reaction procedure described elsewhere [57] to yield the SCLCP homopolymer designated as 10-MeOAzB/AMPS-1/0. Thus, **4** (0.5 g, 1.10 mmol) was dissolved in dimethyl formamide (12.1 g) and 1,1′-azobis(cyclohexane carbonitrile) (0.0132 g) added as initiator. The reaction mixture was flushed with nitrogen for 45 min, then heated at 80 °C in the absence of oxygen to initiate the polymerisation. After 24 h the polymerisation was terminated by precipitation into diethyl ether. The polymer was purified by several reprecipitations from dichloromethane into diethyl ether.

Yield: 68.0%, IR (KBr) ν cm^{-1}: 1726 (C=O), ^1H NMR ($CDCl_3$) δ (ppm): 7.0, 7.9 (m, aromatic, 8 H), 4.1–3.9 (m, CH_2–OOC, OCH_2, 4H), 3.8 (s, $ArOCH_3$, 3H), 1.0–2.0 (m), 0.7–1.1 ($CH_3C(CO.O)$, 3 H).

2.1.2. *Poly[2-Acrylamido-2-methyl-1-propanesulfonic acid]*

The free radical polymerisation of **5** to yield the homopolymer designated as 10-MeOAzB/AMPS-0/1 (PAMPS) was performed using the reaction procedure described earlier. The polymer was purified by precipitation into diethyl ether and dried for several days at 60 °C.

IR (KBr) ν cm^{-1}: 628 (SO_3H), ^1H NMR (D_2O) δ (ppm): 1.5 (s, CH_3, 3H), 2.1 (s, main chain CH_2), 3.7 (s, $\underline{CH_2}SO_3H$, 2H).