



A kinetic study of the formation of smectic phases in novel liquid crystal ionogens



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ABSTRACT

A multi-rate non-isothermal kinetic analysis of the isotropic-melt to liquid crystalline phase transition of novel liquid crystalline ionogenic copolymers, LCIs, the 10-(4-methoxyazobenzene-4'-oxy)decyl methacrylate]-co-2-(acrylamido-2-methyl-1-propanesulfonic acid)s, 10-MeOAzB/AMPS, copolymers, has been performed by means of calorimetric experiments. An analytical methodology which includes the study of the phase transition rate parameter, the determination of the activation energies by using Kissinger and Flynn-Wall-Ozawa models, and the study of the phase transition kinetics by the use of the Avrami theory, has been applied. The formation of the mesophases from the isotropic state occurred close to thermodynamic equilibrium. The results evidence the presence of several individual processes in the formation of liquid crystalline phases from the melt and a strong dependence of phase transition rates and activation energies with acid contents. A decrease in the phase transition rate, related to a decrease in the overall change of the transition entropy, has been observed. The final inhibition of the liquid crystal (LC) behaviour is ascribed to an exponential increase in the activation energy of the phase transition, promoted by strong acid aggregation. An optimum composition of the 10-MeOAzB/AMPS copolymers to achieve the dual characteristics of LCIs (ionogenic and liquid crystalline behaviour) requires acid concentrations capable of promoting structure-forming effects on the LC phases and the evolution of phase separated morphologies.

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1. Introduction

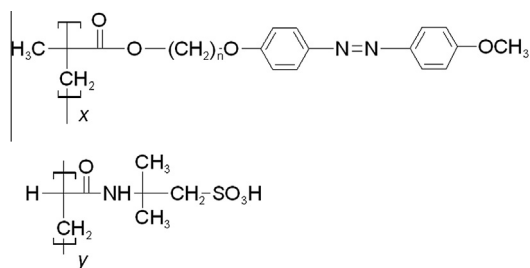
Side chain liquid crystal polymers (SCLCPs) exhibit a unique duality of properties combining those of low molar mass liquid crystals with those of polymers. This combination of properties arises from the structure of SCLCPs in which the mesogenic groups are covalently attached as pendants to a polymer backbone via a flexible spacer. The role of the flexible spacer is to decouple, at least to some extent, the relative tendencies of the mesogenic groups to self-assemble and form the liquid crystal phase from those of the polymer backbone to adopt random coil configurations [1]. The incorporation of nonmesogenic units

along the backbone allows for additional functionalities to be endowed upon the polymer [2–4]. Of particular interest in recent years have been SCLCPs containing ionic and ionogenic units and these are also referred to as liquid crystal ionomers and iononogens (LCIs). This interest stems not only from their considerable application potential in a range of quite diverse areas but perhaps most notably as anisotropic electrolytes, but also because they provide a demanding challenge to our understanding of self-assembly in polymeric systems [5,6].

We recently reported the synthesis and phase behaviour of the 10-(4-methoxyazobenzene-4'-oxy)decyl methacrylate]-co-2-(acrylamido-2-methyl-1-propanesulfonic acid)s, copolymers (Scheme 1), and refer to them using the acronym 10-MeOAzB/AMPS in which 10-MeOAzB refers to the liquid crystal side chain and AMPS to the sulfonic

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Scheme 1.

acid-based group. These copolymers exhibited smectic A phase behaviour over a broad range of compositions, specifically for copolymers containing 0.45 or greater mol fraction of 10-MeOAzB side chains [7]. This observation, in itself, is not unusual and may be accounted for a compression of the backbone in the plane perpendicular to the liquid crystal director which enhances the interactions between the mesogenic groups. Surprisingly, however, the

smectic A-isotropic transition did not simply decrease on increasing the AMPS mol fraction ($X_{\text{AMPS}} = 1 - X_{10\text{-MeOAzB}}$) but instead appeared to reach a limiting value. Such effect was accompanied by changes in the structure of the smectic A phase on increasing the AMPS mol fraction and this was attributed, at least in part, to hydrogen bonding between the sulfonic acid groups. In addition, a phase separated structure was observed consisting of regions of smectic A phase and acid-rich domains.

It appears therefore that the sulfonic acid groups play a central structure-forming role in determining the phase behaviour of these copolymers. Due to the relevance that processing conditions may have on the preparation of materials and membranes with liquid crystalline templates from the melt, this work investigates with more detail the structural formation of the smectic A phase from the isotropic melt for the 10-MeOAzB/AMPS copolymers. To achieve this we performed a calorimetric kinetic study of the non-isothermal isotropic melt-liquid crystal phase transition for the homopolymer (P10-MeOAzB) and the 10-MeOAzB/AMPS copolymers. The Avrami theory [8–10]

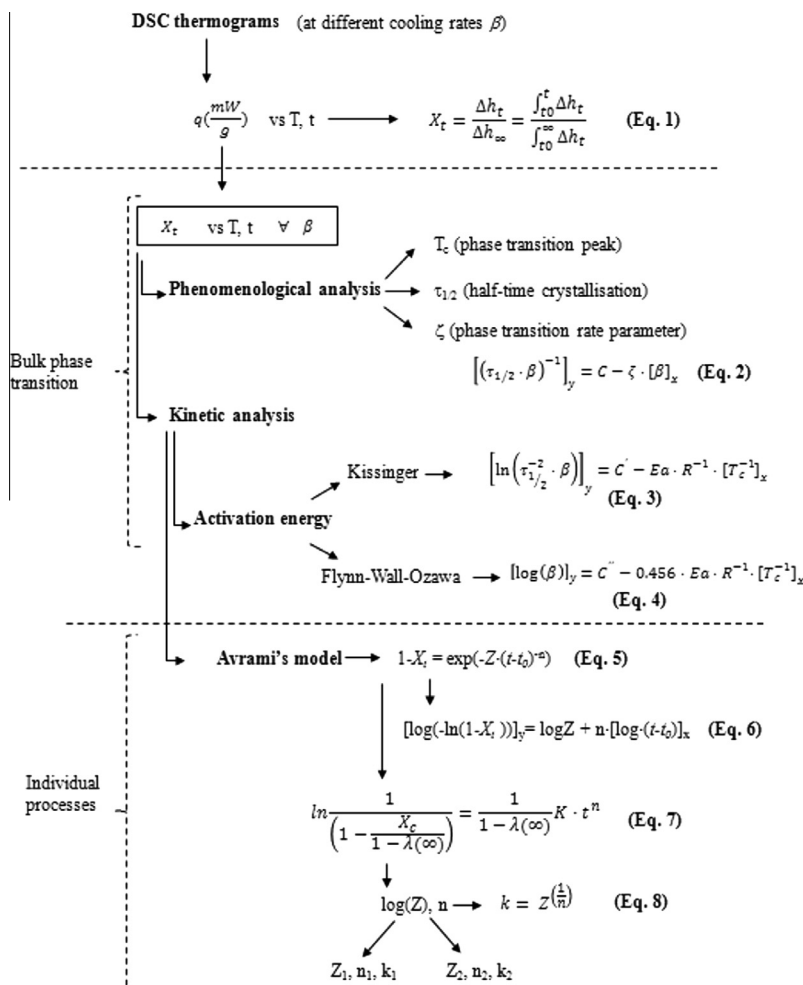


Fig. 1. Schematic representation of the methodology followed for the study of the non-isothermal isotropic-liquid crystal phase transition of the 10-MeOAzB/AMPS copolymers.

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