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Preliminary communication

Induction of the smectic phase in comb-shaped liquid crystalline ionogenic copolymers by hydrogen bond formation

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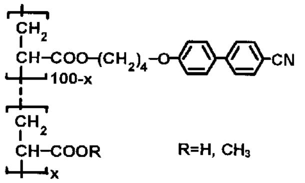
Using a radical copolymerization of 4-(4-cyanobiphenyl-4′-yloxy)butyl acrylate and acrylic acid, a number of new liquid crystalline ionogenic copolymers capable of hydrogen bonding were synthesized. The formation of hydrogen bonds results in an invariant temperature interval of existence for the LC state (up to 52 mol % of acrylic acid) and a rather sudden replacement of the nematic phase by the SmA phase with increase in content of acrylic acid (>35 mol %) in copolymers.

Introduction

Considerable recent attention has been focused on a new type of polymer liquid crystalline (LC) system in which formation of the LC phase is the result of specific non-covalent interactions in the polymer chains and mesogenic fragments [1–10] due to electrostatic [7], donor–acceptor [6], and also hydrogen bonding interactions [1, 4, 8]. On the other hand, the study of ionogenic LC copolymers is of considerable interest because such polymers can combine the highly ordered structure of LC polymers and the very interesting properties of ionogenic polymers. One of the possible ways to incorporate ionogenic groups capable of hydrogen bonding into the macromolecule of an LC polymer is by the radical copolymerization of a mesogenic monomer with a non-mesogenic unsaturated acid. This paper deals with the synthesis of new LC ionogenic copolymers and a study of their phase behaviour.



Copolymers A4CB-AA (R=H)
A4CB-MA (R=CH$_3$)

Experimental part

LC copolymers of the structure given below were synthesized by radical copolymerization of 4-(4-cyanobiphenyl-4′-yloxy)butyl acrylate with acrylic acid (or methyl acrylate) in absolute THF, using the initiator DAC (2%); the average yield was 70–80%. The cyanoacryl monomer was synthesized according to [11]. The copolymers obtained were boiled for a long time in methanol until complete removal of unreacted monomer and low molecular weight products was achieved and further precipitated from solution in chloroform by methanol. The resulting copolymers were dried under vacuum. The copolymers synthesized dissolve readily in chloroform and THF.

The compositions of the copolymers were determined by elemental analysis and by UV spectroscopy by measuring the optical density of the absorption band of the biphenyl group at $\lambda = 285$ nm. The main hydrodynamic characteristics (diffusion coefficients and intrinsic viscosities) of solutions of the homo- and co-polymers in THF are presented in the table. Phase transition temperatures and glass transition temperatures were measured using a Mettler TA-4000 microcalorimeter (heating rate 5°C min^{-1}) and a polarization microscope (Polam-P-112) equipped with a Mettler hot stage. X-ray diffraction patterns were obtained with a URS-55 set-up using a flat-film camera and CuK$_\alpha$ radiation.

Results and discussion

A phase diagram of the copolymers A4CB-AA with different concentrations of acrylic acid (2–80 mol %) is presented in figure 1. The whole range of compositions in the phase diagram can be divided into three separate parts. In the first range of compositions (2–30 mol % of acrylic acid) all copolymer samples are characterized by a nematic mesophase. Figure 1 shows that on increasing

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Table. Some hydrodynamic characteristics of homopolymer A4CB and copolymers A4CB-AA and A4CB-MA in THF solutions.

Characteristics	Homopolymer A4CB	A4CB-AA copolymers, mol % AA 9	34	52	A4CB-MA copolymers, mol % MA 11	22
$[\eta]$/dl/g	0·058	0·058	0·059	0·058	0·058	0·060
$D \times 10^7$/sm^2/s	18·5	24·5	28·0	26·6	—	—

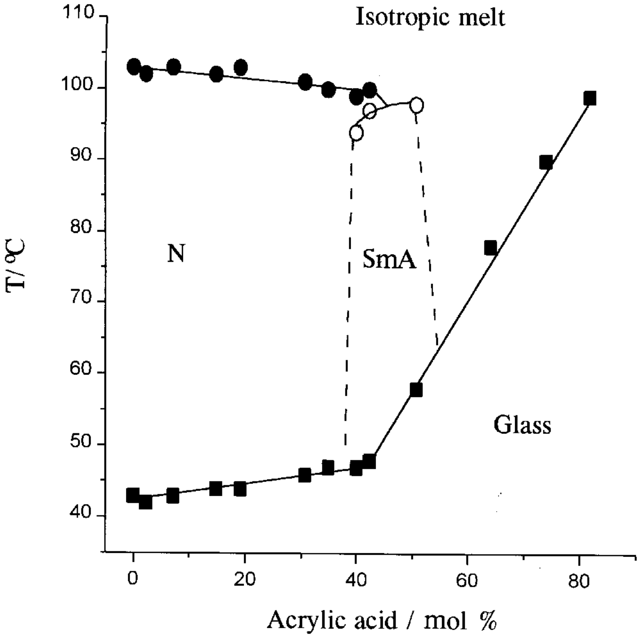

Figure 1. Phase diagram of the copolymers A4CB-AA.

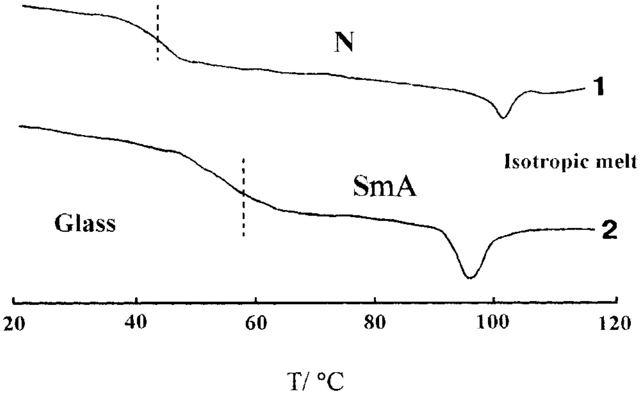

Figure 2. DSC curves for copolymers A4CB-AA with different concentrations of acrylic acid (AA). **1** 9 mol % AA; **2** 52 mol % AA.

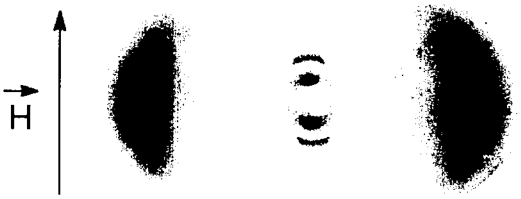

Figure 3. X-ray pattern for copolymer A4CB-AA (AA, 42 mol %) oriented in a magnetic field (H=2·1 T).

the fraction of acrylic acid, a slow rise in the glass transition temperature is observed while the temperature interval of existence of the nematic phase is unchanged. With further increase of acrylic acid concentration (30–52 mol %; the second range of compositions) the appearance of SmA phase is observed. In the third range of compositions, no LC phase is formed and the copolymers are amorphous.

The phase state of all copolymers and the temperatures of the phase transitions N–I and N–SmA were determined by polarization microscopy, DSC and X-ray diffraction. Figure 2 shows the DSC curves of samples of two LC copolymers of different compositions which are characterized by different phase behaviour. In figure 3 the X-ray diffraction pattern of a smectic copolymer pre-oriented in a magnetic field is shown. The layer parameters obtained from the X-ray diffraction experiments were: D=5·0 Å, d_1=33·9 Å, d_2=17·1 Å. Taking into account that the calculated length of the mesogenic group is 17 Å, one can assume that a bilayer packing of the mesogenic groups occurs.

Let us consider the phase diagram of the copolymers with acrylic acid which is characterized by the unusual form in figure 1. In these copolymers the nematic phase is replaced by a smectic phase with increasing concentration of acrylic acid. Since the acrylic acid does not possess any mesogenic properties, then in the copolymers synthesized it must play the role of a 'diluent' of the LC phase, and, as a consequence, the acrylic acid should lead to a decrease in mesophase thermo-stability. However, in fact an increase in concentration of acrylic acid in the copolymers leads to a more ordered mesophase structure and formation of a SmA phase. Such unusual behaviour of LC ionogenic copolymers is apparently the result of inter- and intra-molecular hydrogen

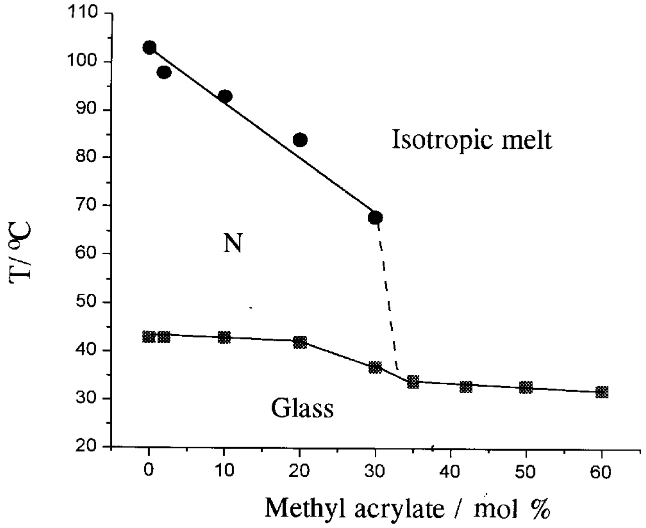

Figure 4. Phase diagram of the copolymers A4CB-MA.

bonds between the free carboxyl groups of acrylic acid monomer units. The formation of hydrogen bonds in the copolymers is confirmed by data from IR spectroscopy. In the IR spectrum of the copolymers there is an absorption at 1710 cm^{-1}, corresponding to a carbonyl group [$\nu_{C=O}$] of a dimer (–COOH)$_2$, and also a group of associated bands [ν_{O-H}] at 2500–3000 cm^{-1}.

To understand the influence of the hydrogen bonding on the phase behaviour of the LC ionogenic copolymers we have synthesized a second series of copolymers which contained the same mesogenic group A4-CB and methyl acrylate MA (figure 4). In these copolymers, hydrogen bonds cannot be formed and due to this fact, only the nematic phase without smectic phase formation was observed. An increase of concentration of methyl acrylate in the copolymers results in a decrease in thermal stability of the nematic state. Moreover the composition range in which the copolymers formed an LC phase was significantly narrower (30 mol %) as compared with the acrylic acid copolymers (52 mol %).

Figure 5 shows a schematic representation of intramolecular hydrogen bond formation for copolymers A4CB-AA built up by a 'head–tail' type of monomer connection in the polymer chain. Hydrogen bonds can be formed in two different ways: (1) between two free carboxyl groups of acrylic acid; (2) between the carboxyl group of an acrylic monomer unit and the carbonyl group of a mesogenic monomer unit. In both cases, the formation of such hydrogen bonds is possible from a geometric point of view; however, intermolecular hydrogen bond formation must not be ruled out.

As can be seen from figure 5, the existence of hydrogen bonds leads to formation of stable 8-membered alicyclic rings resulting in a decrease in kinetic flexibility of the polymer backbone. This in its turn leads to hindrance of movement of mesogenic side groups and probably stimulates their layer packing due to the straightening out of the backbone, with the result that the SmA phase is formed. The decrease in kinetic flexibility of the polymer chain is displayed also by the tendency of the glass transition temperature to rise with increasing concentration of acrylic acid in the copolymers. A maximum increase in glass transition temperature takes place when the polymer chain is sufficiently enriched by acrylic acid, and that becomes possible starting with 50 mol % of acrylic acid in the copolymers. The copolymer containing 52 mol % of acrylic acid is characterized by a considerable jump in glass transition temperature and formation of a 'pure' SmA phase. The increasing structural order

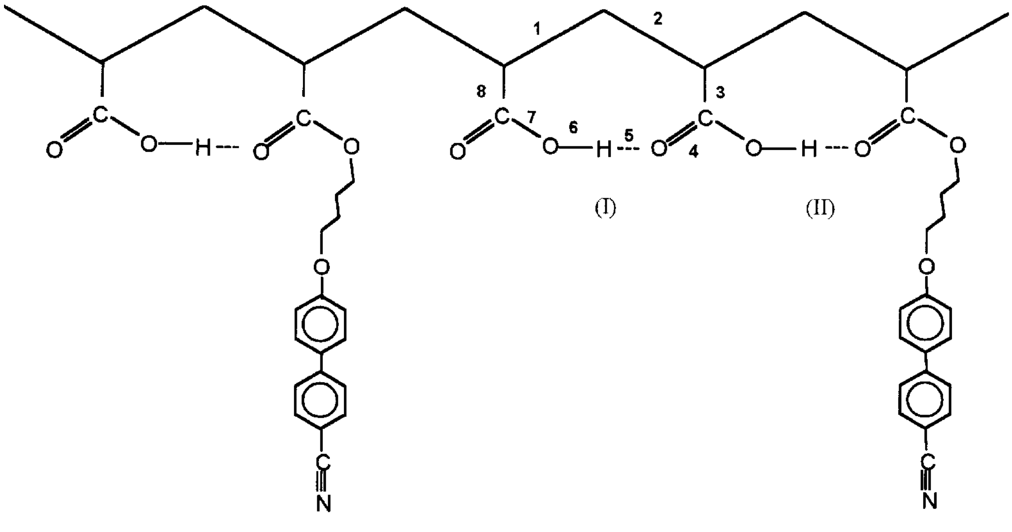

Figure 5. Schematic representation of different types of hydrogen bonds in copolymers A4CB-AA.

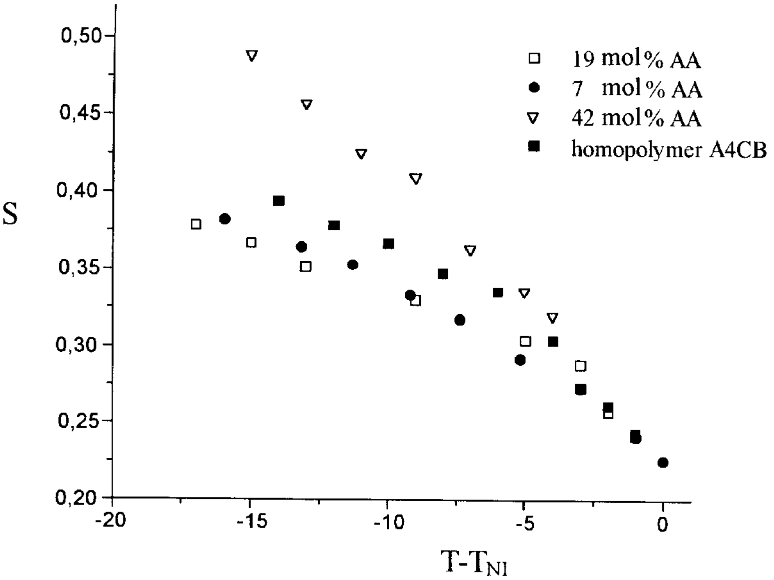

Figure 6. The temperature dependence of the order parameter *S* for copolymers A4CB-AA.

is best demonstrated by a study of the order parameter *S* of the copolymers as a function of temperature. Figure 6 clearly shows that the *S* values in the nematic mesophase of the homopolymer of A4-CB and the copolymers containing between 7 and 19 mol% of AA are essentially lower compared with that in the copolymer containing 42 mol% AA, which forms a smectic A phase. Further increase of acrylic acid content in the copolymers leads to a larger decrease in kinetic flexibility of the polymer backbone. This is confirmed by both the increasingly high glass transition temperatures (>70°C) and the disappearance of the LC phase which has occurred at 64 mol% of acrylic acid. Formation of amorphous copolymers is also caused by the decreasing content of mesogenic groups in the copolymers, and most probably the disappearance of mesophases is a result of both effects.

A number of conclusions can be presented.

(1) An effective method of synthesis of LC ionogenic copolymers by radical copolymerization of a mesogenic monomer and a non-mesogenic monomer containing a functional carboxylic group is suggested.
(2) An unusual phase behaviour of the LC copolymers with acrylic acid was found. Increase of acrylic acid content above 35 mol% drastically changes the phase behaviour of the copolymer; the nematic phase disappears and a SmA phase is formed.
(3) The formation of rigid rings in the ionogenic copolymers by intramolecular hydrogen bonding essentially increases the rigidity of the polymer backbone and predetermines the phase behaviour of the acrylic acid copolymers.

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