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ORIGINAL CONTRIBUTION

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Comb-shaped liquid crystalline ionogenic copolymers

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Abstract A series of new ionogenic liquid crystalline (LC) copolymers (A4CB-AA) was prepared by radical copolymerization of 4-(4-cyanobiphenyl-4′-yloxy) butyl acrylate (A4CB) and acrylic acid (AA). The presence of the AA units do not prevent the development of the nematic phase, which is typical of the initial cyanobiphenyl homopolymer. At a content of AA of 42–52 mol%, the copolymers produce the S_{Ad} type of mesophase, and this phenomenon is explained by an increased rigidity of the main chain due to the development of intramolecular hydrogen bonds. By increasing the concentration of AA units higher than 55 mol%, the development of mesophase is prevented, and the as-received copolymers are amorphous. A crucial role of intramolecular hydrogen bonds for the development of the S_{A} phase in the copolymers is proved by synthesizing and studying the copolymers, in which the same type of the mesogenic group A4CB is preserved but the second component is provided by methyl ether of acrylic acid; such copolymers are able to produce only a nematic phase. Studying orientation of LC A4CB-AA copolymers in the magnetic field by the method of wide-line ^{1}H NMR spectroscopy allows one to calculate the temperature dependences of order parameter S and to advance a correct interpretation of experimental data.

Key words Liquid crystal polymers – ionogenic polymers – synthesis – hydrogen bond – order parameter

Introduction

In recent years, much interest is focused on working out different approaches for preparation and characterization of new functional LC polymers such as thermochromic LC polymers, polymer piezoelectrics, and ferroelectrics, metal-containing LC systems, electro- and photochromic LC polymers, etc. [1–4].

One of the promising families of such compounds involves the so-called LC copolymers, which contain both mesogenic groups responsible for the development of the LC phase and functional groups, for example, carboxyl groups, which transform LC polymers into a specific class of functionalized LC biphilic copolymers [3, 5–15]. The presence of functional carboxylic groups in the LC matrix offers wide possibilities for the controlled modification of their physico-chemical properties.

Actually, combination of hydrophobic mesogenic fragments with their tendency for self-organisation and hydrophilic groups capable of the development of hydrogen bonds within one and the same macromolecule allows one to control their hydrophobic–hydrophilic balance by varying the ratio between the components. This makes it possible to develop a certain character of supramolecular structure, i.e., the type of a liquid-crystalline organization.

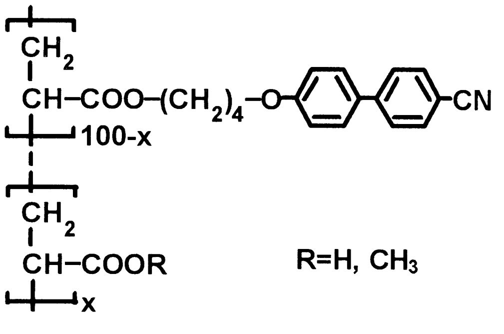
Studying such systems presents a great independent scientific interest making such systems closer to well-known ionomers, in which, as a rule, a small amount of carboxyl groups is randomly distributed in macromolecules of polyolefins.

On the other hand, the presence of highly reactive functional groups opens up wide possibilities for the modification of the properties of such compounds due to chemical or noncovalent binding by various low-molecular-mass substances with a certain "functional potency" [5–12, 15]. Such substances involve low-molecular-mass liquid crystals, dyes, chiral species, non-linear optical fragments, salts of some metals, etc.

Such functionalized LC copolymers constitute rather attractive systems for the development of new types of materials, which combine the tendency for self-organization and development of various LC phases and the ability to "demonstrate" functional properties provided by the second component involved in the LC polymer matrix.

The first attempts to synthesize such LC polymer ionogenic compounds were reported by Zhao [13, 14] and were recently described in our publications [16–18]. In the former works, the LC copolymers were prepared by partial alkaline hydrolysis of the two samples of comb-shaped LC polyacrylates [13] as well as by copolymerization of a mesogenic monomer with methacrylic acid [14]. However, both the methods encountered were serious difficulties associated with carrying out the controlled reaction of polymer-analogous transformation, with composition inhomogeneity of the reaction products as well as with a low degree of substitution of mesogenic groups (to 12%). As a result, the authors failed to examine such copolymers in a wide range of their compositions.

In this work, we propose a simple and effective method for the synthesis of the LC ionogenic copolymers with various compositions by copolymerization of a mesogenic cyanobiphenyl-containing monomer (A4CB) with acrylic acid (AA), which tends to produce hydrogen bonds. Furthermore, to estimate the effect of hydrogen bonds on the character of LC ordering, the model copolymers containing the same mesogenic monomer with methylacrylate (MA) were synthesized. The structural formulae of the synthesized copolymers are presented below:



A4CB-AA (R=H)

A4CB-MA (R=CH_3)

The objective of this work is to synthesize the above two series of copolymers containing the same mesogenic groups but with different chemical structure of the second component as well as to study the specific features of the phase behavior of the copolymers and their tendency for orientation in the magnetic field.

Experimental

Synthesis

In this work, LC copolymers were prepared by radical copolymerization of 4-(4-cyanobiphenyl-4′-yloxy)butyl acrylate with AA or MA in absolute THF (DAC 2% was used as an initiating agent). The mesogenic monomer was prepared according to the procedure described in [19]; m.p.: 91 °C; the monomer displays a monotropic nematic phase at 50 °C. The as-synthesized copolymers were boiled in methanol until the monomer species and low-molecular-mass products were removed. Then, the samples were precipitated with methanol from their solutions in chloroform. The resultant copolymers are easily solved in chloroform and THF.

The composition of the as-received copolymers was studied by the elemental analysis and UV spectroscopy by measuring the optical density of the absorption band of the biphenyl group $\lambda = 285$ nm.

Instrumentation

Molecular mass of the copolymers were estimated by GPC on a "Knauer" instrument using the polystyrene standard. Microcalorimetric studies were performed with a "Mettler" differential scanning calorimeter TA4000; heating rate was 10 K/min. Microscopic studies were carried out with a "Polam" polarization microscope equipped with a "Mettler" FP 82 hot stage. In this work X-ray patterns of the polymers were obtained with an URS-55 instrument (Cu K_α radiation); wavelength was 1.5 Å.

Wide-line ^{1}H NMR spectra were recorded with a "Bruker" MSL-90 NMR spectrometer equipped with the external stabilization of the magnetic field using a reference sample. The standard temperature unit allows one to control the temperature in the range of 300–450 K with an accuracy of 1 K. Orientational order parameter S was estimated by the classical method from the doublet splitting of the wide-line NMR spectra $\delta_f (S = \delta_f / A,\ A = 25.6\,\mathrm{kHz})$ [20]. The coefficients of rotational viscosity γ_1 were determined from the angular and kinetic dependences of the shape line of the NMR spectrum according to the procedure described in [21, 22].

Results and discussion

Thermal behavior and phase transitions

Figure 1 shows the DSC thermograms of the corresponding copolymers. Let us mention that cyanobiphenyl homopolymer A4CB is characterized by the nematic type of mesophase, which covers a rather wide temperature interval from glass transition temperature $T_g = 43\,^\circ\mathrm{C}$ to clearing temperature $T_{cl} = 104\,^\circ\mathrm{C}$ (Fig. 1, curve 1).

Introduction of up to 35 mol% of acrylic acid units to macromolecules has almost no effect on the phase behavior of the copolymers. Figure 1 (curve 2) shows the DSC scan for the test sample containing 18 mol% of AA units in the copolymer. This profile of the DSC curves is typical for all other copolymers with low (to 2 mol%) and high content (to 35 mol%) of AA units. The corresponding thermograms of such copolymers show an inflection point associated with glass transition temperature and a small endothermic peak with enthalpy $\Delta H = 1.2$–$1.4\,\mathrm{J/g}$ associated with clearing temperature of the nematic phase. By increasing the content of AA units (42 mol%), glass transition temperature T_g increases, and two overlapping endothermic peaks with the total enthalpy $\Delta H = 2.2\,\mathrm{J/g}$ are observed (Fig. 1, curve 3).

To characterize the phase state of the copolymers in the temperature range from T_g to T_{cl}, optical microscopic observations and X-ray studies were carried out. Figure 2 shows the schematic representation of the X-ray pattern of the sample of the copolymer containing 42 mol% of AA units. It follows from Fig. 2 that the corresponding small-angle pattern exhibits two well-pronounced meridional reflections ($d_1 = 33.9$ Å, $d_2 = 17.1$ Å), whereas the wide-angle X-ray pattern shows a wide diffuse equatorial scattering ($D = 5.0$ Å). Comparing this data with the calculated length of the mesogenic group (~18 Å) and taking into account the detailed structural studies concerning the copolymer with a similar structure containing the same type of mesogenic group but with a longer spacer (six ethylene groups) [23], one may assume the development of smectic mesophase with partial overlapping of mesogenic groups (S_A) for this and other samples of copolymers containing 42–52 mol% of AA units.

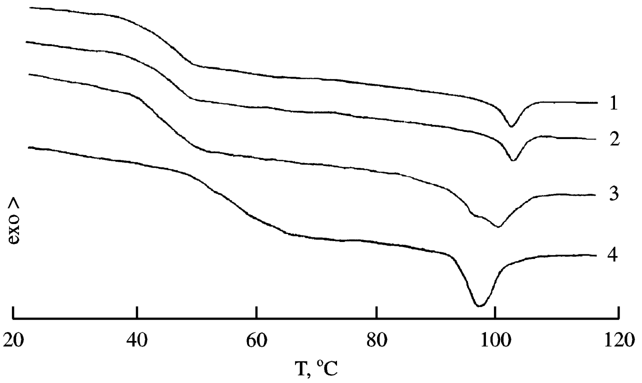


Fig. 1 DSC curves of the homopolymer A4CB (1) and copolymers A4CB-AA containing 18 (2), 42 (3) and 52 (4) mol% AA

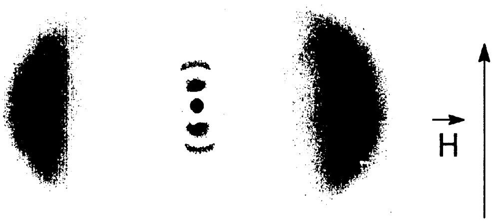


Fig. 2 Scheme of the X-ray pattern for the copolymer A4CB-AA-42 oriented in the magnetic field ($T = 25\,^\circ\mathrm{C}$)

This evidence obtained for a series of synthesized samples of A4CB-AA copolymers allowed one to construct the phase diagram for these copolymers in the wide range of their compositions (from 2 to 84 mol%). It follows from Fig. 3 that copolymers containing up to 34 mol% as well as the initial homopolymer A4CB produce nematic type of mesophase. By increasing the content of AA units, a slight increase in glass transition temperature is observed, and nematic mesophase is preserved.

However, by increasing the concentration of AA units in the copolymers above 34 mol%, in addition to the nematic phase, the S_A phase appeared, whereas the copolymer containing 52 mol% of AA units gives only the S_A phase. A further increase in the content of AA units in the copolymer (above 52 mol%) results in the "degeneration" of the liquid-crystalline phase, and the synthesized copolymers appear to be amorphous.

Considering the phase diagram, the transition from the slightly ordered nematic phase to the highly ordered smectic mesophase as observed when the content of AA units increases is noteworthy. Acrylic acid does not possess any mesogenic properties and, in the copolymers studied, it serves as a "diluent" for the LC phase and, as a result,

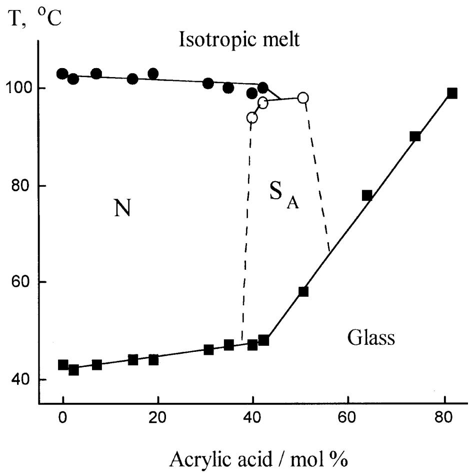


Fig. 3 Phase diagram of the copolymers A4CB-AA

should reduce its thermal stability. However, quite a reverse phenomenon takes place: by increasing the concentration of the AA units, the LC structure of the copolymer becomes more perfect. The latter phenomenon may be associated with an increase in the degree of polymerization of the copolymers with higher content of AA units and, as a result, the clearing temperature increases. However, as evidenced by the estimates of the molecular masses of the samples studied (Table 1), by increasing the content of AA units, no marked changes in the molecular mass are observed.

This unusual phase behavior of ionogenic LC copolymers is likely to be associated with the presence of free carboxyl groups, which tend to produce hydrogen bonds. The development of hydrogen bonds in the copolymers is proved by the data of IR spectroscopy: by the appearance of the absorption band at a frequency of 1710 cm^{-1} corresponding to the stretching of the carbonyl bond [$\nu_{C=O}$] of the dimer $(COOH)_2$ as well as by the appearance of a set of overlapping bands [ν_{O-H}] at 3000–3500 cm^{-1}.

The effect of hydrogen bonds on the phase behavior of acrylic copolymers is also proved by studying the copolymers containing the same mesogenic group A4CB but another type of nonmesogenic fragment. As nonmesogenic fragment, we used methyl ether of acrylic acid (MA), which is unable to produce hydrogen bonds.

Table 1 Molecular mass characteristics of the homopolymer A4CB and copolymers A4CB-AA-mol% and A4CB-MA-mol%

Samples	$M_n \times 10^3$ [a]	$M_w \times 10^3$ [a]	M_w/M_n [a]	$M_{SD} \times 10^3$ [b]
A4CB	3.39	5.59	1.65	—
A4CB-AA-9	3.25	4.73	1.45	9.2
A4CB-AA-18	3.24	5.45	1.68	11.1
A4CB-AA-38	3.43	4.64	1.35	9.1
A4CB-AA-52	2.38	3.67	1.54	7.2
A4CB-MA-10	3.20	5.11	1.60	—
A4CB-MA-20	3.30	5.59	1.69	—
A4CB-MA-35	3.28	5.46	1.66	—

[a] GPC data.
[b] Combination of sedimentation and diffusion methods.

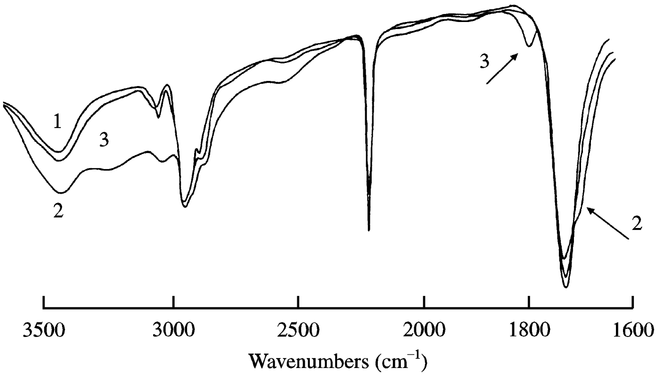


Fig. 4 Fragment of the IR-spectra of the homopolymer A4CB (1) and copolymers A4CB-AA-52 before (2) and after (3) annealing at 130 °C

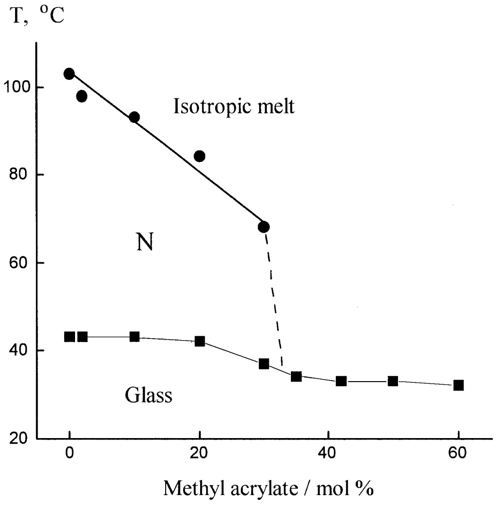


Fig. 5 Phase diagram of the copolymers A4CB-MA

As follows from the corresponding phase diagram (Fig. 5), by increasing the content of MA in the copolymers, a marked decrease in the thermal stability of the nematic phase is observed. Figure 5 shows (as compared with Fig. 4) that the glass transition temperature slightly decreases (a weak plasticizing effect of MA units). As a result of the marked decrease in clearing temperatures, the temperature interval of the existence of the mesophase “shrinks” and the interval of the compositions, where the copolymers produce the mesophase, decreases (30 mol% as compared with 52 mol% for copolymers containing AA units).

This marked difference between the behavior of two families of copolymers containing AA and MA units is likely to be rationalized by the development of intramolecular and intermolecular hydrogen bonds. The development of these bonds is likely to be accomplished in two ways: interaction between two carboxyl groups of AA units (i) and interaction between the carboxyl group of the acrylic acid and the carbonyl group of the mesogenic fragment (ii). Figure 6a shows the schematic representation of the character of intramolecular hydrogen binding between the individual units in the copolymer.

At low concentration of AA units, intramolecular hydrogen bonds are likely to provide the principle contribution to the stabilization of nematic mesophase and development of smectic (layered) packing of mesogenic groups.

From Fig. 6a it follows that the development of hydrogen bonds results in the formation of stable alicyclic rings, and this formation should have a certain effect on the kinetic flexibility of the polymer chain. This conclusion is proved by a slight increase in the glass transition temperature of copolymers by increasing the content of AA units (to 42 mol%) as well demonstrated by Fig. 3. The increased rigidity of the polymer chain is likely to result in the development of the continuous more "stretched" conformations in macromolecules, which markedly restrict the translational motion of mesogenic groups and assist the formation of smectic layers. In all probability, just within this interval of compositions (2–42 mol% of AA units), intramolecular hydrogen bonds assume a predominant role.

However, with further increase in the concentration of AA units in copolymers, intermolecular hydrogen bonds come into play. As a result, a copolymer with the content of AA units higher than 52 mol% shows a marked increase in glass transition temperature. The development of intermolecular hydrogen bonds is equal to the development of the network of "physical cross-links" in the LC polymer.

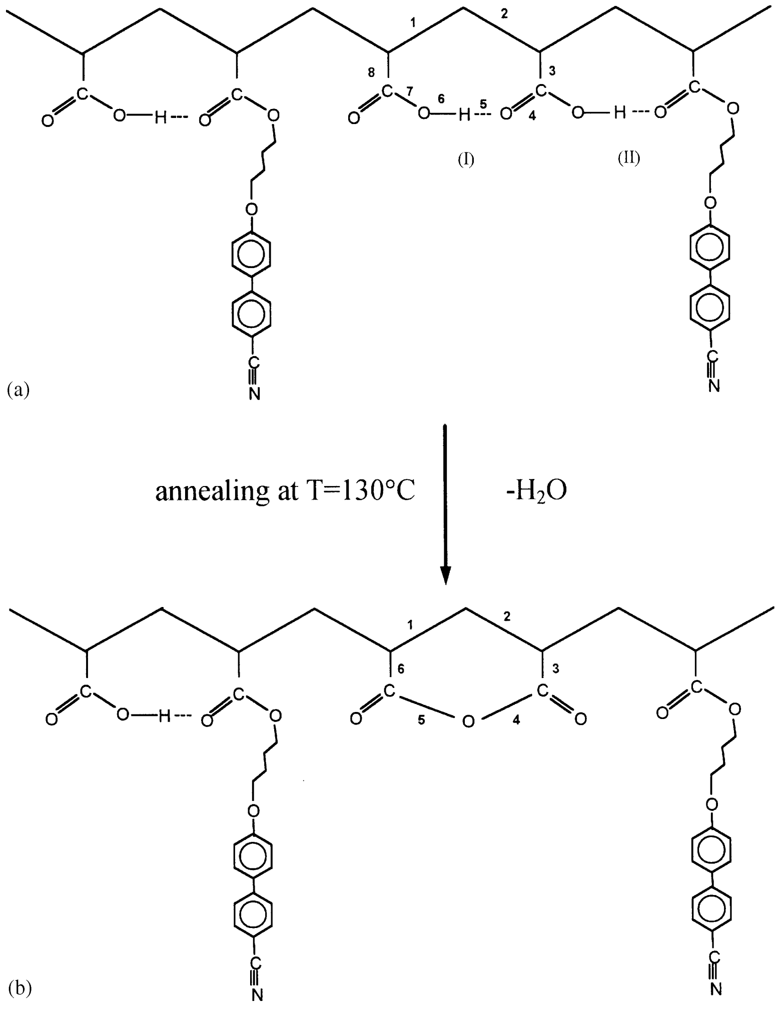


Fig. 6 Schematic representation of the polymer chain fragment before (a) and after (b) the formation of anhydrides in A4CB-AA copolymers

When the concentration of AA units exceeds 52 mol%, copolymers lose their ability to produce the LC phase. In this case, their glass transition temperatures markedly increase, and the copolymers become amorphous.

Formation of anhydrides in A4CB-AA copolymers

It is well-known that at temperatures below 250 °C, polyacrylic acid experiences the reactions of intramolecular transformation [24]. The products of these reactions are water (dehydration reaction) and carbondioxide CO_2 (decarboxylation reaction). Depending on the conditions of these reactions (temperature below 140 °C), this reaction primarily proceeds via water elimination and formation of anhydride groups. The formation of anhydrides for copolymers containing 34 and 52 mol% of AA units is proved by the appearance of a signal in the corresponding ^{13}C NMR spectra at 176 ppm, which is associated with the chemical shift of the carbon atom in the anhydride. The formation of cyclic anhydride is also suggested by the corresponding IR spectra, which show a typical signal at a frequency of 1802 cm^{-1}, and this signal is attributed to stretching of carbonyl group [$\nu_{C=O}$] in a six-ring cycle [25] (Fig. 4). At a content of AA units of 9 mol%, no formation of anhydride groups is observed. After prolonged annealing at 130 °C, all samples preserve their solubility in THF, and this fact also suggests the development of intramolecular anhydride cycles. Hence, the above evidence proves the conclusion concerning the development of intramolecular hydrogen bonds in LC copolymers containing AA units.

The development of true six-ring cycles (Fig. 6b) in the macromolecules of copolymers leads to a further increase in the rigidity of the polymer chain as compared with the effect of the intramolecular hydrogen bonds. This effect manifests itself in an increase in glass transition temperature of the copolymers (Table 2) after dehydration. At the same time, clearing temperature slightly increases. However, on the whole, the temperature interval of the LC phase (between the glass transition temperature and the clearing temperature) decreases.

Table 2 Phase transition temperatures of ionogenic LC copolymers A4CB-AA after prolonged annealing at the 130 °C

Samples	Annealing time [h]		
	0	6	24
A4CB-AA-9	G 43 N 101 I	G 43 N 101 I	G 43 N 101 I
A4CB-AA-34	G 47 N 101 I	G 53 N 101 I	G 57 N 102 I
A4CB-AA-52	G 54 S_A 96 I	G 64 S_A 100 I	G 78 S_A 108 I

G – glass temperature, N – nematic phase, S_A – smectic A phase, I – isotropic melt.

Investigation of orientation behavior of ionogenic LC copolymers in the magnetic field

Specific features of liquid crystals are associated with their ability to produce highly oriented structures under the action of the external magnetic field.

Let us consider the principal orientation ability of ionogenic LC polymers with hydrogen bonds. In our earlier works concerning the orientation of LC comb-shaped polymers under the action of external magnetic field, orientational order parameter of comb-shaped LC nematic polymers was shown to be independent of molecular mass [22, 26, 27]. For example, for homopolymer A4CB, in the interval of molecular masses from 180 000–810 000 g/mol, the order parameter remains unchanged [26].

Figure 7 shows the temperature dependencies of the order parameter for the LC homopolymer and the copolymers as measured by wide-line NMR spectroscopy. Orientation of the samples of copolymers was set by slow cooling (1 K/min) from isotropic melt to nematic mesophase in the magnetic field provided by the NMR spectrometer ($\mathbf{H} = 2.1$ T). For the nematic LC copolymers (Fig. 7, curves 2 and 3), the order parameter tends to decrease with increasing content of AA units. This deterioration in the quality of orientation is associated with the "dilution" of the copolymer by structural fragments (acrylic acid) with zero anisotropy of diamagnetic susceptibility $\Delta\chi$, which leads to a decrease in $\Delta\chi$ of the test sample. For the LC copolymer containing 42 mol% of AA units (Fig. 7, curve 4), the corresponding values of order parameter are higher than those of the LC homopolymer (Fig. 7, curve 1). This behavior is associated with the development of the S_A phase in a given copolymer. The copolymer, which produces a "pure" smectic phase in the whole temperature interval of mesophase (52 mol% of AA units), shows no orientation in the magnetic field.

The composition of copolymers also affects the reorientation of the samples of nematic LC ionogenic copolymers in the magnetic field. Figure 8 shows the dependence of the ratio of coefficients of rotational viscosity γ_1 and anisotropy of magnetic susceptibility $\Delta\chi$ on the composition of the copolymer at a temperature of 95 °C. It follows from Fig. 8 that by increasing the content of AA units in the copolymers, the ratio $\gamma_1/\Delta\chi$ increases, and this behavior is explained by a decrease in $\Delta\chi$ of the sample. However, nonlinear dependence (including, the dependence in the logarithmic coordinates) allows one to conclude that reorientation of the LC director is controlled

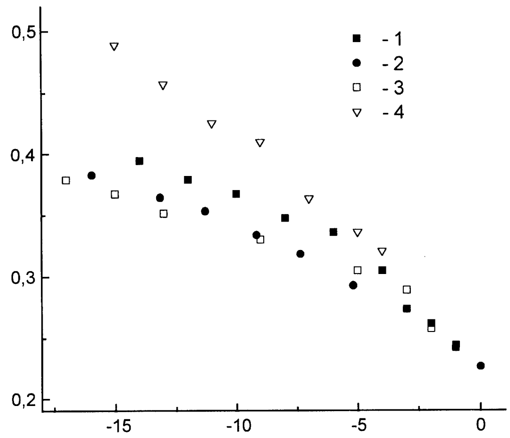


Fig. 7 The dependences of the order parameter S for the homopolymer A4CB(1) and copolymers A4CB-AA-7 (2), A4CB-AA-19 (3) and A4CB-AA-42 (4) on relative temperature ΔT

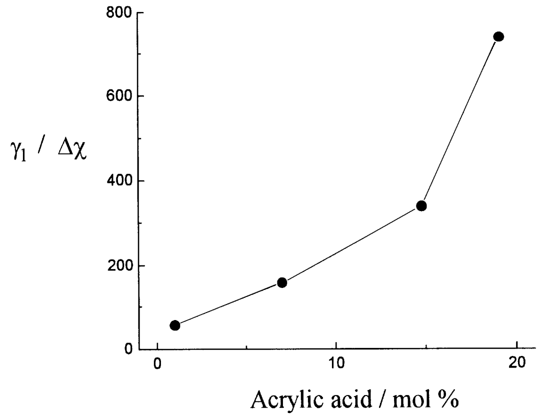


Fig. 8 The dependences of the ratio of the rotation viscosity γ_1 and the anisotropy of magnetic susceptibility $\Delta\chi$ on the compositions of the copolymers A4CB-AA at 95 °C

not only by the changes in $\Delta\chi$ but also by the hydrogen bonds, which prevent reorientation of the LC copolymer sample in the magnetic field.

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