T.P. Stepanova [1], G.I. Nosova [1], N.A. Solovskaya [1],
V.M. Kapralova [2], A.V. Yakimansky [1]

[1] Institute of Macromolecular Compounds RAS

[2] St. Petersburg Polytechnic University

THE CONSTANT ELECTRIC FIELD EFFECT
ON THE DIPOLE MOMENT OF A COMB-LIKE POLYMER
WITH CHROMOPHORE GROUPS IN SIDE CHAINS

The study of conformational properties and tendency to association for chromophore-containing comb-like copolymer of β-(3,4-dicyanophenylazobenzenethyazole) methacrylate (A) and amylmethacrylate (B) (1:1) has been carried out. The copolymer AB is of particular interest because of nonlinear optical properties of its films. Dielectric permittivity and dipole moment temperature dependences in dilute cyclohexanone solutions in the temperature range from 20 to 70 °C, in the electric field $E \leq 10^4$ V/cm were investigated by means of static dielectric polarization. It was shown that temperature and concentration dependences of dielectric permittivity for the solvent, copolymer AB, monomer A and polymer B were linear indicating low molecular interactions at temperatures and fields used. The invariable stoichiometry of components in solution for concentration lower than 10^{-3} mol/mol was proved. The values of dielectric permittivity were extrapolated to infinite dilution and increments $\alpha = (\Delta\varepsilon_{12}/\Delta x_2)_{x2=0}$ were calculated. The solvent dipole moments were calculated in terms of the Onsager theory whereas dipole moments of AB, A and B were calculated in terms of the Backingham statistical theory of dielectric polarization. Intramacromolecular conformational transition was found to be at ~40 °C. Dipole moment of A was shown to increase with both temperature and electric field strength. Copolymer side chains trans-location takes place due to intramacromolecular association resulting in the compensation of dipole moments and Kirkwood factor $g \approx 0.6$. The association of A units increases in the electric field reducing the dipole moment per monomer unit significantly and g values approximately twice.

COMB-LIKE POLYMER, DIELECTRIC POLARIZATION, DIPOLE MOMENT, ASSOCIATION.

1. Introduction

Nowadays, the investigation of the correlation between comb-like polymers properties and molecular structure is of great interest for polymer physics. Various functional groups like imine, chromophore, mesogenic ones with specific molecular interactions can be included into the side-chains of macromolecules, so it is possible to synthesize new polymers with liquid-crystalline, nonlinear optical, bioactive properties, etc. for the up-to-date engineering and medicine [1– 3].

The task of the paper was to investigate the solution of a chromophore-containing comb-like polymer by means of static dielectric polarization method in order to find correlations between the conformation as well as association tendency in a single macromolecule coil and nonlinear optical properties of the polymer material. External orienting electric field was used to gain additional information about orientation dielectric polarization of the polymer.
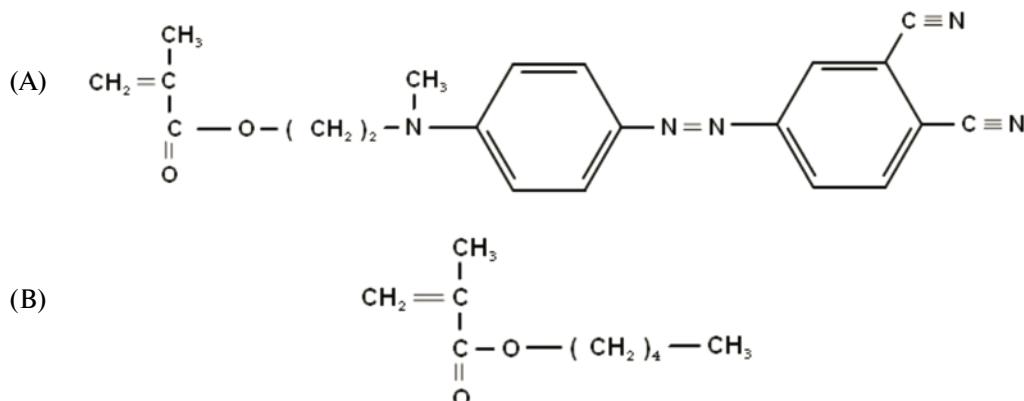
Scheme 1. Structural formulae of the objects

The comb-like copolymer of (dicyanophenyl) azobenzenethyazolemethacrylate (A) and amyl-methacrylate (B) 50 : 50 (see Scheme 1) was studied.

Films of this copolymer polarized in the corona discharge demonstrate the second order nonlinear optical properties [3].

The comparative study of temperature dependences of dielectric permittivity and dipole moments for copolymer AB, polymer B and monomer A under the electrical field $|\mathbf{E}| = 10^4$ kV/cm and $\mathbf{E} = 0$ in the cyclohexanone dilute solutions was carried out.

2. Experimental

2.1. Copolymer AB synthesis technique

Chromophore-containing monomer A was synthesized in two steps:

(a) synthesis of 4-{4-[methyl(2-hydroxy-ethyl)amino]-phenylazo}-phthalonitrile (MAPN) from N-methyl-N-(2-hydroxyethyl)aniline and 3-aminophthalonitrile using the technique described in Ref. [4]. Some properties of this compound are as follows: melting temperature $T_m = 169 - 171$ °C; wavelength of the absorbance spectra maximum $\lambda_{max} = 483$ nm;

(b) synthesis of {{4-{4-[methyl(2-hydroxy-ethyl)amino]-phenylazo}-phthalonitrile}}meth-acrylate from MAPN and methacrylic acid chloride in dimethylacetamide at 0 °C. Reaction yield was as high as 83 %.

Copolymer AB was synthesized by radical polymerization of chromophore-containing monomer A and amylmethacrylate B with the ratio of 50 : 50 in the 30 mass. % dimethylacet-amide solution using dinitrileazoisobutyric acid as initiator (1 mass.%) at 70 °C. Water precipitation was used. After drying the polymer was purified by the precipitation from the cyclohexanone solution into the water-methanol 1 : 3 mixture. The copolymer intrinsic viscosity [η] in the cyclohexanone was 0.72 cm³/g. Structure and composition of monomer A and copolymer AB were verified by means of NMR spectroscopy.

The technique of measuring solution dielectric permittivity in the external field as well as specific volume evaluation is described in Refs. [5−8].

2.2. The equations used

The dipole moment of the solvent (cyclohexanone) was calculated in terms of Onsager theory of dielectric polarization [9]:

$$\mu^2 = \frac{9kT}{4\pi N_A} \cdot \frac{M}{\rho} \cdot \frac{(2\varepsilon + n^2)(2\varepsilon - n^2)}{\varepsilon(n^2 + 2)^2}. \quad (1)$$

Copolymer AB was considered regular. Both monomers contain polar side groups joined with the same methacrylate chain. In this case, the summarized dipole moment of the macromolecule $(AB)_n$ is

$$\mu_{ef\,cop} = \sum_{i=1}^{n} (\mu_{A_i} + \mu_{B_i}), \quad (2)$$

and the mean square dipole moment in the first approximation (the first term of the series) is given by

$$\frac{\overline{\mu_{ef\,cop}^2}}{n} = (\overline{\mu_A^2} + \overline{\mu_B^2}), \quad (3)$$
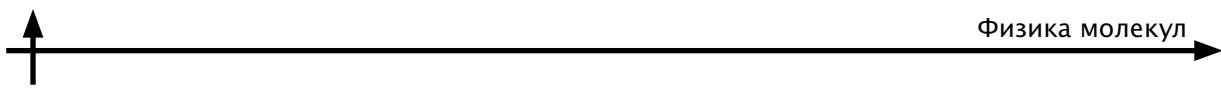
where $\overline{\mu_A^2}$ is the mean square of the monomer A dipole moment and $\overline{\mu_B^2}$ is the mean square of the dipole moment of monomer unit B included into the copolymer chain.

The mean square dipole moments of copolymer AB and homopolymer B macromolecules per monomer unit and that of monomer A molecule were calculated in terms of Frochlich − Buckingham theory of statistical polarization [10−13] for a two-component system (dissolved substance − solvent) in the case of infinite dilution:

$$\lim_{x_2 \to 0} \mu_{ef}^2 = \frac{kT}{4\pi N_A} \left\{ \frac{(\varepsilon_1 - 1)(2\varepsilon_1 + 1)}{\varepsilon_1} \times \right.$$

$$\times \left[M_1 \left(\frac{dv}{dx_2} \right)_{x_2=0} - M_1 v_1 + M_2 v_2 \right] +$$

$$+ V_1 \frac{2\varepsilon_1^2 + 1}{\varepsilon_1^2} \left(\frac{d\varepsilon}{dx_2} \right)_{x_2=0} -$$

$$- 6V_1 \frac{(n_1^2 - 1)^2}{(2\varepsilon_1 + n_1^2)^2} \left(\frac{d\varepsilon}{dx_2} \right)_{x_2=0} + \tag{4}$$

$$+ \frac{3(2\varepsilon_1 + 1)(n_1^2 - 1)}{2\varepsilon_1 + n_1^2} V_1 -$$

$$\left. - \frac{3(2\varepsilon_1 + 1)(n_2^2 - 1)}{2\varepsilon_1 + n_2^2} V_2 \right\}.$$

In Eqs. (1) and (4) and below the following symbols are used: ε is a dielectric permittivity; n is a refraction index; V is a molar volume ($V = M v_{sp}$, v_{sp} is a specific volume; M is a molecular mass); $\frac{\partial \varepsilon_{12}}{\partial x_2}\Big|_{x_2=0}$ and $\frac{\partial v_{12sp}}{\partial x_2}\Big|_{x_2=0}$ are in-

crements of the dielectric permittivity and the specific volume in the case of infinite dilution; x is a mole fraction; T is a temperature; N_A is the Avogadro number; k is the Boltzmann constant; μ is a dipole moment; lower indices 1 and 2 refer to the solvent and the dissolved substance respectively.

Refraction indices were determined from the molar refraction R by the Lorentz − Lorence equation:

$$R_D = \frac{n^2 - 1}{n^2 + 2p} \frac{M}{\rho}. \tag{5}$$

The molar refraction R_D for the molecules of cyclohexanone and monomer A as well as monomeric units A and B were calculated as a sum of bond increments and atomic refractions [10].

3. Results and discussion
3.1. The dipole moment of cyclohexanone molecule

Temperature dependences of experimental values for the cyclohexanone dielectric constant, the density, the dipole moment and the Kirkwood factor are presented in Table 1. Dielectric permittivity values are in the close agreement with those given in Ref. [12].

The correlation factor in the orientation of dipolar cyclohexanone molecules

$$g = (\mu_{liquid})^2 / (\mu_{gas})^2$$

was calculated using the tabulated value of the dipole moment μ_{gas} of gaseous cyclohexanone molecules; $\mu_{gas} = 2.8$ D [11].

As indicated in Table 1, the cyclohexanone dipole moment increased from 2.87 to 2.89 D

Table 1

Temperature dependence of cyclohexanone physical properties

| T °C	ε	ρ, g/cm³	v, cm³/g	n^2	μ, D	g
20	15.102	0.94654	1.0521	2.072710	2.87	1.050
25	14.811	0.94209	1.0615	−	2.88	1.060
30	14.520	0.93764	1.0614	2.059060	2.88	1.060
35	14.229	0.93319	1.0716	−	2.89	1.060
40	13.939	0.92874	1.0708	2.045500	2.89	1.065
50	13.357	0.91984	1.0804	2.032039	2.89	1.066
60	12.776	0.91094	1.0902	2.018663	2.89	1.060
70	12.195	0.90204	1.1002	2.005375	2.88	1.060
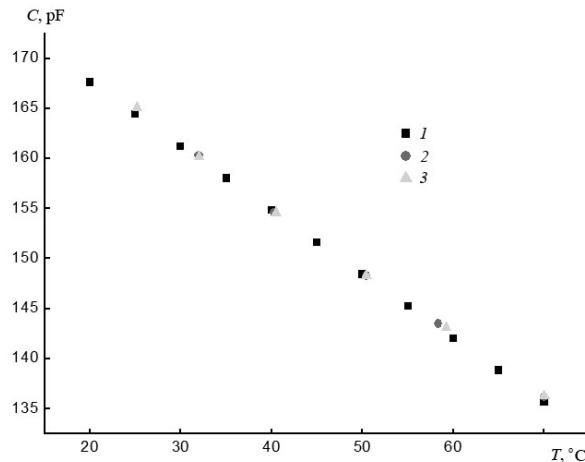
Fig. 1. Plots of the electrical capacitance, C, of the measuring cell filled with cyclohexanone, vs temperature, T, at 500 (*1*), 750 (*2*), and 1000 (*3*) V

with increase in temperature from 25 to 60 °C. This change can be caused by the variation of statistical weights of the "boat" and more polar "chair" conformers. The g value being of the order 1.1 shows a certain correlation in the orientation of dipole moments of cyclohexanone molecules which causes a high value of the dielectric permittivity $\varepsilon = 15.1$ at the temperature of 20 °C.

Electrical capacitance C of the measuring cell filled with cyclohexanone under the external orienting constant electric field at the voltage of $U = 500$, 750 and 1000 V in the temperature range from 25 to 60 °C is shown in Fig. 1. It can be seen that the field mentioned above does not affect C values and, therefore, does not change the orientation of the dipole moment vector for the $>C = O$ group in the cyclohexanone molecule and also does not influence on the ratio of the "boat" and "chair" conformers statistical weights in the chosen temperature and voltage range.

3.2. The dipole moment of monomer A. External electric field influence

Temperature and concentration dependences for the electrical capacitance of the measuring cell filled with the solutions of monomer A in cyclohexanone at $E = 10^4$ V/cm are shown in Fig. 2. The identical dependences measured at $E = 0$ are similar. The linearity of these de-

pendences confirms the invariable stoichiometry of the solution composition at the constant temperature, making possible to extrapolate the data to infinite dissolution and to evaluate increments of dielectric permittivity $(\Delta\varepsilon)/(\Delta x_2)|_{x2=0}$. Here $\Delta\varepsilon = (\Delta C)/C_0$; $C = \varepsilon C_0 + C_{par}$; C_0 is a self-capacitance of the cell determined by the interelectrode gap geometry; C_{par} is a wire capacitance. C_0 and C_{par} values were calculated from the data of capacitance measurements for the cell filled with standard liquids with the tabulated dielectric permittivity.

a)
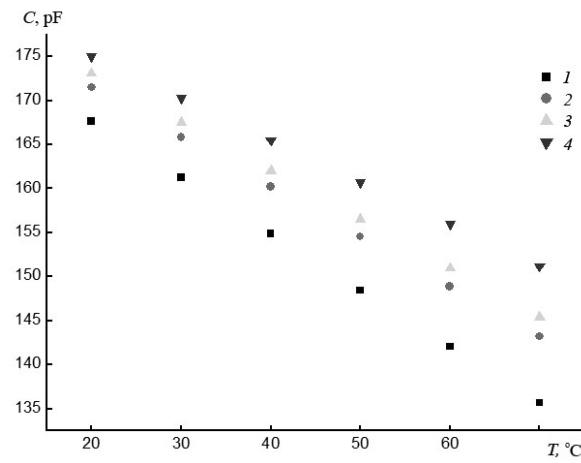
b)
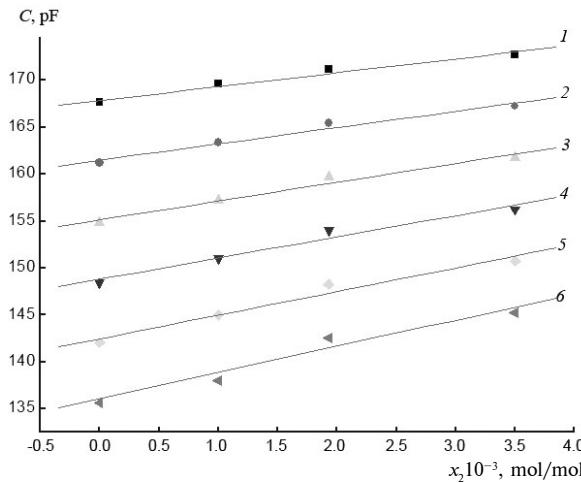
Fig. 2. Plots of the electrical capacitance, C, of the measuring cell filled with cyclohexanone solution of monomer A, at $E = 10^4$ V/cm, vs temperature (*a*) and concentration (*b*); the concentration $x_2 = 0$ (*1*); 1 (*2*); 2 (*3*); 3 (*4*) mol/mol (*a*); the temperature $T = 20$ (*1*); 30 (*2*); 40(*3*); 50 (*4*); 60 (*5*); 70 (*6*) °C (*b*)
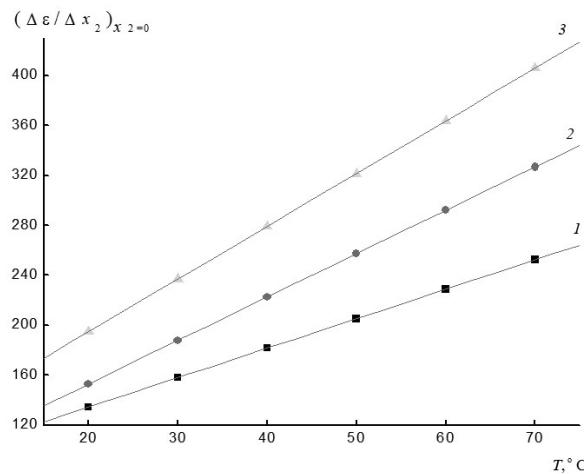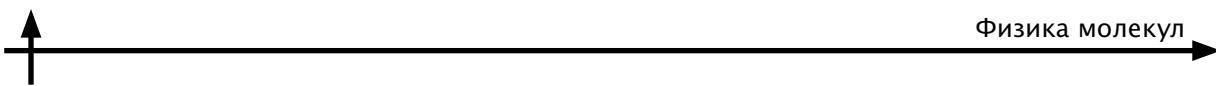
Fig. 3. Plots of the dielectric permittivity increments for cyclohexanone solution of monomer A vs temperature at 0 (*1*), 750 (*2*), 1000 (*3*) V
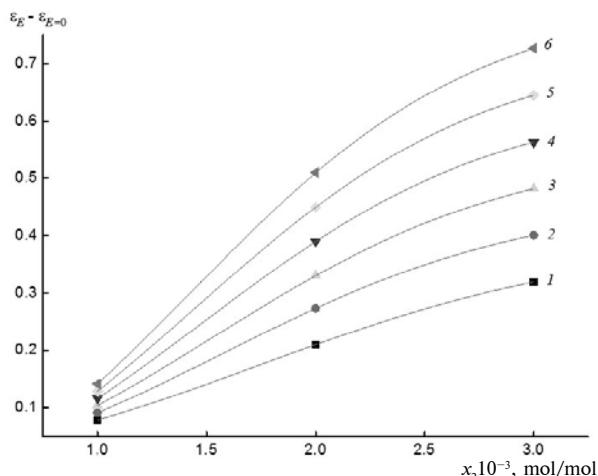

Fig. 4. Plots of the differential static dielectric permittivity of cyclohexanone solution of monomer A at $E = 10^4$ V/cm, vs solution concentration, x_2, at 20 (*1*), 30 (*2*), 40(*3*), 50 (*4*), 60 (*5*), and 70 (*6*) °C

Temperature dependences of dielectric permittivity increments for monomer A at different E values are shown in Fig. 3. It is well-known that the dielectric permittivity increment is in direct proportion to squared dipole moment. Obviously (see Fig. 3), the dipole moment of monomer A increases with temperature at $E = 0$. The tendency remains the same at non-zero field. Increment values also rise when E is increased.

The molecule A structure is rather complicated; it contains several polar groups and axes

of internal rotation. Previous investigations [14 −16] of low molecular liquid crystals with the same polar cyanophenyl end groups both in solution and in condensed state by means of dielectric polarization method showed the formation of associates with antiparallel laying of dipole moments (about 4 D) of cyanophenyl groups.

The increasing temperature gives rise to the disordering the antiparallel orientation of the polar groups. The external electric field has the same effect forcing the orientation of the end cyanophenyl groups along the field. Also, one can suppose that the external electric field forces the appearance of the induced dipole

a)
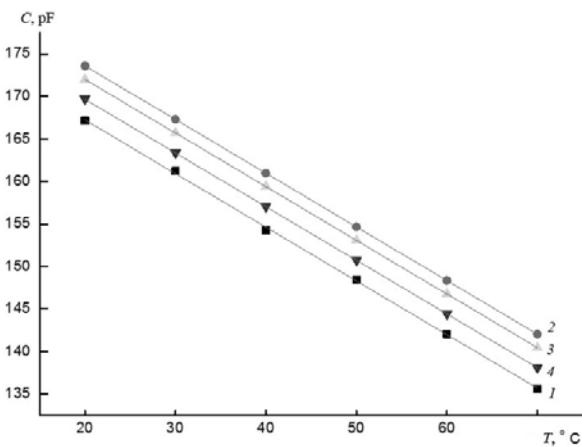
b)
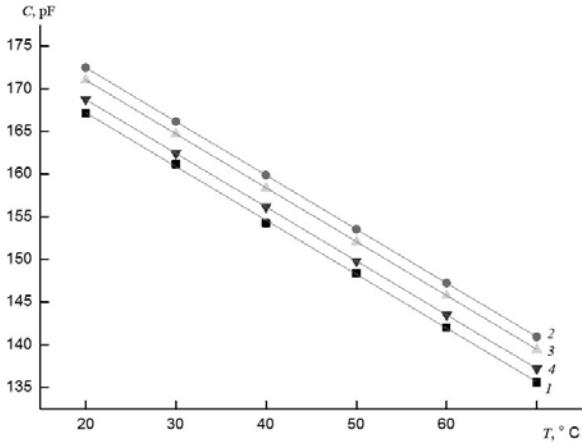
Fig. 5. Plots of the electrical capacitance, C, of the measuring cell filled with cyclohexanone solution of copolymer AB at $E = 0$ (*a*) and $E = 10^4$ V/cm (*b*) vs temperature, T; concentration $x_2 = 0$ (*1*), 0.00649 (*2*), 0.00359 (*3*), 0.00253 (*4*) mol/mol

a)

б)
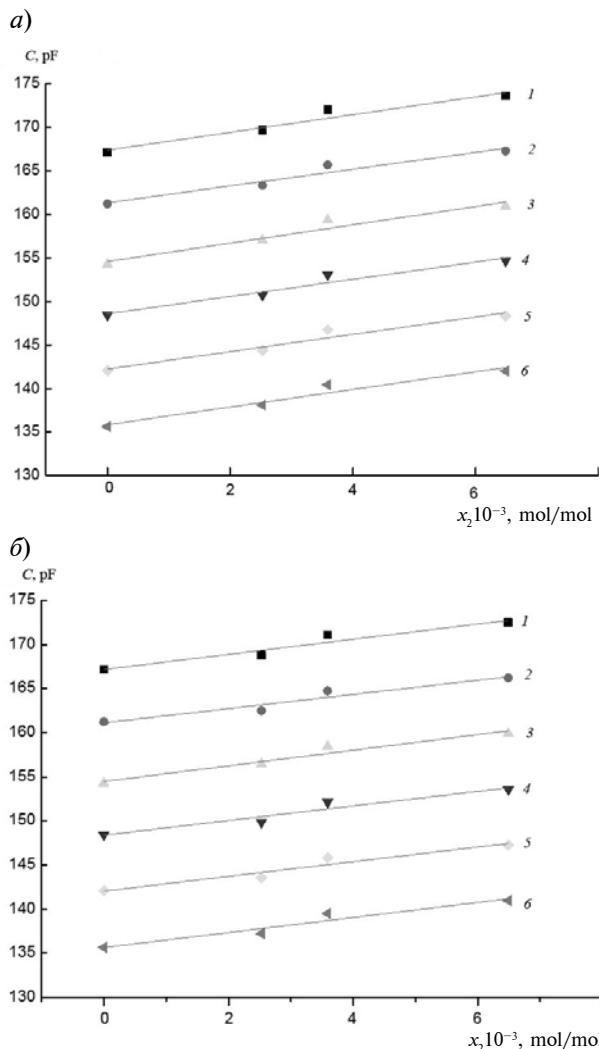
Fig. 6. Plots of the electrical capacitance, C,
of the measuring cell filled with cyclohexanone
solution of copolymer AB at $E = 0$ (*a*) and
$E = 10^4$ V/cm (*b*) vs concentration, x_2.
Temperature $T = 20(1)$, 30 (*2*), 40(*3*), 50 (*4*), 60 (*5*),
and 70 (*6*) °C

moment from the chromophore groups which
makes the whole dipole moment value of the
molecule or associate larger.

Concentration dependences of the static po-
larization for the monomer A at $E = 10^4$ V/cm
are presented in Fig. 4. One can see that the
monomer A polarization increases with tem-
perature nonlinearly and tends to have a limit
as the monomer concentration in solution rises.
This seems to be coupled with the associa-
tion and partial dipole moments compensation
caused by it.

3.3. The effect of the external electric field on the dielectric polarization of the copolymer AB

Temperature and concentration depen-
dences for the electrical capacitance of the
measuring cell filled with copolymer AB so-
lutions in cyclohexanone at $E = 0$ and
$E = 10^4$ V/cm are shown in Figs. 5 and 6.
The dependences are linear, and this makes it
possible to calculate the dielectric permittivity
increment $(\Delta\varepsilon)/(\Delta x_2)\big|_{x2=0}$ for the copolymer AB
solutions in cyclohexanone.

The temperature dependences of $(\Delta\varepsilon)/(\Delta x_2)\big|_{x2=0}$ for infinitely diluted solutions of the
copolymer AB without external orienting elec-
tric field and in the field are presented in Fig.
7. One can see that temperature behavior of the
dielectric permittivity increment for the copo-
lymer is quite different from that of the mono-
mer A. The values of $(\Delta\varepsilon)/(\Delta x_2)\big|_{x2=0}$ decline in
the temperature range of 20−40 °C and then
increase with temperature. The change of the
temperature rate of the $(\Delta\varepsilon)/(\Delta x_2)\big|_{x2=0}$ depen-
dence at 40 °C is caused by the intramacromo-
lecular conformational transition and reflects
the change of the intramolecular structure as
well as the ratio of statistical weights of con-
formers with different dipole moments. This ef-
fect is typical for previously investigated comb-
like homopolymethacrylates, side chains of
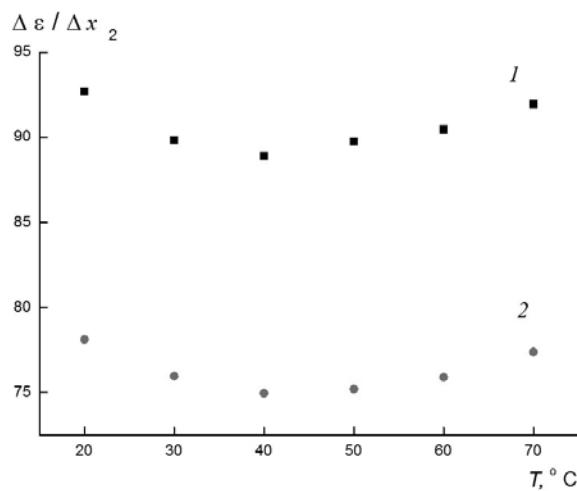
Fig. 7. Plots of the dielectric permittivity
increments of the cyclohexanone solution
of the copolymer AB at $E = 0$ (*1*), and 10^4 V/cm
(*2*) vs temperature
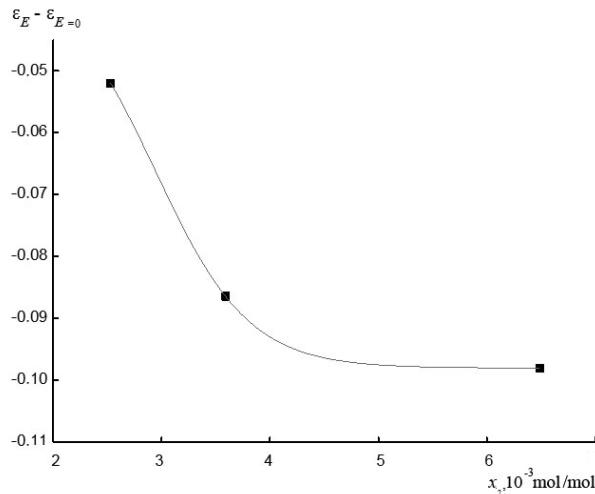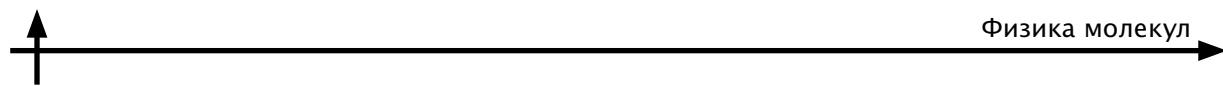
Fig. 8. Plots of the static dielectric permittivity of the cyclohexanone solution of the copolymer AB at $E = 10^4$ V/cm, vs solution concentration

which contain fragments of the same structure as low-molecular liquid crystals do [17−23].

When external electric field is applied, the temperature dependence of $(\Delta\varepsilon)/(\Delta x_2)|_{x2=0}$ is the same. However, the values of $(\Delta\varepsilon)/(\Delta x_2)|_{x2=0}$ are less in the whole temperature range. It can be caused by the fact that in electric field the value of projection of the monomer unit effective dipole moment on the field direction decreases. At the same time the ratio of the conformer statistical weights in copolymer is not affected by the applied external electric field.

As it was shown in Refs. [19, 22], side chains intramacromolecular association in comb-like polymers was rather typical because of molecular groups specific interactions inside the polymer coil. Moreover, the intramolecular conformational transitions in comb-like polymers determine further structure formation in dilute solutions on the intermolecular level and lead to the gel formation when the thermodynamic parameters of the solution are changed [24, 25].

Table 2

The temperature dependence of the properties of the investigated compounds in cyclohexanone solutions

| T, °C	v_2, cm³/g	n_2^2	$\alpha = (\Delta\varepsilon/\Delta x_2)_{x2=0}$		$-\beta = (\Delta v/\Delta x_2)_{x2=0}$	μ^2, D	
			$E = 0$	10^4 V/cm		$E = 0$	10^4 V/cm
Copolymer AB							
20	1.1000	1.979101	92.70	78.11	0.0435	8.54	7.92
30	1.1104	1.967664	89.84	75.96	0.0438	8.61	7.99
40	1.2080	1.955824	88.90	74.95	0.0440	8.77	8.12
50	1.1312	1.944271	89.77	75.19	0.0440	9.00	8.20
60	1.4160	1.932993	90.46	75.89	0.0438	9.26	8.55
70	1.5200	1.921982	91.94	77.37	0.0434	9.51	8.79
Polymer B							
20	0.9493	2.20727	26.06	42.74	0.107	3.54	4.83
30	0.9500	2.20602	26.18	42.94	0.116	3.74	4.96
40	0.9507	2.20478	26.30	43.14	0.126	3.74	5.10
50	0.9515	2.20336	26.43	43.33	0.136	3.88	5.25
60	0.9522	2.20212	26.54	43.53	0.146	3.98	5.40
70	0.9529	2.20088	26.66	43.72	0.156	4.10	5.55
Monomer A							
20	1.0052	2.13289	134.409	194.705	0.0439	10.27	12.05
30	1.0096	2.11889	157.973	236.949	0.0428	11.25	13.48
40	1.0192	2.10489	181.552	279.193	0.0516	12.23	14.88
50	1.0288	2.09089	205.139	321.436	0.0516	13.22	16.27
60	1.0384	2.07689	228.751	363.707	0.0518	14.22	17.67
70	1.0480	2.06289	252.345	405.951	0.0522	15.22	19.06
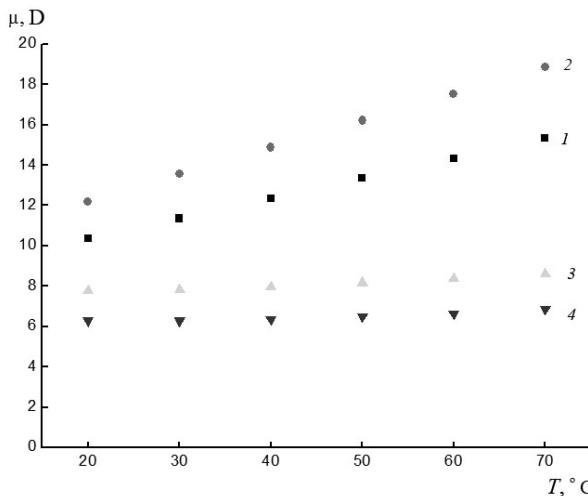
Fig. 9. Plots of the dipole moment
of the monomer A (*1, 2*), and of the partial
dipole moment of monomer unit A included
into the copolymer AB (*3, 4*), measured in the
cyclohexanone solution $E = 0$ (*1, 3*), and
10^4 V/cm (*2, 4*) vs temperature, T.

The intramolecular association is reflected also in the nonlinear effect of dielectric polarization. The concentration dependence of the ε_E and $\varepsilon_{E=0}$ difference is depicted in Fig. 8. The abrupt decrease of the difference of the dielectric permittivity in the field and without the field as the polymer concentration increases and the plateau at $x_2 > 0.004$ mol/mol is due to the association of the monomeric units A with the compensation of the tangential partial dipole moments on the intramolecular level [6, 22, 23].

3.4. The dipole moment and the internal rotation of monomer units A in the copolymer macromolecule

It is well known [10, 14, 26] that the orientation of the polar monomer units in polymers depends on the internal rotation hindering in the chain and is determined by the macromolecule conformation properties. As a result, the dipole moment per monomer unit is different from the dipole moment of a free monomer molecule.

As it was mentioned above, the presence of monomer units A in the copolymer macromolecules AB gives nonlinear optical properties of the copolymer in the condensed state. Therefore, it is important to know the conditions of monomer units A internal rotation in the copolymer chain, which gives information about structure formation in the single molecular coil and order of the copolymer in the condensed state.

According to Eq. (3), it is possible to calculate molar orientation polarization of the monomer unit A in the copolymer macromolecule by subtracting molar orientation polarization of polymer units B from the copolymer molar orientation polarization (see Table 2). Calculated values of orientation dielectric polarization (dipole moment squared) of monomer unit A in copolymer AB are also given in Table 2.

Dipole moments of isolated monomer A and monomer unit A in the copolymer AB are compared in Fig. 9 in the absence and in the presence of the electric field. The Kirkwood factor
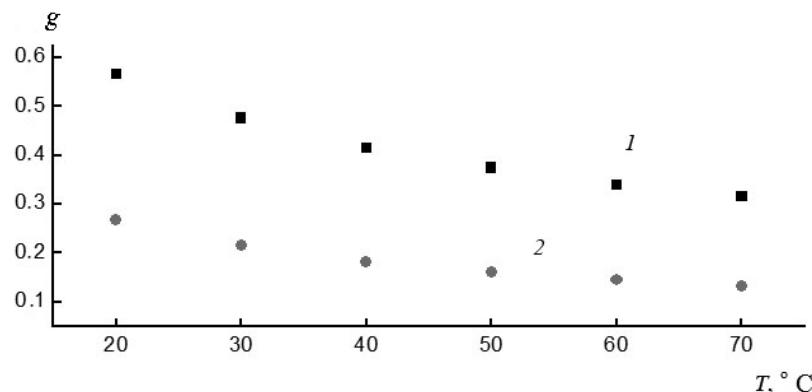

Fig. 10. Plots of the Kirkwood factor of the monomer unit A included into
the copolymer AB measured in the cyclohexanone solutions at $E = 0$ (*1*)
and 10^4 V/cm (*2*) vs temperature
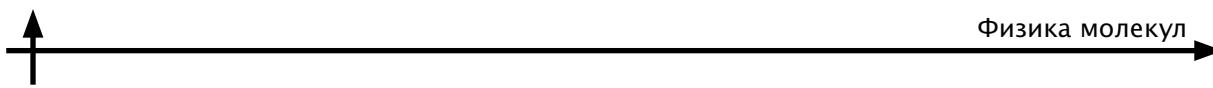
$$g = (\mu_{(A)cop})^2/(\mu_{(A)isol})^2$$

values are presented in Fig. 10 for the same two cases. It can be seen that the correlation factor values g of polar monomer unit A are typical for the polymethacrylate homologous series being equal to approximately 0.6 at $T = 20$ °C [6, 21−23]. When electric field is applied, the g value decreases to about 0.35 reflecting the larger degree of association in the molecular coil. The received value $g < 1$ characterizes the tendency to antiparallel orientation of the monomer A side chains and the increase of the units A association when the solution is in the electric field.

4. Conclusions

Thus, the analysis of experimental data on comparative study of the dielectric polarization of the copolymer AB, the polymer B and the monomer A leads to the following conclusions.

(1) There are associates of constant stoichiometry at given temperature due to intermolecular interactions in the monomer A solutions, and their dipole moments increase both with temperature and with external electric field.

(2) In the copolymer solution, intra-macromolecular association of chromophore-containing side chains in *trans* conformation takes place leading to dipole moment compensation. The Kirkwood factor is less than 1. When external electric field is applied, intramolecular association increases: g values decrease almost twice.

(3) The dipole moment of the copolymer molecule per monomer unit AB decreases under the external electric field.

(4) The intramacromolecular conformational transition takes place at the temperature of about 40 °C.

REFERENCES

[1] **J.K. Moscicki,** Liquid crystal polymers: from structure to applications, in Dielectric Relaxation in Macromolecular Liquid Crystals, ed. by Collyer A.A., Elsevier Applied Science, London, 1992, pp. 143−236.

[2] **N.A. Nikonorova, A.V. Yakimansky, N.N. Smirnov, V.V. Kudryavtsev, R. Diaz-Calleja, P. Pissis,** Dielectric relaxation in copolymethacrylates containing side-chain nonlinear optical chromophores, Polymer. 48 (2007) 556−563.

[3] **N.A. Nikonorova, R. Diaz-Calleja, A.V. Yakimansky,** Molecular mobility in comb-like copolymethacrylates with chalcone-containing side-chains, Polym. Int. 60 (2011).

[4] **V.B. Lyskov, I.G. Abramov, O.V. Dobrokhotov, G.I. Nosova, A.V. Yakimanskiy, V.V. Kudryavtsev,** Khromofory na osnove zameshchennykh 4-fenilazoftalonitrilov dlya polimerov s nelinejnymi opticheskimi svojstvami [Chromophores based on substituted 4-phenylazophthalonitriles for polymers with nonlinear optical properties], Chemistry and chemical technology. 51 (8) (2008) 86.

[5] **T.I. Borisova, L.L. Burstein, T.P. Stepanova, N.A. Nikonorova,** Influence of the external oriented (electric or mechanic) fields on the dielectric relaxation in LC side-chain polymers, Intern. J. Polymeric materials. 22 (1−4) (1993) 103−112.

[6] **T.P. Stepanova, L.L. Burstein,** Dipole polarization and molecular structure of main- and side-chain liquid-crystalline polymers in dilute solu-

tions. Chinese Journal of Polymer Science. 14 (1) (1996) 1−18.

[7] **T.P. Stepanova, A.N. Pogrebnaya, V.M. Kapralova, S.S. Skorokhodov,** External orienting electric field influence on dielectric relaxation of segmented polyesters in diluted solution, Polymer Science. A. 49 (2) (2007) 321−328.

[8] **T.P. Stepanova, M.M. Glazdovskaya, V.M. Kapralova,** External orienting electric field influence on dipole moment of mesogen-containing polymer, St. Petersburg Polytechnical University Journal: Physics and Mathematics. 4(162) (2011) 134−165.

[9] **L. Onsager,** Electrical moments of molecules in liquids, J. Amer. Chem. Soc. 58 (8) (1936) 1468.

[10] **M.V. Vol'kenshtein,** Stroenie i fizicheskie svojstva molekul [Structure and physical properties of molecules], USSR Academy of Sciences Publishing House, Moscow, Leningrad, 1955.

[11] **S.A. Osipov, V.I. Minkin, A.D. Garshevskij,** Spravochnik po dipol'nym momentam [Handbook on dipole moments], Vysshaya shkola, Moscow, 1971.

[12] **S.O. Morgan, W.A. Yager,** Dielectric Properties of Organic Compounds. Relation to Chemical Composition and Physical Structure, Industrial & Engineering Chemistry. 32 (11) (1940) 1519.

[13] **A.D. Buckingham,** A Theory of the Dielectric Polarization of Polar Substances, Proc.Roy. Soc. A., Mathem.a. Phys. Sci. A 38 (1213) (1956) 235−244.

[14] **G.P. Mikhailov, L.L. Burstein,** Sovremennye teorii dipol'noj polyarizatsii molekulyarnykh kondensirovannykh system [Modern theories of dipole polarization of molecular condensed systems], Uspekhi fiz.nauk, 74 (1961) 3.

[15] **T.P. Stepanova, A.E. Bursian, V.M. Denisov,** Molecular Dipole Moment and mobility in Nematic Liquid Crystal of 4-n-butyl ester [4'-n-hexyloxyphenyl]benzoic acid in the absence of external orienting fields, Solid State Physics. 44 (10) (2002) 1900−1907.

[16] **J.A. Malecki, J. Novak,** Intermolecular interactions in benzene solutions of 4-heptyl-3'-cyano-biphenyl studied with non-linear dielectric effects, J. Molecular Liquids. 81 (1999) 245.

[17] **T.I. Borisova, L.L. Burstein, T.P. Stepanova, V.M. Moiseenko, V.P. Shibaev,** O konformatsionnom perekhode v rastvorakh poli-N-oktadetsilakrilamida [On conformation transition in N-octadecylacrylamide solutions], Polymer Science. B. 18 (7) (1976) 550−553.

[18] **T.I. Borisova, L.L. Burstein, T.P. Stepanova, Ya.S. Freidzon, V.P. Shibaev, N.A. Plate,** Dipol'nyj moment i vnutrimolekulyarnyj orientatsionnyj poryadok v makromolekulakh kholesterinovogo efira poli-N-polimetakriloil-ω-aminolaurinovoj kisloty [Dipole moment and intramolecular orientational order in macromolecules of cholesterine ester of poly-N-polymethacryloyl-ω-aminolaurylic acid], Polymer Science. B. 18 (8) (1976) 628−631.

[19] **T.I. Borisova, L.L. Burstein, T.P. Stepanova, Ya.S. Freidzon, V.P. Shibaev,** Vnutrimolekulyarnaya uporyadochennost' kholesterinsoderzhashchikh sopolimerov [Intramolecular ordering of cholesterin-containing copolymers], Polymer Science. A. 20 (6) (1978) 1380−1384.

[20] **Ya.S. Freidzon, V.P. Shibaev, I.M. Agranovich, V.D. Pautov, E.V. Anufrieva, N.A. Plate,** Strukturoobrazovanie v kholesterinsoderzhashchikh zhidkokristallicheskikh polimerakh [Structure formation in cholesterol-containing liquid crystal polymers], Polymer Science. A. 20 (11) (1978) 2601.

[21] **T.I. Borisova, L.L. Burstein, T.P. Stepanova, V.P. Shibaev,** O konformatsionnykh perekhodakh v rastvorakh grebneobraznykh polimerov [On conformation transitions in solutions of comb-like polymers], Polymer Science. B. 21 (3) (1979) 186−190.

[22] **T.I. Borisova, L.L. Burstein, T.P. Stepanova, S.G. Kostromin, V.P. Shibaev,** Konformatsionnoe sostoyanie grebneobraznogo zhidkokristallicheskogo polimera s tsiandifenil'nymi bokovymi gruppami [Conformation state of comb-like LC polymer with cyandiphenyl side groups], Polymer Science. A. 28 (5) (1986) 1331−1332.

[23] **T.I. Borisova, L.L. Burstein, V.P. Malinovskaya, T.P. Stepanova, B. Kriuke,** Dipol'nyj moment i vzaimnaya orientatsiya polyarnykh mezogennykh fragmentov v grebneobraznykh polimerakh [Dipole moment and orientation of polar mesogenic fragments in comb-like polymers], Polymer Science. B. 32 (6) (1990) 406−410.

[24] **T.I. Borisova, L.L. Burstein, T.P. Stepanova, V.P. Shibaev, N.A. Plate,** Issledovanie dielektricheskoj polyarizatsii gelej nekotorykh grebneobraznykh polimerov [Investigation of dielectric polarization of some comb-like polymer gels], Polymer Science. A. 19 (2) (1977) 286−290.

[25] **T.P. Stepanova, L.L. Burstein,** Dielectric polarization in gelforming liquid-crystalline polymers and their monomers, Proceedings of the Workshop on non equilibrium phenomena in super cooled fluids, glasses and amorphous materials. (Pisa. Italy, 25-29 September, 1995). Series in Contemporary Chemical Physics. 12 (1995).

[26] **O.B. Ptitsyn, T.M. Birshtein,** Konformatsii makromolekul [Conformations of macromolecules], Nauka, Moscow, 1960.

THE AUTHORS

STEPANOVA Tamara P.
Institute of Macromolecular Compounds RAS
31 Bolshoy Ave. V.O., St. Petersburg, 199004, Russian Federation
t_stepanova2005@mail.ru

NOSOVA Galina I.
Institute of Macromolecular Compounds RAS
31 Bolshoy Ave. V.O., St. Petersburg, 199004, Russian Federation
nosova@physicist.net

SOLOVSKAYA Nina A.
Institute of Macromolecular Compounds RAS
31 Bolshoy Ave. V.O., St. Petersburg, 199004, Russian Federation
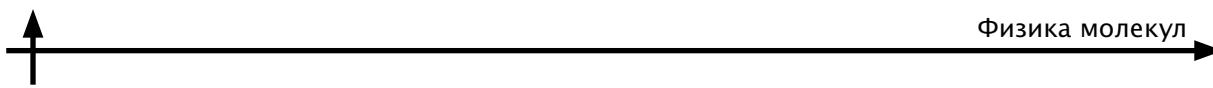
KAPRALOVA Victoriia M.
St. Petersburg Polytechnic University
29 Politekhnicheskaya St., St. Petersburg, 195251, Russian Federation
kapralova2006@yandex.ru

YAKIMANSKY Alexander V.
Institute of Macromolecular Compounds RAS
31 Bolshoy Ave. V.O., St. Petersburg, 199004, Russian Federation
yak@hq.macro.ru

Степанова Т.П., Носова Г.И., Соловская Н.А., Капралова В.М., Якиманский А.В.
ВЛИЯНИЕ ПОСТОЯННОГО ЭЛЕКТРИЧЕСКОГО ПОЛЯ НА ДИПОЛЬНЫЙ МОМЕНТ ПОЛИМЕРА ГРЕБНЕОБРАЗНОГО СТРОЕНИЯ С ХРОМОФОРНЫМИ ГРУППАМИ В БОКОВЫХ ЦЕПЯХ.

Работа посвящена исследованию конформационных свойств и тенденции к ассоциации макромолекул хромофорсодержащего гребнеобразного сополимера дицианфенилазобензтиазолметакрилата (А) и амилметакрилата (В) в соотношении 1 : 1, пленки которого обладают нелинейно-оптическими свойствами. Методом статической диэлектрической поляризации изучены температурные зависимости диэлектрической проницаемости и дипольных моментов сополимера АВ, полимера В и мономера А в разбавленных растворах в циклогексаноне, в том числе во внешнем постоянном ориентирующем электрическом поле. Показано, что в сополимере происходит внутримолекулярная ассоциация хромофорсодержащих фрагментов с компенсацией их дипольных моментов, которая усиливается при наложении электрического поля. Дипольный момент макромолекулы в расчете на мономерное звено уменьшается под действием поля. При температуре около 40 ºС имеет место внутримакромолекулярный конформационный переход.
ГРЕБНЕОБРАЗНЫЙ ПОЛИМЕР, ДИЭЛЕКТРИЧЕСКАЯ ПОЛЯРИЗАЦИЯ, ДИПОЛЬНЫЙ МОМЕНТ, АССОЦИАЦИЯ.

СПИСОК ЛИТЕРАТУРЫ

[1] **Moscicki J.K.** Liquid crystal polymers: from structure to applications, in Dielectric Relaxation in Macromolecular Liquid Crystals, ed. By Collyer A.A., Elsevier Applied Science, London, 1992. Pp. 143–236.

[2] **Nikonorova N.A., Yakimansky A.V., Smirnov N.N., Kudryavtsev V.V., Diaz-Calleja R., Pissis P.** Dielectric relaxation in copolymethacrylates containing side-chain nonlinear optical chromophores // Polymer. 2007. Vol. 48. Pp. 556–563.

[3] **Nikonorova N.A., Diaz-Calleja R., Yakimansky A.V.** Molecular mobility in comb-like copolymethacrylates with chalcone-containing side-chains // Polym. Int. 2011. Vol. 60.

[4] **Лысков В.Б., Абрамов И.Г., Доброхотов О.В., Носова Г.И., Якиманский А.В., Кудрявцев В.В.** Хромофоры на основе замещенных 4-фенилазофталонитрилов для полимеров с нелинейными оптическими свойствами // Химия и химическая технология. 2008. Т. 51. Вып. 8. С. 86.

[5] **Borisova T.I., Burstein L.L., Stepanova T.P., Nikonorova N.A.** Influence of the external oriented (electric or mechanic) fields on the dielectric relaxation in LC side-chain polymers // Intern. J. Polymeric materials. 1993. Vol. 22. No. 1–4. Pp. 103–112.

[6] **Stepanova T.P., Burshtein L.L.** Dipole polarization and molecular structure of main- and side-chain liquid-crystalline polymers in dilute solutions. Chinese Journal of Polymer Science. 1996. Vol. 14. No. 1. Pp. 1–18.

[7] **Степанова Т.П., Погребная А.Н., Капралова В.М., Скороходов С.С.** Влияние внешнего ориентирующего электрического поля на диэлектрическую релаксацию сегментированных полиэфиров в разбавленном растворе // Высокомолек. соед. А. 2007. Т. 49. № 2. С. 321–328.

[8] **Степанова Т.П., Глаздовская М.М., Капралова В.М.** Влияние внешнего постоянного ориентирующего электрического поля на дипольный момент мезогенсодержащего полимера // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2011. № 4(162). С. 162–165.

[9] **Onsager L.** Electrical moments of molecules

in liquids // J. Amer. Chem. Soc. 1936. Vol. 58. No. 8. P. 1468.

[10] **Волькенштейн М.В.** Строение и физические свойства молекул. М.-Л: Изд-во АН СССР. 1955.

[11] **Осипов С.А., Минкин В.И., Гаршевский А.Д.** Справочник по дипольным моментам. М.: Высшая школа, 1971.

[12] **Morgan S.O., Yager W.A.** Dielectric properties of organic compounds. Relation to chemical composition and physical structure // Industrial & Engineering Chemistry. 1940. Vol. 32. No. 11. P. 1519.

[13] **Buckingham A.D.** A Theory of the dielectric polarization of polar substances // Proc. Roy. Soc. A., Mathem.a. Phys. Sci. 1956. Vol. A 38. No. 1213. Pp. 235−244.

[14] **Михайлов Г.П., Бурштейн Л.Л.** Современные теории дипольной поляризации молекулярных конденсированных систем // Успехи физ. наук, 1961. Т. 74. С. 3.

[15] **Степанова Т.П., Бурсиан А.Э., Денисов В.М.** Дипольный момент и подвижность молекул в нематическом жидком кристалле 4-*н*-бутилового эфира [4'-*н*-гексилоксифенил] бензойной кислоты в отсутствие внешних ориентирующих полей // Физика твердого тела. 2002. Т. 44. Вып. 10. С. 1900−1907.

[16] **Malecki J.A., Novak J.** Intermolecular interactions in benzene solutions of 4-heptyl-3'-cyano-biphenyl studied with nonlinear dielectric effects // J. Molecular Liquids. 1999. Vol. 81. P. 245.

[17] **Борисова Т.И., Бурштейн Л.Л., Степанова Т.П., Моисеенко В.М., Шибаев В.П..** О конформационном переходе в растворах поли-N-октадецилакриламида // Высокомолек.соед. Б. 1976. Т. 18. № 7. С. 550−553.

[18] **Борисова Т.И., Бурштейн Л.Л., Степанова Т.П., Фрейдзон Я.С., Шибаев В.П., Платэ Н.А.** Дипольный момент и внутримолекулярный ориентационный порядок в макромолекулах холестеринового эфира поли-N-полиметакрилоил-ω-аминолауриновой кислоты // Высокомолек. соед. Б. 1976. Т. 18. № 8. С. 628−631.

[19] **Борисова Т.И., Бурштейн Л.Л., Степанова Т.П., Фрейдзон Я.С., Шибаев В.П.** Внутримолекулярная упорядоченность холестеринсодержащих сополимеров // Высокомолек.соед. А. 1978. Т. 20. № 6. С. 1380−1384.

[20] **Фрейдзон Я.С., Шибаев В.П., Агранович И.М., Паутов В.Д., Ануфриева Е.В., Платэ Н.А.** Структурообразование в холестеринсодержащих жидкокристаллических полимерах // Высокомолек. соед. А. 1978. Т. 20. № 11. С. 2601.

[21] **Борисова Т.И., Бурштейн Л.Л., Степанова Т.П., Шибаев В.П..** О конформационных переходах в растворах гребнеобразных полимеров // Высокомолек.соед. Б. 1979. Т. 21. № 3. С. 186−190.

[22] **Борисова Т.И., Бурштейн Л.Л., Степанова Т.П., Костромин С.Г., Шибаев В.П.** Конформационное состояние гребнеобразного жидкокристаллического полимера с циандифенильными боковыми группами // Высокомолек. соед. А. 1986. Т. 28. №5. С. 1331−1332.

[23] **Борисова Т.И., Бурштейн Л.Л., Малиновская В.П., Степанова Т.П., Крюке Б.** Дипольный момент и взаимная ориентация полярных мезогенных фрагментов в гребнеобразных полимерах // Высокомолек.соед. Б. 1990. Т. 32. № 6. С. 406−410.

[24] **Борисова Т.И., Бурштейн Л.Л., Степанова Т.П., Шибаев В.П., Платэ Н.А.** Исследование диэлектрической поляризации гелей некоторых гребнеобразных полимеров // Высокомолек. соед. А. 1977. Т. 19. № 2. С. 286−290.

[25] **Stepanova T.P., Burstein L.L.** Dielectric polarization in gelforming liquid-crystalline polymers and their monomers // Proceedings of the Workshop on non equilibrium phenomena in super cooled fluids, glasses and amorphous materials. (Pisa. Italy, 25-29 September, 1995). Series in Contemporary Chemical Physics. 1995. Vol. 12.

[26] **Птицын О.Б., Бирштейн Т.М.** Конформации макромолекул. М.: Наука. 1960.

СВЕДЕНИЯ ОБ АВТОРАХ

СТЕПАНОВА Тамара Павловна − *кандидат физико-математических наук, старший научный сотрудник лаборатории люминесценции, релаксационных и электрических свойств полимерных систем Института высокомолекулярных соединений РАН.*

199004, Российская Федерация, г. Санкт-Петербург, Большой пр. В.О., 31
t_stepanova2005@mail.ru

НОСОВА Галина Ивановна − *кандидат физико-математических наук, старший научный сотрудник лаборатории люминесценции, релаксационных и электрических свойств полимерных систем Института высокомолекулярных соединений РАН.*

199004, Российская Федерация, г. Санкт-Петербург, Большой пр. В.О., 31
nosova@physicist.net
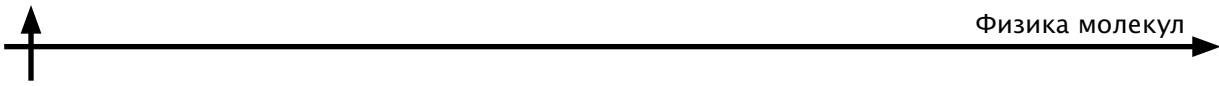
СОЛОВСКАЯ Нина Аркадьевна — *кандидат химических наук, старший научный сотрудник лаборатории синтеза полимерных наноматериалов и композиций для оптических сред Института высокомолекулярных соединений РАН.*

199004, Российская Федерация, г. Санкт-Петербург, Большой пр. В.О., 31

КАПРАЛОВА Виктория Маратовна — *кандидат физико-математических наук, доцент кафедры интегральной электроники Санкт-Петербургского государственного политехнического университета.*

195251, Российская Федерация, г. Санкт-Петербург, Политехническая ул., 29

kapralova2006@yandex.ru

ЯКИМАНСКИЙ Александр Вадимович — *заведующий лабораторией синтеза полимерных наноматериалов и композиций для оптических сред Института высокомолекулярных соединений РАН.*

199004, Российская Федерация, г. Санкт-Петербург, Большой пр. В.О., 31

yak@hq.macro.ru