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St. Petersburg Polytechnical University Journal: Physics and Mathematics 1 (2015) 92–100

www.elsevier.com/locate/spjpm

The constant electric field effect on the dipole moment of a comb-like polymer with chromophore groups in side chains

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Available online 11 March 2015

Abstract

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 non-linear 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.

Keywords: 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, non-linear 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 chromophore-containing comb-like polymer by

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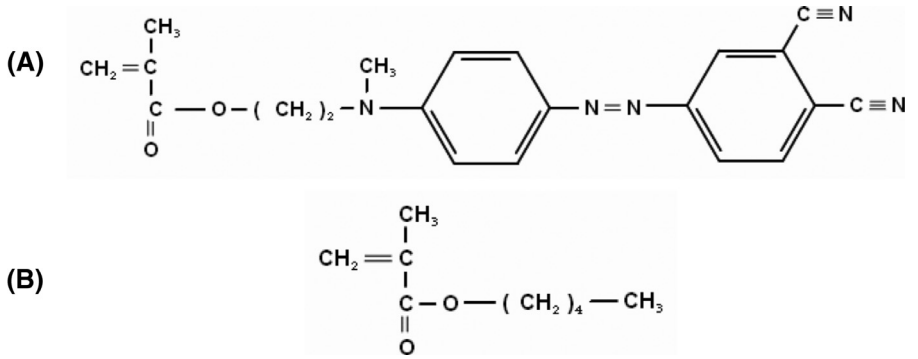
http://dx.doi.org/10.1016/j.spjpm.2015.03.008

(Peer review under responsibility of St. Petersburg Polytechnic University).



Scheme 1. Structural formulae of the objects.

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 non-linear optical properties of the polymer material. External orienting electric field was used to gain additional information about orientation dielectric polarization of the polymer.

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

Films of this copolymer polarized in the corona discharge demonstrate the second order non-linear 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-hydroxyethyl) 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-hydroxyethyl) amino]-phenylazo}-phthalonitrile}}methacrylate 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.% dimethylacetamide 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 $[\eta]$ in the cyclohexanone was 0.72 cm^3/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]:

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

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

$$\mu_{ef\,cop} = \sum_{i=1}^{n}(\mu_{Ai} + \mu_{Bi}), \tag{2}$$

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

$$\frac{\overline{\mu^2_{ef\,cop}}}{n} = \left(\overline{\mu^2_A} + \overline{\mu^2_B}\right), \tag{3}$$

where $\overline{\mu^2_A}$ is the mean square of the monomer A dipole moment and $\overline{\mu^2_B}$ is the mean square of the dipole