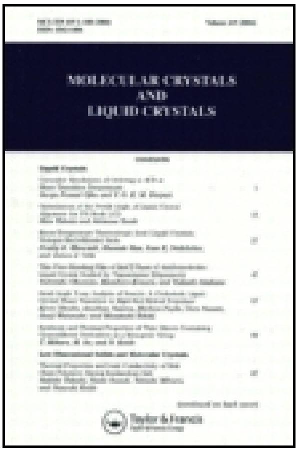

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Temperature Influence on Properties of Side-Chain Polymethacrylates with Azobenzene Mesogenic Groups and Their Polycomplexes with Cobalt (II)

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Temperature Influence on Properties of Side-Chain Polymethacrylates with Azobenzene Mesogenic Groups and Their Polycomplexes with Cobalt (II)

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Azopolymers and polycomplexes with cobalt based on them are synthesized, thermal behavior of the side chain polymethacrylates and their polycomplexes containing substituted azobenzene units as mesogens attached directly to the polymeric backbone and the influence of temperature on the photoelectric effect in films of these materials are investigated. The influence of the electric field on the transmission of polarized light is attributed to the appearance of forces affecting the dipole moments of photoisomers of azobenzene groups and metallic ions. The synthesized polymer materials showed a good thermal stability. The introduction of substituents of the different nature or spacers decreases the influence of metallic ions on the electro-optical properties of polycomplex films.

Keywords Azopolymer; dipole moment; DSC measurements; electro-optical effect; photo isomerization; polycomplexes; temperature

1. Introduction

Nowadays, the polymers with photoactive chromophores have been a subject of intensive researches. In this domain, azobenzene-containing polymers are of interest due to the extreme response to incoming electromagnetic fields [1–3] and a widespread usage in various fields such as nonlinear optics [4–5], photoswitches [6–7], and holographic data storage devices [8–10].

Till now, many approaches have been used to introduce liquid crystalline and photoactive azounits to a polymer framework. The first approach is the doping of chromophores into a polymeric matrix ("guest-host system") [11–12]. The main problem of this system is that the glass transition temperature of the host (polymer) decreases due to the plasticization by a guest (chromophore) [13]. In addition, the dye dispersed in the host polymer matrix is distributed nonhomogenously, by

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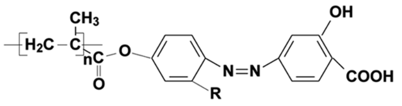
causing significant scattering losses. The second approach is the utilization of the polymer system, where the chromophores are covalently attached as a pendant side group or to the polymer backbone along the main chain. The latter approach helps in getting the very high film homogeneity. The synthesis of a photoactive monomer followed by the polymerization was found to be a convenient approach to build up azobenzene containing side chain liquid crystalline polymers.

It is known that polymers with azobenzene side groups are promising materials for optical applications due to anisotropic properties induced in polymer films by irradiation with linearly polarized light [14–15]. The temperature influence on the process of *trans*-*cis*- isomerization of azobenzene is known from the literature [16], but the effect of the temperature on electro-optical properties of these polymers was not investigated.

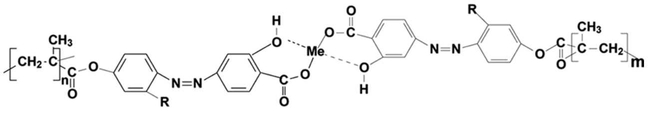
In this article, we report our results on the synthesis and the thermal behavior of side chain polymethacrylates and their polycomplexes containing substituted azobenzene units as mesogens attached directly to the polymeric backbone. The aim of this work was to study optical and electrical properties of metal-containing polymeric systems depending on the temperature.

Poly-4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene (A1), poly-4-methacryloyloxy-2-(N,N-diethylamino)-(4′-carboxy-3′-hydroxy)azobenzene (A2), poly-4-methacryloyloxy-2-chlor-(4′-carboxy-3′-hydroxy)azobenzene (A3), poly-4-methacryloyloxy-2-nitro-(4′-carboxy-3′-hydroxy)azobenzene (A4), poly-4-methacroyloxy-(2′-carboxy)-azobenzene (A5), poly-4-(6-methacroyloxyhexyloxy)-4′-carboxy-azobenzene (A6), poly-4-methacryloyloxy-2-methyl-5-nitro-(4′-carboxy-3′-hydroxy)azobenzene (A7), poly-4-{ethyl[2-(methacroyloxy)ethyl]amino}-(4′-carboxy-3′-hydroxy)azobenzene (A8), and their polycomplexes were synthesized:

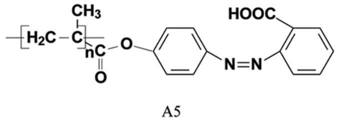


R = H (A1), $N(C_2H_5)_2$ (A2), Cl (A3), NO_2

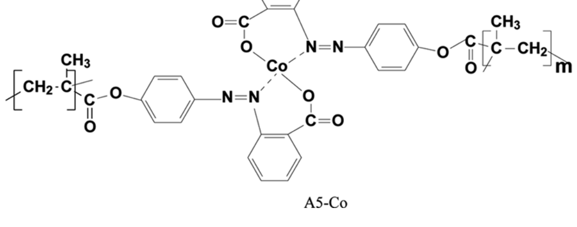
(A4)



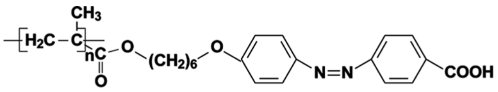
R = H (A1-Co), $N(C_2H_5)_2$ (A2-Co), Cl (A3-Co), NO_2 (A4-Co)



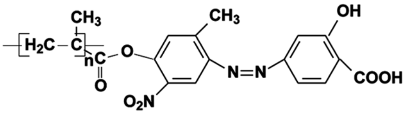
A5



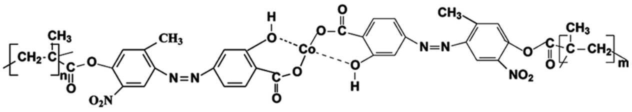
A5-Co



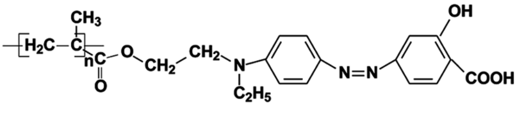
A6



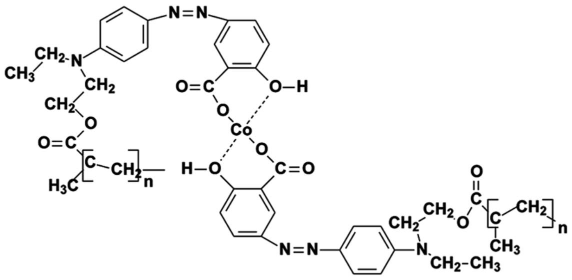
A7



A7-Co



A8



A8-Co

The structures of the monomers, polymers, and metal complexes were confirmed by data obtained by NMR- and infrared spectroscopies.

2. Experimental

2.1. *Synthesis*

The syntheses of the polymers and polycomplexes under study were reported in [17–18] earlier.

2.2. *Characterization Methods*

Infrared spectra were measured with a Fourier transform infrared (FTIR) spectrophotometer (Perkin– Elmer 1600) using KBr pellets. The 1H (500 MHz) spectra were recorded on a Bruker 500-MHz FT-NMR spectrometer with dimethyl sulfoxide-d_6 (DMSO-d_6) and $CDCl_3$ as solvents and tetramethylsilane as an internal standard.

Differential Scanning Calorimetry (DSC): A Q20 model DSC (TA Instruments) with a continuous N_2 purge was used to determine the glass and phase transition temperatures (T_g) of all polymers. The sample was initially stabilized and, after the first scan, was heated at a rate of 10°C/min up to 200°C and then cooled to 20°C. Finally, the second scan was performed at a heating rate of 10°C/min up to 250°C giving the values of T_g. The glass transition temperatures by the midpoint of the heat capacity jump are given.

Thermogravimetric analysis (TGA) was carried out with a Q500 apparatus (TA Instruments) in the nitrogen atmosphere at a heating rate of 10°C/min from room temperature up to 800°C.

2.3. *Spectral Measurements*

Samples with the free surface (glass substrate – conducting layer SnO_2:In_2O_3 – polymeric film) were prepared and used in our investigations. The thickness of the polymeric films was 2–4 mμ. These samples were used for the following measurements: the spectra of optical density D of the polymeric films over the range of light wavelengths $\lambda = 350–900$ nm; the value $I_E/I_{0,}$ where I_0 and I_E are the monochromatic light intensities before and after the action of the electric field, respectively. Polarized light was used for the exposure of samples. In this case, the sample was located between two polarizers at an angle of ninety degrees. The value δI_E was determined after a long-term exposure (60 min) of the samples by polarized light with $\lambda = 530$ nm. The electric field ($E = 1 \cdot 10^8$ V/m) was produced by a corona discharge. The value δI_E was determined depending on (and the temperature (T). For temperature measurements of δI_E, a special thermostat with optical apertures was used for the exception of the influence of depolarized properties of layer SnO_2:In_2O_3 and the corona discharge. The temperature was measured in range 20–100°C.

3. Results and Discussion

3.1. *Thermal Properties*

The thermal properties of the polymers and polycomplexes were studied by a combination of DSC and TGA. The DSC thermograms of the polymer are given in Figure 1. The glass transition temperatures of the samples obtained by DSC are summarized in Table 1.

Figure 1 shows the DSC traces for the second heating of the samples. All samples showed obvious crystalline-phase melting endotherms during the heating process, whereas polymethylmethacrylate was completely amorphous. The glass transition temperatures (T_g) for A2, A1-Co, and A3-Co were obtained to be 58°C, 151°C, and 152°C, respectively (Fig. 1). Endothermic transitions at 182°C, 183°C, and 217°C, respectively, are attributed to T_m (melting temperature).

Practically the same $T_g = 153$°C, 148°C, and 151°C were observed for A2-Co, A4-Co, and A5-Co, respectively (Fig. 1). For A6, the greater intermolecular interaction due to the COOH substitution takes place (hydrogen bonding between neighboring chain segments), which leads to decreasing the fractional free volume between the chains. As a result, T_g of one of them is higher than 156°C. This may be due to the interchain dimerization of carboxylic acid groups (IR spectra: 1690–1700 cm^{-1}) through the hydrogen bonding which can involve the physical crosslinking leading to higher transition temperatures. The endothermic transitions were observed for **A6**, A2-Co, **A4-Co**, and **A5-Co** at 231°C, 205°C, 189°C, and 175°C, respectively. A comparison of DSC traces of polymers and polycomplexes

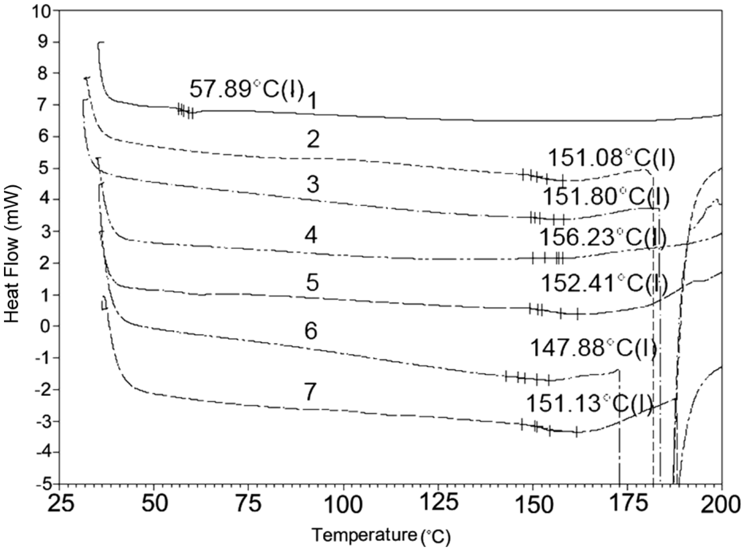


Figure 1. Differential scanning calorimetry curves for the second heating of A2 – 1, A1-Co – 2, A3-Co – 3 A6 – 4, A2-Co – 5, A4-Co – 6, A5-Co – 7.

indicates that metal ions and the presence of substituents attached to the pendant side chains have a certain influence on the phase transitions.

The thermal stability of some polymers and polycomplexes was characterized by TGA. The decomposition temperatures of samples are given in Table 1.

In Figure 2, the weight changes of samples A2, A1-Co, and A3-Co in nitrogen atmosphere as functions of the temperature are clearly seen. The TGA results indicate that the thermal decomposition of A2 in nitrogen occurs in 3 major steps (Fig. 3).

The first step was a weight loss of about 37.75% in the temperature range 47–250°C which represents the evolution of the degradation, and the other step at 250–429°C was a weight loss of 34.89% which represents the main thermal degradation of polymer **A2** and the carbonization of the products to ash in the temperature range 429–795°C with a weight loss of 9.54%. It can be seen that A2 has only a 5% weight loss at 205°C and a 10% weight loss at a temperature of 212°C, which indicates its good thermal stability.

Table 1. Characterization temperature data for the synthesized polymers and polycomplexes

Polymer	DSC, T_g°C	DSC, T_m°C	TGA, T_5°C	TGA, T_{10}°C
A1-Co	151	183	107	207
A2	58	182	205	212
A2-Co	153	205	–	–
A3-Co	152	217	132	193
A4-Co	148	189	–	–
A5-Co	151	175	–	–
A6	156	231	–	–

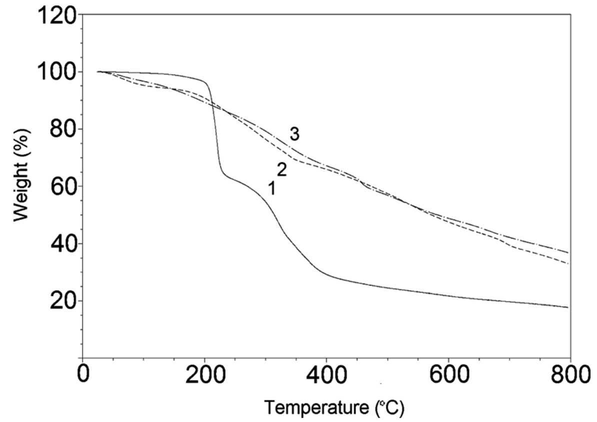


Figure 2. TGA thermograms of polymers A2 – 1, A1-Co – 2, A3-Co – 3 in nitrogen atmosphere.

The initial weight losses of polymers A1-Co and A3-Co are due to the adsorbed moisture. The temperatures for the 5-% and 10-% gravimetric losses which are an important criterion for the evaluation of thermal stability were found to be 107°C and 207°C for A1-Co and 132°C and 193°C for A3-Co, respectively. The char yields of polymers at 790°C were about 17–37%.

3.2. *Spectral Properties*

The absorption of polymeric films is determined by light excitation of azobenzene groups, and it is not sensitive to the presence of metallic ions in polymers. The considerable bathochromic shift absorption observed for A6 testifies to the development of the aggregation in this polymer (class of J-aggregates).

The electric field had a more appreciable effect on the light transmission, if the samples were pre- irradiated by polarized light in the absorption range of azobenzene groups ($\lambda < 550$ nm). The most significant change in I_0 induced by an external electric

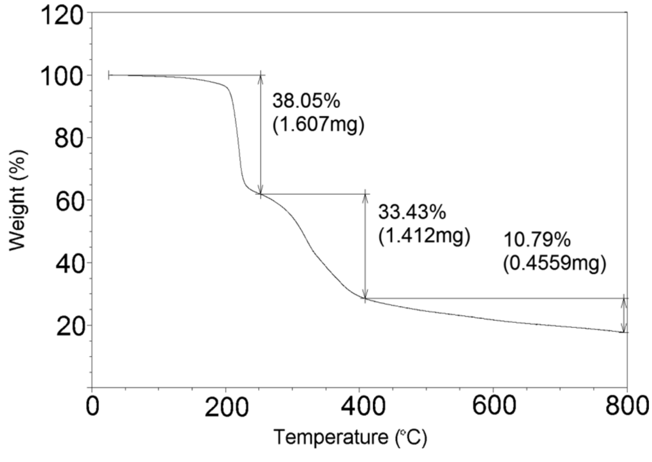


Figure 3. Weight change of polymers A2 (TGA thermograms).

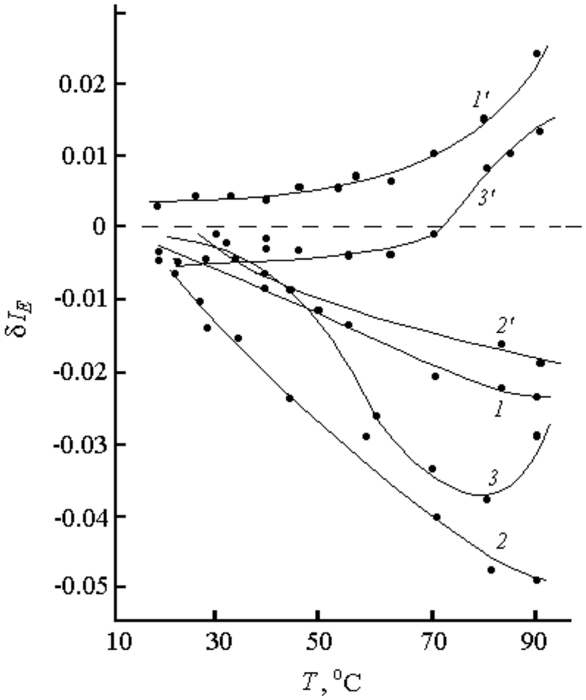


Figure 4. Dependence of δI_E on the temperature T ($\lambda = 620$ nm) in the samples with films A1 (*1*), A1-Co (*1'*), A7 (*2*), A7-Co (*2'*), A8 (*3*), and A8-Co (*3'*). The samples were illuminated by linearly polarized light with $\lambda = 530$ nm during 60 min.

field is observed after the exposure of samples to light transmitted through a polarizer during $t > 30$ min. The influence of an electric field on the light transmission is increased after the long-term irradiation by polarized light in the long-wave part of the absorption range of the investigated polymeric films ($\lambda = 400$–750 nm).

When the electric field is switched-off, the kinetics of light intensity changes from I_0 to I_E and can be described by the simple relations $I(t) = I_0 + (I_E - I_0)(1 - \exp(-t/\tau_E))$ and $I(t) = I_0 + (I_E - I_0)\exp(-t/\tau_E))$, in which the time constant τ_E is 60 ± 10 s for A1 and A1-Co, 90 ± 10 s for A7 and A7-Co, and 40 ± 10 s for A8 and A8-Co. When the electric field is switched-on, the kinetics of light intensity changes for A6 has two components: the fast component with the time constant 7.5 ± 1.5 s and the slow component with the time constant 160 ± 20 s; but when the electric field is switched-off, only the slow component is observed.

With increase in the temperature, the value of τ_E is decreased, and the value of $|\delta I_E|$ is increased (Fig. 3). The influence of the temperature on $|\delta I_E|$ is intensified in the series A1, A7, and A8, and the value δI_E is negative. Polycomplexes with Co A1-Co, A7-Co, and A8-Co have a positive value of $\delta I_{E.}$

4. Conclusions

We have synthesized and characterized side chain polymethacrylates and their polycomplexes containing substituted azobenzene units as mesogens attached directly to the polymeric backbone.

In the investigated polymeric samples, the electro-optical effect is revealed as a result of the appearance and the accumulation of light-induced dipole moments of azobenzene groups. The orientation of photoinduced dipoles changes relative to the electric vector of an incident light wave in an external electric field, which results in a change of the optical anisotropy of these films.

A growth of the "spacer" length (A6) and the capability to form hydrogen bonds between substituents in azobenzene groups cause the growing changes of optical characteristics of the films in an external electric field.

An increase in the temperature results in a growth of the mechanical mobility of polymeric side chains and, as a consequence, in an enhancement of the electro-optical effect.

Thus, azopolymers and complexes based of them including chromophore groups in every polymeric unit are promising for optical storage applications.

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