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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Interpolymeric Complexes of Polyoctamethyleneacetamidine with Polyethers Terminally Modified with Chromophore Groups and Their Nonlinear Optical Properties

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Abstract—Ionic interpolymeric complexes of polyoctamethyleneacetamidine with polyethers terminally modified with 4-[5-(4-hydroxyphenyl)-3-oxopenta-1,4-dienyl]benzoyl (chromophore) groups were prepared. The complexes exhibit third-order nonlinear optical properties. Factors affecting the third-harmonic generation efficiency were revealed.

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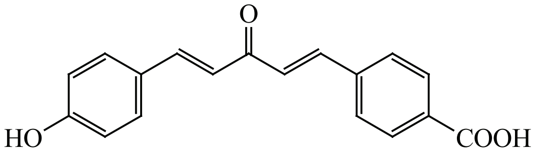
The modern nonlinear optics requires new materials for use in photonic information processing devices and for the development of optical switches and optical shutters based on nonlinear adsorption. Among materials with nonlinear optical (NLO) properties, polymers exhibit indubitable advantages over inorganic materials. They are cheap and relatively easy in processing; they have film-forming and other useful properties. In preparation of organic NLO materials, it is important to ensure their high service characteristics and chemical and optical stability. The development of procedures for preparing polymers modified with chromophores capable of nonlinear interaction with electromagnetic radiation and the search for ways to stabilize such composite materials without covalent binding of the components remain priority problems of nonlinear optics. When tackling these problems, it is important to take into account the chromophore distribution in the matrix, the nature of intermolecular interactions, and the capability of the chromophore component for self-organization. These aspects were not given due attention previously.

To prevent microphase segregation caused by thermodynamic incompatibility of the polymeric matrix and low-molecular-weight chromophore, covalent binding or strong noncovalent interactions of the chromophore with the polymer are ensured [1–4]. Taking into account the fact that hydrogen bonding or ionic interactions between the components strongly affect the enthalpy of mixing, compatibility, and stability of polymer–chromophore systems, we suggested in this study a new approach to preparing NLO-active organic materials, based on formation of ionic interpolymeric complexes (IPCs) between two polymers, of which one contains covalently bound anionic chromophore groups and the other acts as a cationic matrix. As applied to NLO materials, IPCs were not considered as promising objects until recently.

To prepare IPCs, we used in this study bifunctional polyethers containing two terminal anionogenic chromophore 4-[5-(4-hydroxyphenyl)-3-oxopenta-1,4-dienyl] benzoyl groups, and as cationogenic matrix polymer we used polyoctamethyleneacetamidine.

EXPERIMENTAL

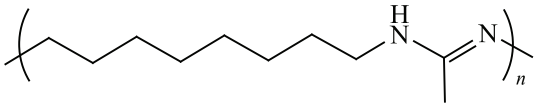
The polyethers modified with chromophore groups (anionic NLO-active polymeric components of IPCs) were prepared by modification of a series of polyethers ($M = 0.6 \times 10^3$, 2×10^3, and 4×10^3) containing two terminal amino groups (Jeffamines®, Huntsman). As starting chromophore for the polyether modification we used 4-[5-(4-hydroxyphenyl)-3-oxopenta-1,4-dienyl] benzoic acid:



The chromophore was synthesized by two-step aldol condensation. First, by the reaction of 4-hydroxybenzaldehyde with acetone we prepared 4-(4-hydroxyphenyl)-but-3-en-2-one [5], which was treated in the second step with the excess of 4-carboxybenzaldehyde to obtain the chromophore [6].

The chromophore linking via terminal amino groups of the polyether was performed after preliminary acetyl protection of the hydroxy group of the chromophore, followed by activation of the carboxy group [7] (Scheme 1).

The synthesis of the matrix cationogenic polymer, polyoctamethyleneacetamidine (polyamidine), was described previously [8, 9]:

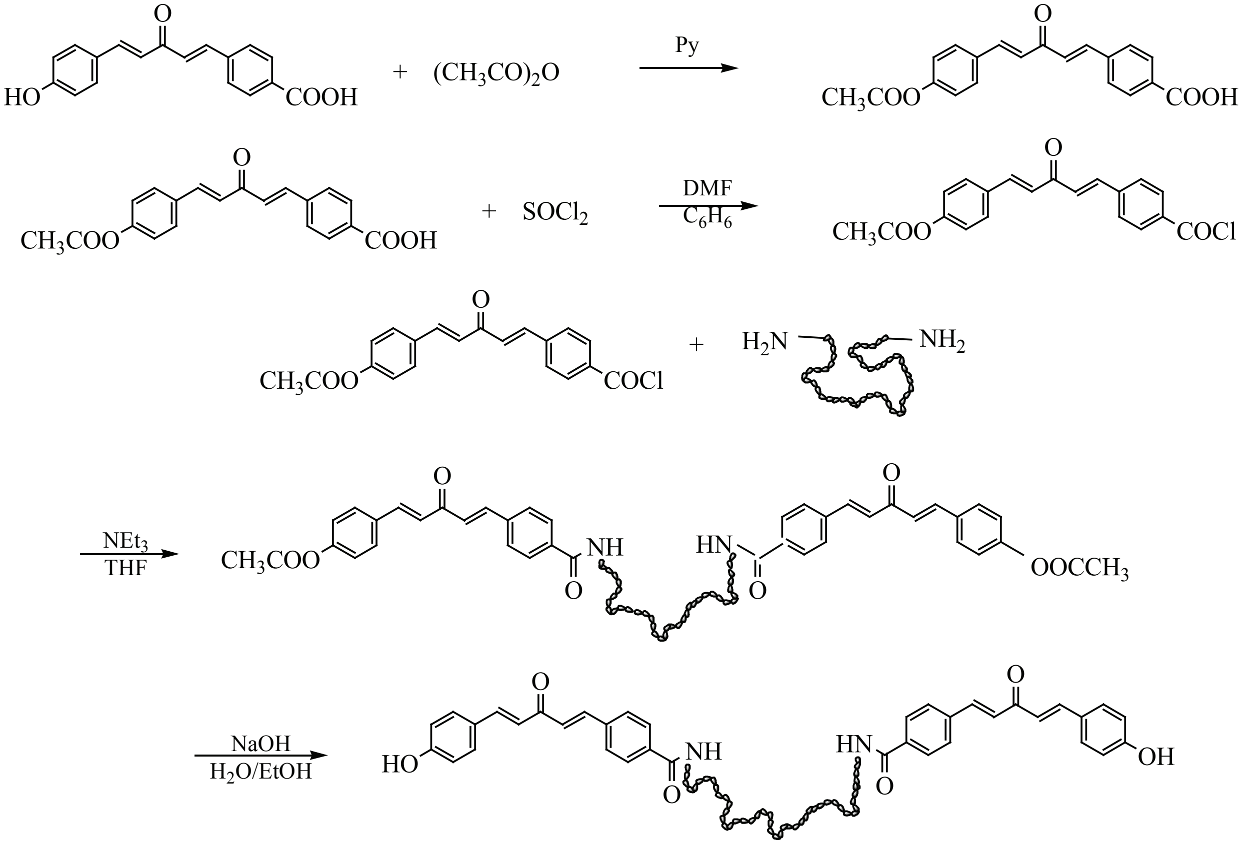


Film samples were prepared by casting from solutions of the components in a common solvent (ethanol) onto glass supports [cover glass, 18 × 18, GOST (State Standard) 6672–75], followed by solvent evaporation. Prior to measurements, the films were dried in a vacuum (5 mm Hg) to constant weight to remove residual solvent.

The third-order nonlinear optical coefficients $\chi^{(3)}$ were estimated by the method of third-harmonic generation (THG) [10, 11]. The harmonic was excited in the samples with a YAG : Nd^{3+} pulse laser with the emission wavelength $\lambda = 1064$ nm.

Calorimetric studies of the complexes of the modified polyethers with polyamidine were performed with a Mettler TA20 scanning calorimeter. Measurements were made in the course of heating and cooling (four runs) in

Scheme 1.



the interval from room temperature to 180°C at a scanning rate of 5 deg min^{-1}.

The optical properties of the films are largely determined by complexation and formation of supramolecular structures on mixing the solutions of the starting components. Therefore, we paid particular attention to these processes. As we showed in the previous studies [12–14], the chromophore tends to aggregation owing to formation of a hydrogen bond system and to intermolecular π–π interactions. According to [13, 15], the chromophore in methanol solutions is associated to form structures with the hydrodynamic radius $R_h > 450$ nm. Upon complexation, these structures undergo partial deaggregation with the formation of smaller particles.

Terminal chromophore groups of the modified polyethers are also capable of aggregation. For example, a study of the interaction of polyamidine with the chromophore and chromophore-containing polyethers in methanol by static and dynamic light scattering [13] showed that the formation of ionically bonded complexes in solutions leads to the formation of supramolecular polymer–chromophore structures of colloidal size (hydrodynamic radius $R_h \sim 200$ nm). The chromophore components in such structures are in the aggregated state.

Mixing of alcoholic solutions of the polyamidine and of the polyethers modified with chromophore groups leads to a sharp change in the solution color from yellow to red, suggesting fast proton transfer from the phenol group of the chromophore to amidine fragments (deprotonation) (Scheme 2).

The spectral changes observed in solutions of the modified polyether and chromophore itself on interaction with the polyimidine are essentially similar (Fig. 1).

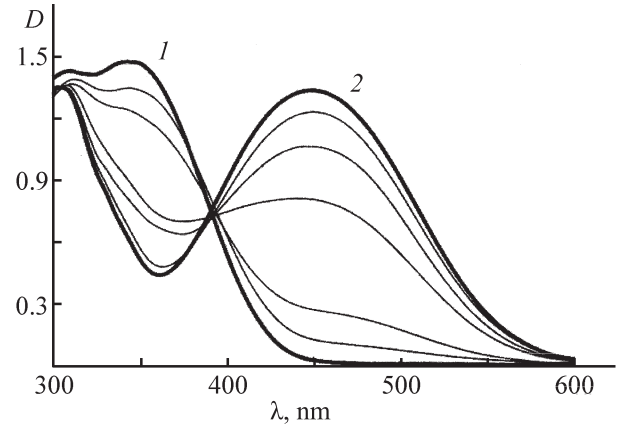
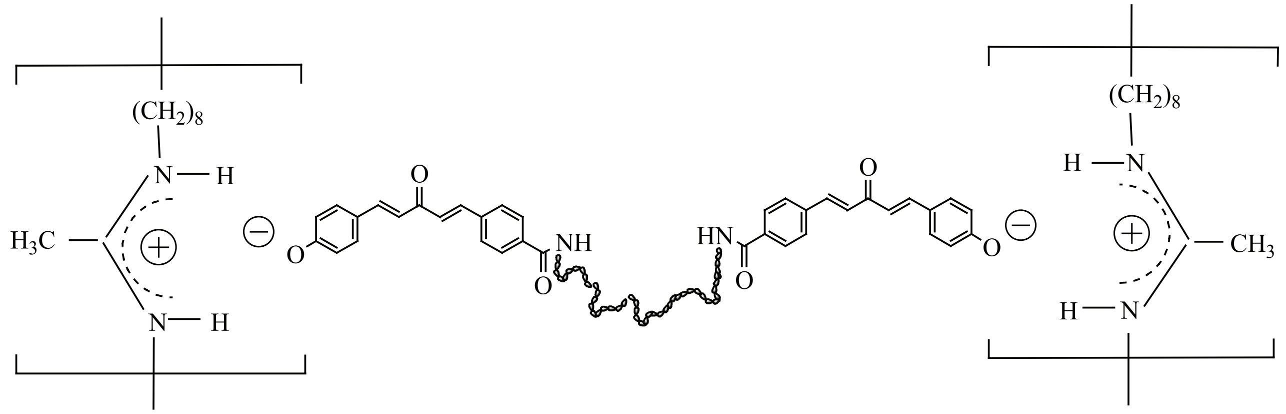


Fig. 1. Change in the UV spectrum of the solution of the chromophore-modified polyether ($M = 4 \times 10^3$, $c = 4 \times 10^{-5}$ mM) in the course of titration with a polyamidine solution. (*D*) Optical density and (λ) wavelength. Form: (*1*) neutral and (*2*) anionic.

On adding the polyamidine to solutions of the modified polyethers or initial chromophore, the intensity of the absorption band of the protonated form at λ = 350 nm decreases and that of the deprotonated form at λ = 450 nm increases. Analysis of the spectra allows these bands to be assigned to the phenolic moiety of the chromophore fragment [16]. In the UV spectra of the complexes in the solid phase (films), the longer-wave absorption band undergoes bathochromic shift to λ = 460 nm.

By measuring the optical density *D* of the deprotonated form at λ = 450 nm, we obtained the titration curves of the chromophore-containing components with the polyamidine (Fig. 2). As can be seen, full deprotonation of the shortest-chain polyether ($M = 0.6 \times 10^3$) requires the largest excess of the polyamidine. For the polyethers in which the length of the polyether spacer chain between

Scheme 2.



the chromophore groups is the largest ($M = 4 \times 10^3$), the required amount of the polyamidine appeared to be practically the same as for the deprotonation of the free chromophore. This is due to the fact that, with an increase in the length of the polyether spacer chain, the chromophore groups become more labile and more accessible to the polyamidine.

For studying the NLO properties by the THG method, we used thin films (0.5–5 μm) prepared from solutions of the complexes of the modified polyethers with polyamidine in ethanol. By varying the concentration of the chromophore component and the film thickness, we obtained samples with the same optical density D ~0.5 at $\lambda = 460$ nm, corresponding to the absorption maximum of the ionic form of the chromophore in the solid state. For the films studied, the Beer law is observed:

$$D = kcl = knl/V,$$

where k is the absorption coefficient of the NLO component, c is the NLO component concentration, l is the film thickness, n is the number of particles, and V is the volume.

For comparison, using the similar method, we studied films of complexes of the initial chromophore with the polyamidine. The third-order nonlinear optical susceptibility coefficients $\chi^{(3)}$ of the complexes were measured in the presence of excess polyamidine to shift the equilibrium toward full deprotonation of the chromophore component (see table). Because of the difference in the molecular weights of the modified polyethers, such films were characterized by different content of the NLO-active component. The polyether/polyamidine films with the longest-chain polyether ($M = 4 \times 10^3$) had the lowest content of the chromophore component and, therefore, the lowest values of $\chi^{(3)}$.

It is known that the microstructure of films formed in the course of solution evaporation depends on the state of the components in the starting solution [17]. The common feature of complexation processes in solutions is partial deaggregation of the chromophore component and formation of perplexed ionically bonded polymeric structures within which the chromophore component forms small aggregates [13]. We expected that, in going to a solid system (film), the particle aggregation will be enhanced, but certain features characteristic of solutions will be preserved. Therefore, to determine how the polyether chain length affects the nonlinear optical properties of interpolymeric complexes, we additionally prepared films with a fixed content of the NLO-active component in the solid phase (~14 wt %). As follows from our results (Fig. 3), the THG efficiency $\chi^{(3)}$ for films of polyether/

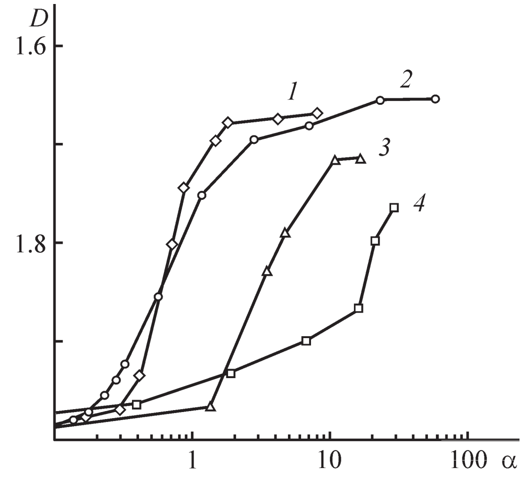


Fig. 2. Titration curves of solutions of (*1, 3, 4*) modified polyether and (*2*) chromophore with a solution of polyamidine in ethanol. (*D*) Optical density at $\lambda = 450$ nm. Here and in Fig. 4, $\alpha = n/2m$, where n is the number of polyamidine amino groups, and $2m$ is the number of chromophore groups of the polyethers (the coefficient 2 takes into account the presence of two chromophore groups per polyether molecule). M: (*1*) 4×10^3, (*3*) 2×10^3, and (*4*) 0.6×10^3.

Third harmonic generation in films of interpolymeric complexes

Complex	Molar ratio of ionogenic groups	$\chi^{(3)} \times 10^{14}$, CGS units
Polyamidine : chromophore	1 : 0.17	133
	1 : 0.26	430
	1 : 0.51	720
Polyamidine : polyether: $M = 0.6 \times 10^3$	1 : 0.12	82
	1 : 0.28	295
	1 : 0.53	293
$M = 2 \times 10^3$	1 : 0.16	14.0
	1 : 0.25	21.1
	1 : 0.47	25.9
$M = 4 \times 10^3$	1 : 0.13	5.8
	1 : 0.28	4.6
	1 : 0.51	4.3

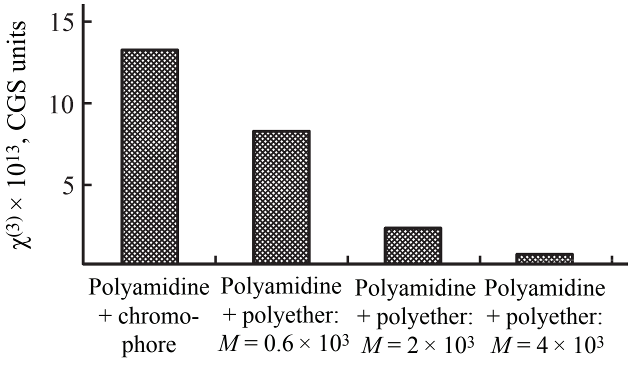


Fig. 3. Parameter $\chi^{(3)}$ of the films of the complexes as a function of the polyether chain length. NLO component content 14 wt %.

polyamidine complexes decreases with an increase in the polyether spacer length. Because the films contained the same amount of the chromophore component, the observed differences in $\chi^{(3)}$ can be attributed to features of aggregation of the chromophore component. Probably, with an increase in the polyether chain length, the capability of the chromophore groups for the intermolecular interactions and formation of aggregated structures decreases.

Our previous study of the NLO properties of model systems, chromophore potassium salt in poly-N-vinylpyrrolidone matrix [14], showed that the cubic susceptibility $\chi^{(3)}$ in the films increase with an increase in the size of the chromophore component aggregates. Apparently, in polyether/polyamidine films prepared using the polyether with the larger length of the spacer between the chromophore groups ($M = 4 \times 10^3$), the aggregates formed by the NLO-active component are the smallest. These data convincingly show that specifically the capability for aggregation and the cooperative effects observed in the aggregates, and not only the NLO component concentration, are responsible for the manifestation of the NLO properties.

The interpolymeric complexes combine two thermodynamically incompatible polymers: polyamidine and polyether. It is known that blends of these polymers exhibit two glass transition points corresponding to those of the individual components [18]. A study of the polyether/polyamidine complexes by differential scanning calorimetry showed a well-defined peak in the region of 120°C, corresponding to an endothermic phase transition of first order (melting) (Fig. 4). This fact means that modification of one of the components of a blend of incompatible polymers by introducing anionogenic chromophore groups leads not only to stabilization of interpolymeric complexes due to ionic interactions, but also to an increase in the degree of ordering, leading to enhancement of the heat resistance of the compounds (upper temperature limit of service properties).

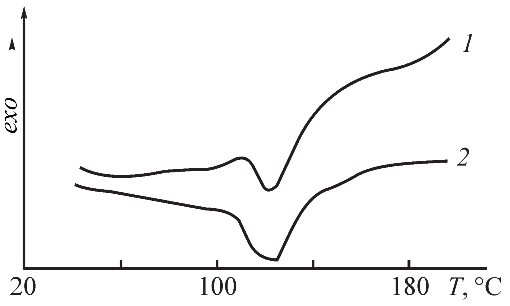


Fig. 4. Thermograms of polyamidine/polyether complexes ($M = 0.6 \times 10^3$). (*T*) Temperature. Component molar ratio α: (*1*) 2 and (*2*)10.

CONCLUSIONS

(1) New interpolymeric complexes of polyoctamethyleneacetamidine with polyethers terminally modified with 4-[5-(4-hydroxyphenyl)-3-oxopenta-1,4-dienyl]-benzoyl chromophore groups, exhibiting third-order nonlinear optical properties, were synthesized.

(2) A study of how the length of the polymeric spacer between the terminal chromophore groups of the polyethers affects the nonlinear optical properties of their interpolymeric complexes with polyoctamethyleneacetamidine showed that the efficiency of the third harmonic generation in the complexes is determined not only by the concentration of the NLO component, but also by the capability of the chromophore groups for aggregation and by the cooperative effects manifested in the aggregates.

(3) Introduction of anionogenic chromophore groups into the structure of one of the components of blends of incompatible polymers leads both to stabilization of interpolymeric complexes via ionic interactions and to an increase in the degree of ordering, making the compounds more heat-resistant.

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