Photochemical transformation of polyphenylacetylene ✽

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Photochemical transformation of polyphenylacetylene (PPA) was studied. Irradiation of a toluene solution of PPA with the light λ = 365 nm induces the cleavage of PPA polymeric chains and *cis*-transoidal—*trans*-cisoidal isomerization. Intense photoluminescence appears after irradiation of the polymer.

Key words: polyphenylacetylene, photochemical reactions, chain cleavage, photoluminescence, *cis—trans*-isomerization.

Conjugated polymers, such as polyacetylene (PA) and polyphenylacetylene (PPA), are of interest for creating photoconducting polymeric materials.[1,2] The optical and semiconducting properties of these polymers are due to electron delocalization and, therefore, to the conformational structure of the main conjugation chain. One of the methods for studying the conformational structure of polymers is photoluminescence (PL). Photoluminescence and photoconductivity in the *cis*-transoidal (*cis*) and *trans*-transoidal (*trans*) conformations of polyacetylene $(CH)_x$ have been studied.[3] Recombination luminescence is observed in *cis*-$(CH)_x$. Photoluminescence disappears and photoconductivity appears in *trans*-$(CH)_x$ obtained by heating of *cis*-$(CH)_x$ at 120 °C for 10 min. The soliton model was used to explain these properties. The photoluminescence properties of the PPA series with different concentrations of the *cis*-transoidal and *trans*-cisoidal segments (from 67 to 100% of the *cis*-form) have been studied.[4,5] It was found that both absorption and emission in the 350—650 nm spectral region are caused by the presence of the *cis*-segments in the polymeric chain. The intensity and duration of PL in the samples under study decrease linearly with an increase in the content of *cis*-fragments. The source of nonradiative recombination was not determined for all samples except for 100% *cis*-PPA. These results cannot be explained by the soliton theory. A decrease in the degree of stereoregularity with a decrease in the content of the *cis*-fragments plays an important role. The violation of stereoregularity leads to the formation of short *cis*-segments of PPA, which are the source of intense PL appeared due to the cage effect.

The problem of phototransformation of the polymer during photoirradiation has not been considered in the literature. In this work, we found the photodestruction of the polymeric chain and the conformational transitions of the *cis*-transoidal form to the *trans*-cisoidal form in fragments of the PPA chain.

Experimental

Synthesis of polyphenylacetylene. Polyphenylacetylene was synthesized by phenylacetylene polymerization in the presence of the $MoCl_5$ catalyst. Phenylacetylene was stored above molecular sieves, distilled *in vacuo* above CaH_2 (b.p. 41—43 °C (10 Torr)), and kept under argon at temperatures at most 0 °C. Toluene was triply treated with H_2SO_4, washed with water, a 10% solution of NaOH, and again with water, and dried for several days above sieve 4A. Anhydrous toluene was distilled above sodium. Before experiment, toluene was frozen and thawn out above $LiAlH_4$. Molybdenum pentachloride was doubly sublimed in a quartz tube in a dry chlorine flow at 210 °C. This procedure gave dark brown needle-like crystals with m.p. 194—195 °C consistent with the published data. All procedures with $MoCl_5$ were carried out in a dry box in an Ar atmosphere with magnetic stirring. Components were introduced in the following order: $MoCl_5$ ($1.5 \cdot 10^{-2}$ mol L^{-1}), toluene, and phenylacetylene (1.6 mol L^{-1}). The reaction temperature was 30 °C. The polymer was triply precipitated from toluene with methanol in a ratio of 1 : 10 (vol/vol) and dried at 60 °C *in vacuo* (1 Torr) to a constant weight.

Samples in standard quartz cells were irradiated with the light from a DRSh-1000 mercury lamp using a glass light filter. The irradiation duration was varied from 2 to 30 min. The light intensity with λ = 365 nm was 0.05 W cm^{-2}. The presence or absence of air oxygen in the samples had no effect on the course of photochemical transformations under the experimental conditions.

Absorption spectra of PPA solutions in toluene were recorded on a Specord M40 spectrophotometer. Fluorescence spectra were studied on a setup described previously.[6] IR spectra of PPA were recorded on a Specord 75 IR spectrophotometer in a region of 400—4000 cm^{-1}. Samples were prepared as thin films deposited on KBr windows. The molecular weight distribution of PPA before and after irradiation with the light λ = 365 nm

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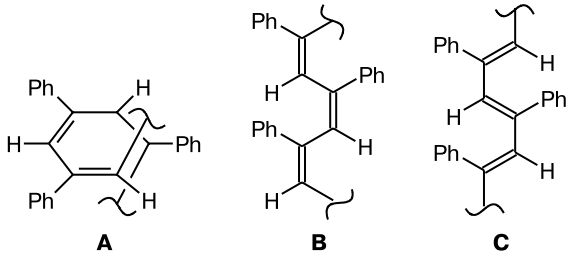
was determined by GPC.[7] NMR spectra of solutions of the starting and irradiated PPA in CCl_4 were recorded on a Bruker AC-200 instrument using Me_4Si as internal standard.

Results and Discussion

As known, PPA can have structures with different positions of the chain with respect to the double and ordinary bonds: *cis*-cisoidal (**A**), *cis*-transoidal (**B**), and *trans*-cisoidal (**C**).



These stable isomeric structures form helicoidal conformations of chains with three double bonds in the segment.[8–10]

The IR and NMR spectroscopic data were used to reveal the structure of PPA chains. The IR spectrum of the starting PPA contains absorption bands at 3060 and 3028 (ν_{CH}), 1595 ($\nu_{(C=C)_{arom}}$), 1490, and 1445 ($\nu_{C=C}$), 750 and 740 (ν_{CH}), and 695 cm^{-1} ($\delta_{(CH)_{arom}}$). The ratio of absorbances is $D_{1490}/D_{1445} < 1$. The NMR spectra exhibit signals at δ 6.85 (4 H, H arom.), 6.73 (1 H, H arom.), and 5.63 (1 H, C=C<u>H</u>).

The data obtained from the IR and NMR spectra indicate the predominant formation of the *cis*-transoidal structure **B**.[8–10]

The electronic absorption spectrum of a toluene solution of the starting PPA (Fig. 1) exhibits an absorption up to 520 nm with a shoulder at 350—360 nm (electronic π—π*-transition in the conjugated polymeric chain). A toluene solution of the starting PPA does not virtually luminesce. When a solution of PPA ($4 \cdot 10^{-5}$ mol L^{-1}) is irradiated with the light λ = 365 nm, the absorption at 310—520 nm decreases monotonically, and the intensity of blue luminescence increases. After 4-min irradiation, a toluene solution of PPA changes its color from orange to light yellow. The absorbance at 310—520 nm disappears (see Fig. 1). A blue luminescence of the whole volume of the solution is observed upon excitation with the light λ = 365 nm (luminescence spectrum is presented in Fig. 2).

During irradiation, the photoluminescence intensity at λ_{exc} = 365 nm increases (~10-fold), and the PL maximum of the product formed shifts by ~50 nm toward the short-wave region. The decrease in the absorbance in the visible region indicates that the conjugation in the polymeric chain is violated.

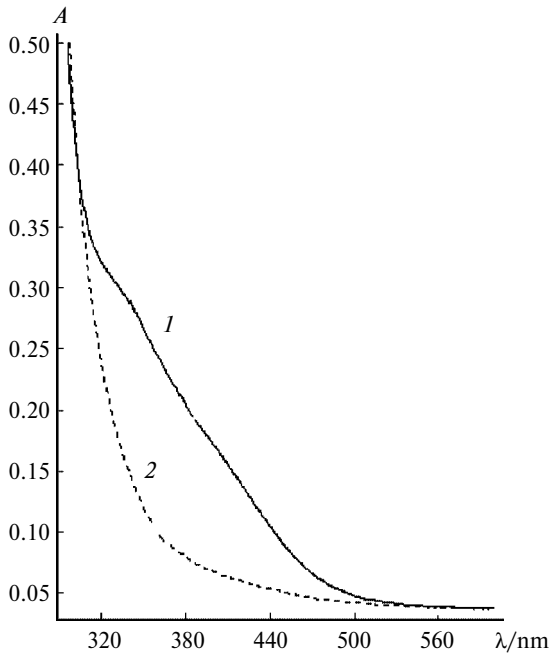


Fig. 1. Electronic absorption spectra of a toluene solution of PPA ($4 \cdot 10^{-5}$ mol L^{-1}) before (*1*) and after irradiation with the light λ =365 nm (*2*).

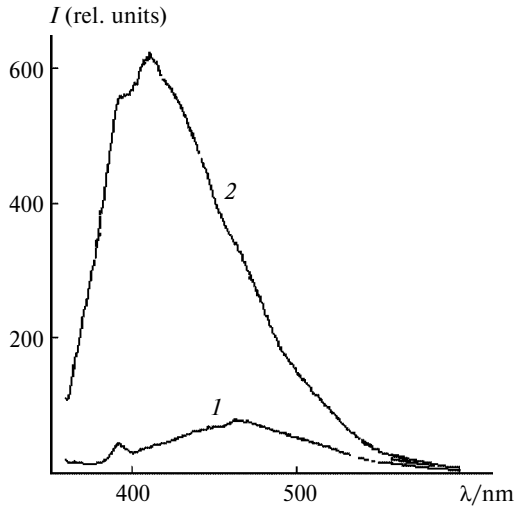


Fig. 2. Photoluminescence spectra of a toluene solution of PPA ($4 \cdot 10^{-5}$ mol L^{-1}) before (*1*) and after irradiation with the light λ =365 nm (*2*) (λ_{exc} = 350 nm).

The IR spectrum of the irradiated PPA differs from the spectrum of the starting polymer by the ratio of intensities of absorption bands at 1490 and 1445 cm^{-1} (I_{1490}/I_{1445} = 0.86 and 1.30 in the starting and irradiated PPA, respectively), the appearance of an absorption band at 1265 cm^{-1}, and the almost complete disappearance of the absorption band at 740 cm^{-1}. The appearance of the absorption band of stretching vibrations of C=O at 1725

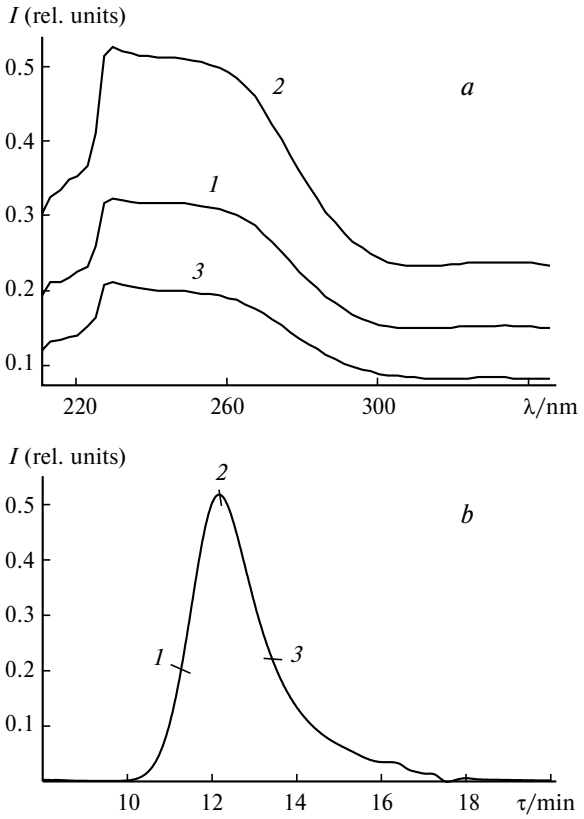


Fig. 3. Electronic absorption spectra of fractions *1—3* (*a*) and the chromatogram (*b*) of a solution of the starting PPA in THF (10^{-3} mol L^{-1}).

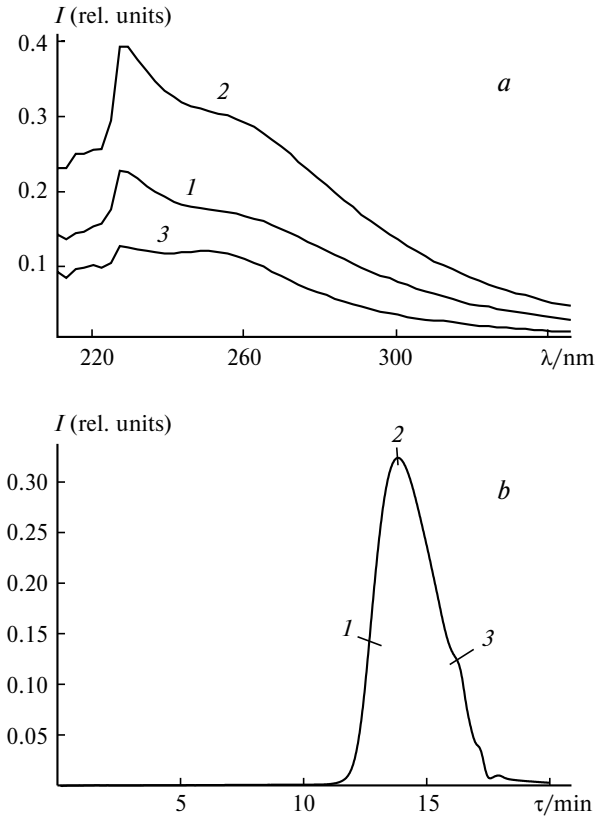
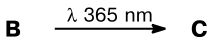


Fig. 4. Electronic absorption spectra of fractions *1—3* (*a*) and the chromatogram (*b*) of a solution of the irradiated PPA in THF (10^{-3} mol L^{-1}).

and 1690 cm^{-1} in the spectrum of the irradiated polymer can be related to the cleavage of PPA chains and their partial oxidation during irradiation. In the NMR spectrum (Fig. 3), the signal at δ 5.63 disappears, and the overall signal of other protons exhibits a downfield shift to ~6.95 ppm.

The changes in the characteristics of PPA after irradiation indicate the conformational transition from the *cis*-transoidal form to the *trans*-cisoidal form.[8,9]



The GPC data for solutions of PPA in tetrahydrofuran before and after irradiation are presented below.

PPA	M_n	M_w	Polydispersity
Starting	5100	28000	5.48
Irradiated	1220	2170	1.78

The starting PPA contains a set of homologs with different molecular weights, which have almost the same chemical compositions (see Fig. 3) but differ by the length of the polymeric chain. The GPC data for a solution of PPA in tetrahydrofuran after irradiation and the short-wave shift of the PL maximum indicate that the *trans—cis*-isomerization of the main polymeric chain is accompanied by a decrease in the conjugation length due to the cleavage of polymeric chains during irradiation. According to the UV spectra and the chromatogram presented in Fig. 4, 95% PPA undergo photochemical transformations. The polydispersity decreases from 5.48 to 1.78, *i.e.*, after irradiation, the polymer represents a mixture (more uniform in length) of macromolecules with lower molecular weights. Processes of fractionation and isomerization of polymeric chains increase the number of luminescent centers and decrease the contribution of nonradiative deactivation of excited states. It is clear from the dynamics of the PL spectra that the photoluminescence is most intense in a conjugated system with a restricted size of the *trans*-cisoidal conformation.

Thus, the irradiation of a solution of PPA with the light λ = 365 nm induces the cleavage of PPA polymeric chains and *cis*-transoidal—*trans*-cisoidal isomerization. The intense photoluminescence appeared after irradiation of the polymer is caused by conformational transformations and cleavages of the main chain. When using PPA as photomaterials, one should take into account its photochemical transformations during photolysis.

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