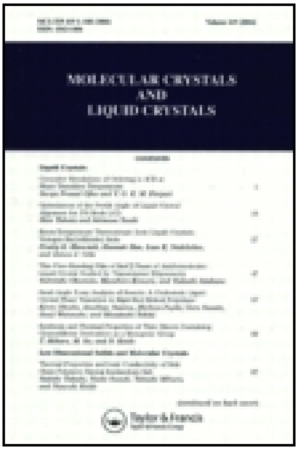

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Tymish Yu. Ogul'chansky, Valeriy M.(N.) Yashchuk, Anatoliy F. Maslyuk, Georgiy K. Bereznitskii & Olexiy D. Kachkovsk (2001): Peculiarities of Triplet Exciton Jump Mechanism in Unconjugated Polymers with Pendant Benzophenone-Type Groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 361:1, 25-30

Mol. Cryst. and Liq. Cryst., 2001, Vol. 361, pp. 25-30
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Peculiarities of Triplet Exciton Jump Mechanism in Unconjugated Polymers with Pendant Benzophenone-Type Groups

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Copolymer of methylmethacrylate with methacrylate of monopropandiole ether of benzophenonecarbone acid (BCA-MMA) with different contents of the benzophenone-type groups has been studied. Investigation of absorption and luminescence spectra of solutions of BCA-MMA, dependence of phosphorescence intensity on intensity of exciting light and dependence of polarization degree on content of BCA links in copolymer macromolecule has been carried out. Basing on data obtained it was found that the migration of *t*-excitons and their effective annihilation in macromolecules of BCA-MMA took place starting from 32.6% content of the benzophenone-type links. Using computer calculation for a geometry optimization of the studied polymers the average distance between chromophores for BCA-MMA containing ~20% and ~33% of the benzophenone-type links was determined. It is asserted that the critical jump distance for the triplet excitons in studied polymers is in these limits and is equal approximately 20 Å.

Keywords: electronic excitation energy transfer; triplet excitons; polymers with pendant benzophenone-type groups

INTRODUCTION

An electronic excitation energy transfer in unconjugated polymers containing π-electron systems in side chain is known[1,2] to realize by the singlet (*s*) and triplet (*t*) excitons. Their spreading along macromolecule is random walks in a character[3-5]. Number of works[6,7] has pointed to an importance of the triplet electronic excitation transport in polymers. In particular, in the most of cases, photochemical reactions in macromolecules may occur just at the expense of triplet energy deactivation[8]. Some parameters of t-excitons in aromatic-containing polymers were determined in our laboratory[9,10]. However, electronic energy transfer has been mainly examined for the polymers in which both singlet and triplet excitons exist. It seems to be interesting to study a triplet exciton migration in polymers where *s*-excitons do not exist due to a high value of singlet-triplet conversion in a pendant link π-electron system (benzophenone can be considered as an example of chromophore possessing above properties). This suggests the possibility to determine the "pure" t-exciton parameters in polymers. On the other hand, polymers with pendant benzophenone-type links are well-known polymeric photoinitiators[11]. Such photoinitiators are usually considered to display a higher efficiency with respect to the low molecular counterparts, in particular, due to energy migration along the polymer backbone[12]. However, as far as we know, characteristics of electron excitation energy transfer in polymeric macromolecules containing benzophenone-type groups in side chain were not determined adequately. In this connection a copolymer of methylmethacrylate with methacrylate of monopropandiole ether of benzophenonecarbone acid (BCA-MMA) with different content of the benzophenon-type groups have been synthesized and studied.

EXPERIMENTAL

We have investigated the solutions of copolymer BCA-MMA with different (8%, 19.8%, 32.6%, 46%, 75%, 100%) contents of the BCA groups as well as solutions of isobutyle ether of benzophenonecarbone acid (IBBCA) which is an analogue of a polymer link. Structures of compounds under study are given in Figure 1, A. Absorption spectra were recorded by Specord UV VIS spectrophotometer and luminescence was studied using a spectrometer for steady-state luminescence designed in our laboratory. As a source of excitation of examined compounds a nitrogen laser with set of neutral filters was used. Glan prisms were applied both as polarizer and analyzer. The polarization degree measurements were carried out at 77 K in glassy rigid solutions. A special solvent which consist of tetrahydrofurane, diethyl ether and ethanole in ratio 3:3:1 was used.

The software package HyperChem 5.0 was applied for the calculations and for generating figures. The geometry optimization for investigated molecules has been realized by the MM+ and semiempirical PM3 methods.

RESULTS AND DISCUSSION

MMA links in copolymer investigated do not absorb light in the studied spectral region. They serve as neutral insertions between pendant benzophenone-type BCA chromophores. A likeness of BCA-MMA and IBBCA absorption spectra (Figure 1, B) proves that mainly BCA links absorb light in copolymer system. Taking into account a closeness of copolymerization constants we consider that BCA groups are situated

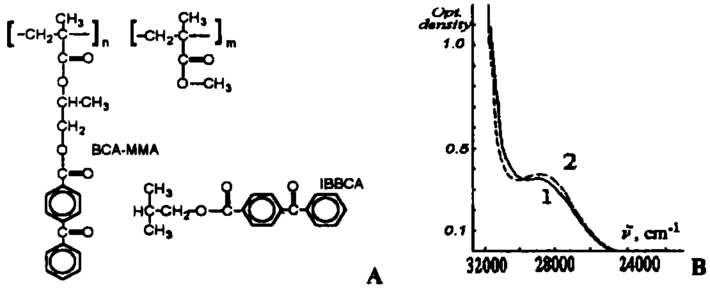

FIGURE 1 Structure (A) and absorption spectra (B) of the compounds investigated: 1- BCA-MMA (46 % content of BCA groups); 2- IBBCA. Dioxane solutions, $C = 5\cdot10^{-4}$ mole/liter (counting on elementary unit).

approximately uniformly along the macromolecule. That is why we believe that increasing a number of MMA insertions causes an increase in the average distance between BCA links.

Emission of BCA-MMA as well as that of IBBCA at 77 K (Figure 2) is phosphorescence, the spectrum shape and spectral position of which, in principle, are near that of benzophenone[13] but red shifted owing to the presence of additional conjugated carbonyl group. It is important to note that the phosphorescence spectra are close for BCA-MMA with all studied contents of BCA-links. Therefore, one can conclude that, at any rate, an emission of BCA-MMA at 77 K is the phosphorescence of benzophenone-type pendant links. The study of the phosphorescence intensity dependence on the intensity of the exciting light has shown that the character of this dependence is close for BCA-MMA with 8% and 19.8%-content of the BCA links and seems to be linear in character. On the contrary, this dependence is non-linear for BCA-MMA with 32.6% , 46% ,75%, 100% -content of the BCA links. From our point of view, this fact testifies to "switching on" the migration of *t*-excitons and their effective annihilation in macromolecules of BCA-MMA starting from 32.6% content of the BCA links. Such annihilation causes the non-linear deviation of phosphorescence intensity dependence on the exciting light intensity (Figure 3, A).

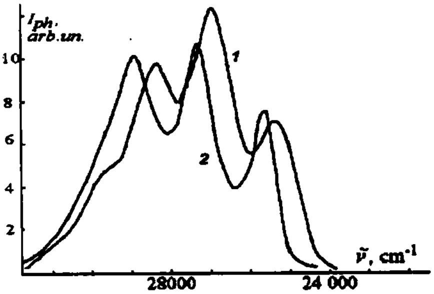

FIGURE 2 Phosphorescence spectra of the compounds investigated: 1- BCA-MMA (46 % of BCA groups); 2- IBBCA. Dioxane solutions, C = $5 \cdot 10^{-4}$ mole/liter (counting on elementary unit).

Studies of the phosphorescence polarization dependence on content of the benzophenone-type links also show the sharp change in the value of phosphorescence polarization passing from BCA-MMA with 19.8%-content of the BCA chromophores to the BCA-MMA with their 32.6%-content (Figure 3, B).

Using computer calculation for a geometry optimization of the polymer macromolecule the average distance between chromophores for BCA-MMA containing ~20% and ~33% of the benzophenone-type links was determined. It is important to note that, according to our calculation, macromolecule of copolymer under study tends to trans-conformation. That is why, taking into account a remoteness of BCA chromophores from the polymer backbone, we have supposed that the electronic excitation energy transfer mainly occurs between next nearest links. Characteristic values of the average distance between next nearest links in BCA-MMA macromolecule are 15 Å for copolymer with ~ 33% BCA content and 25 Å for that with ~ 33% BCA content (Figure 4). We believe that the critical jump distance for the *t*-excitons in polymers studied is in these limits and is equal approximately 20 Å.

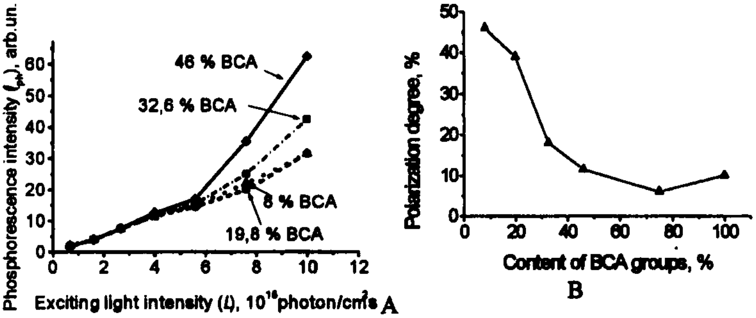

FIGURE 3 A - Dependencies of phosphorescence intensity on exciting light intensity for BCA-MMA with different content of BCA groups; B - Dependence of phosphorescence polarization degree on content of BCA groups in copolymer macromolecule. The lines are there only to guide the eye.

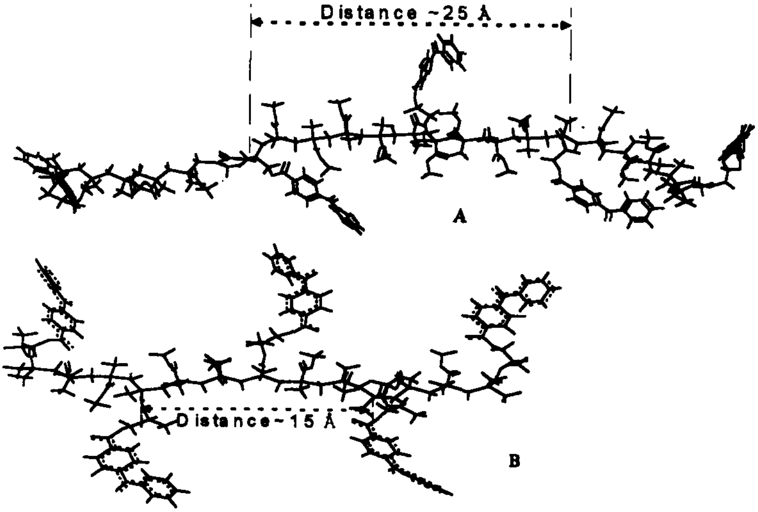

FIGURE 4 Fragments of BCA-MMA macromolecules with ~ 20 % BCA content (A) and ~ 33 % BCA content (B)

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