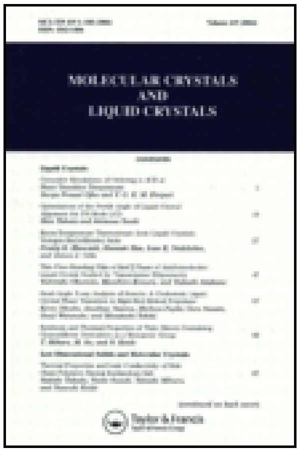

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Direct Energy Supply for Initiation of Some Photochemical Reactions in Macromolecules

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Direct Energy Supply for Initiation of Some Photochemical Reactions in Macromolecules

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The possibility of using the direct electronic excitation energy transfer for energy supply to definite points of molecular systems for initiation of the chemical reactions or, on the contrary, for drainage of electronic excitation energy from the points of molecular systems suitable for reactions with the aim of their stabilization is examined. An analysis of Fries photorearrangement process in investigated compounds confirms the possibility of affecting the rate of Fries photorearrangement by means of electronic excitation energy supply.

Keywords: functional macromolecule, direct electronic excitation energy transfer, Fries photorearrangement.

INTRODUCTION

It is known that in a number of cases the start of chemical reactions demands some initial energy. This energy can be supplied by a light or heat action but one can imagine the situation when these two pathways mentioned above are not suitable because the energy must be transferred to the determined point of the system. In previous works[1-3] we have shown that it is possible to design the macromolecule that can serve as a one-way conductor of electronic energy excitations.

The possibility of direct supply or, on contrary, electronic excitation energy's "sucking off" for initiation or stopping of such photochemical reaction as Fries photorearrangement (F.p.) (Fig.2) in a way of preliminary selection and intramolecular insertion of π-electron systems with the suitable disposition of electronic energy levels has been studied.

EXPERIMENTAL

In connection with the mentioned above we have compared the rate of F.p. in a number of previously synthesized chemical compounds that could be referred to two groups: substituted phenylmethacrylates and substituted naphtylmethacrylates (Fig.1). The processes of energy transfer in these compounds were investigated by studying their fluorescence and phosphorescence spectra. As a source of irradiation and excitation of examined compounds a Hg lamp with a set of optical filters was used. Absorption spectra were recorded by Specord UV VIS spectrophotometer and luminescence was studied using a spectrometer for steady-state luminescence designed in our laboratory.

RESULTS AND DISCUSSION

It is known that the process of F.p. (in compounds that are similar to investigated ones) manifests itself in a characteristic change in absorption spectra[6]. In connection with this we can estimate the rate of F.p. ($V_{F.p.}$) as the rate of photorearrangement product formation and, accordingly, the rate of the F.p. product optical density variation with time $V'_{F.p.} = \partial(D-D_0)/\partial t$.

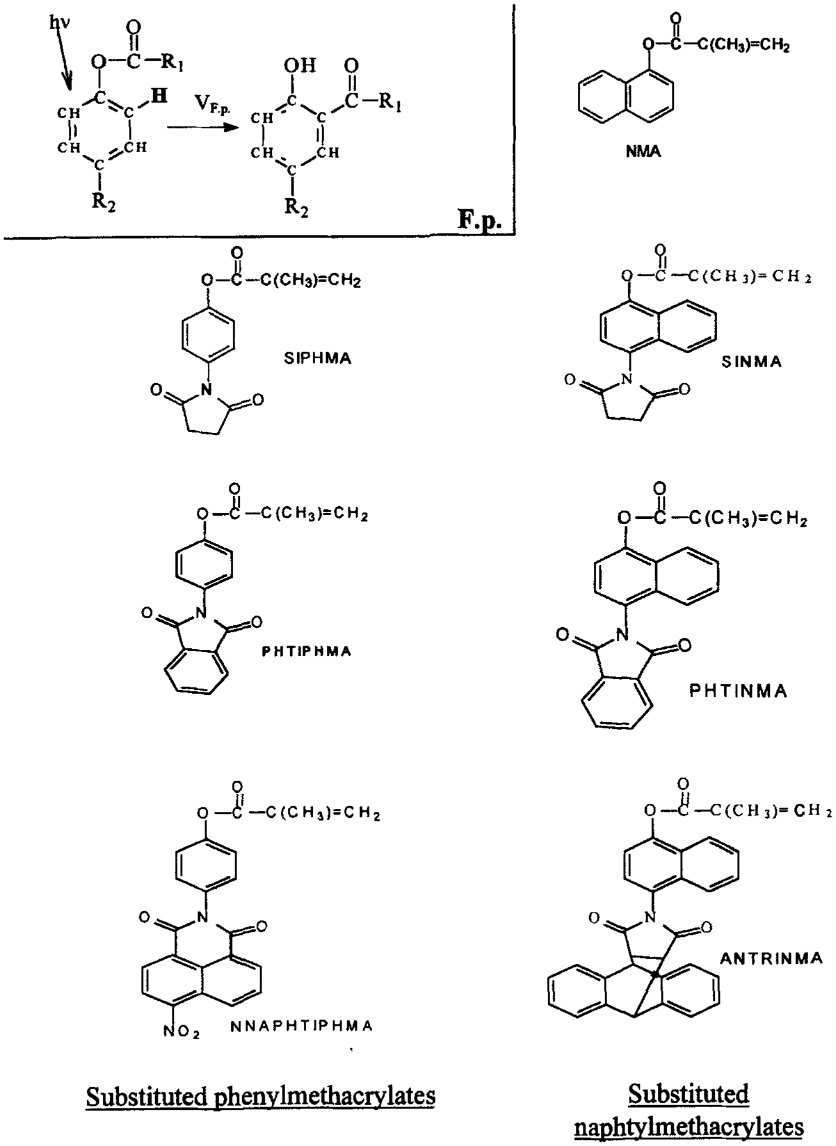
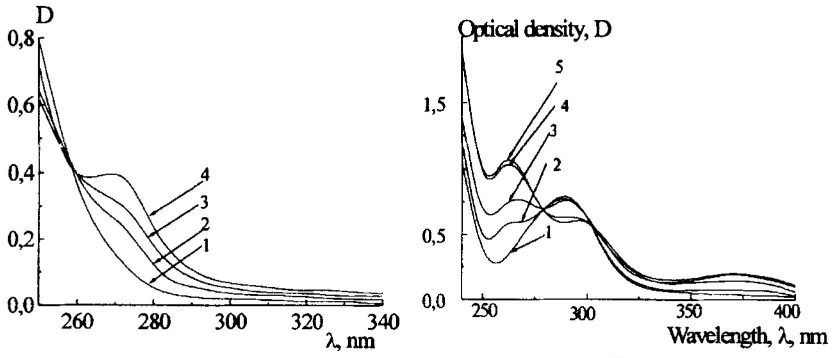


FIGURE 1 The principal scheme of Fries photorearrangement and the structure of the investigated compounds.

In Fig.2 the absorption spectra of SIPHMA and PHTINMA are given that are the representatives of the substituted phenylmethacrylates and substituted naphtylmethacrylates respectively. As one can see, the new bands associated with the formation of F.p. products appear in the absorption spectra after irradiation. We have compared the values of $V'_{F.p.}$ for all the investigated compounds, the variations of F.p. product optical density are considered at the wavelength of the corresponding maxima of the absorption spectra. The analyzed compounds are examined as the combination of sufficiently independent π-electron systems, between which S-S and T-T electronic energy transfer occurs. The examples of such examination were presented in[1-4].

It is known[5] that the rate of F.p. to a great extent depends on an electron - acceptor ability of substitutients in such a way that with increasing substitutient electron - acceptor ability the rate of F.p. also increases.



A

B

FIGURE 2 A - Absorption spectra of SIPHMA (ethanole solution, $C=10^{-4}$ M) before (1) and after UV - irradiation over a period of 4 min (2), 6 min (3), 8 min (4); B - Absorption spectra of PHTINMA (ethanole solution, $C=10^{-4}$ M) before and after UV - irradiation over a period of 0-10 min. 1).-0 min; 2).-1 min; 3).-3 min; 4).-5 min; 5).-10 min.

In this connection we have compared the rate of F.p. by means of the comparison of $V'_{F.p.}$ in the investigated substituted phenylmethacrylates (Fig.1, Tab.1). As one can see from Tab.1 the value of $V'_{F.p.}$ for PHTIPHMA's F.p. is greater than that of the SIPHMA compound. This is understandable if we take into account electron - acceptor ability of the substitutient existing in a PHTIPHMA molecule. On the other hand, under the consideration of the substituted naphtylmethacrylates it has been found that the value of $V'_{F.p.}$ for SINMA, PHTINMA and ANTRNMA is essentially different (Tab.2). It takes place in spite of the fact that the electron - acceptor abilities of these three compounds are approximately equal according to our calculations (it follows from the estimation of charges on carbon atoms). To our point of view the phenomenon of distinguishing $V'_{F.p.}$ (and, accordingly, the rate of the F.p.) for presented compounds is caused by the electronic energy transfer from the π-electron system of substitutient to the naphtyl π-electron system in substituted naphtylmethacrylates. The fact of the existence of such a transfer was established in[4]. Besides that we irradiated NMA, SINMA, PHTINMA and ANTRINMA in such a way that only π-electron system of naphtyl - fragment of molecule was excited (λ=313 nm). It was found that in this case the F.p. rates for the compounds under study were equal with the exception of F.p. rate for NMA (Tab.2).

TABLE 1. Comparison of $V'_{F.p.}$ for substituted phenylmethacrylates

Compound (abbreviation)	$V'_{F.p.} = \partial(D-D_0)/\partial t$ ***(Irradiation by Hg lamp without optical filters)***
SIPHMA	$0.45*10^{-3}$ s^{-1}
PHTIPHMA	$0.9*10^{-3}$ s^{-1}
NNAPHTIPHMA	$0.15*10^{-3}$ s^{-1}

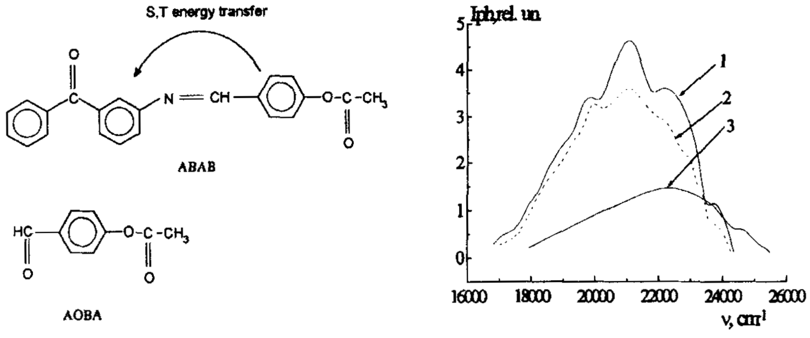
TABLE 2. Comparison of $V'_{F.p.}$ for substituted naphtylmethacrylates

Compound (abbreviation)	$V'_{F.p.} = \partial(D-D_0)/\partial t$ ***(Irradiation by Hg lamp without optical filters)***	$V'_{F.p.} = \partial(D-D_0)/\partial t$ ***(Irradiation by Hg lamp, λ = 313 nm)***
NMA	$1.0*10^{-3}\ s^{-1}$	$0.1*10^{-4} min^{-1}$
SINMA	$2.75*10^{-3}\ s^{-1}$	$0.4*10^{-4} min^{-1}$
PHTINMA	$4.33*10^{-3}\ s^{-1}$	$0.4*10^{-4} min^{-1}$
ANTRINMA	$6.67*10^{-3}\ s^{-1}$	$0.4*10^{-4} min^{-1}$

These data show that if the energy transfer doesn't exist the electron - acceptor ability is only of importance. That's why there is the difference between F.p. rate of NMA and that of other examined compounds.

So, in the compounds presented above the supply of electronic excitation energy to the part of the molecule, in which F.p. occurs, leads to accelerating this photochemical reaction. It is worth waiting for its slowing in the case when the electronic excitation energy "sucking of" takes place. Realization of such situation is observed in substituted phenylmethacrylates (Fig.1, Tab.1). In fact, the electron - acceptor ability of NNAPHTIPHMA approximately equals to that of PHTIPHMA, but it is sufficiently greater than for SIPHMA. In spite of this the rate of F.p. for NNAPHTIPHMA is considerably less than for SIPHMA. To our point of view this fact is explained in a way of electronic excitation energy transfer from phenyl-fragment of molecule NNAPHTIPHMA to nitronaphtylimide - fragment. Similar situation (but intensified) is realized in the compound 4-aceto(3-benzylydenamino)benzophenon (ABAB) (Fig.3,A). It was established, in particular, that owing to the effective S-S and T-T electronic energy transfer to the benzophenon-type π-electron system in ABAB, F.p. didn't occur in contrast to 4-

acetoxybenzaldehyde (AOBA) in which F.p. took place. In Fig.3,B the luminescence spectra of the compounds under study are presented. They prove the existence of electronic excitation energy transfer.



A

B

FIGURE 3 Structure (A) and luminescence spectra (B) of: 1 - benzophenone, 2 - 4-acetoxy-3-(benzylideneamino)benzophenone (ABAB), 3 - 4- acetoxybenzaldehyde (AOBA)

An interesting fact was established concerning F.p. in the compound AOBA. It was found that under air evacuating the rate of F.p. decreased (Fig.4).

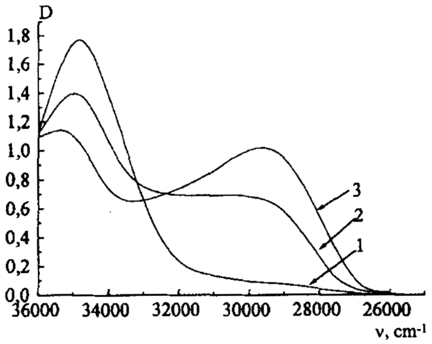


FIGURE 4 Absorption spectra of AOBA (ethanole solution, C=10^{-4} M) before (1) and after UV - irradiation over a period of 40 min without (3) and with (2) air evacuating (P ≈ 0.1 mm Hg).

It is apparently associated with decreasing the number of oxygen molecules contacting with molecules of AOBA. It is possible to presuppose that according to[7], the process of singlet-triplet conversion catalysis takes place by the following scheme:

$^1(\mathrm{AOBA})^* + {}^3\mathrm{O}_2 \rightarrow {}^3[(\mathrm{AOBA})\mathrm{O}_2]_n^*$ *(highest excited triplet exiplex)* $\rightarrow {}^3[(\mathrm{AOBA})\mathrm{O}_2]_l^*$ *(lower excited triplet exiplex)* $\rightarrow {}^3(\mathrm{AOBA})^* + {}^3\mathrm{O}_2$

Thus, the presence of oxygen molecules furthers the creation of triplet excited states and, therefore, to our point of view, Fries photorearrangement in AOBA occurs mainly at the expense of triplet level excitation.

CONCLUSIONS

We can conclude that owing to direct electronic excitation energy transfer in the investigated compounds such photochemical reaction as Fries photorearrangement is accelerated or, on the contrary , slowed or even stopped. It gives the possibility to further stabilization or, contrary, accelerated degradation of polymers and other molecular systems.

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