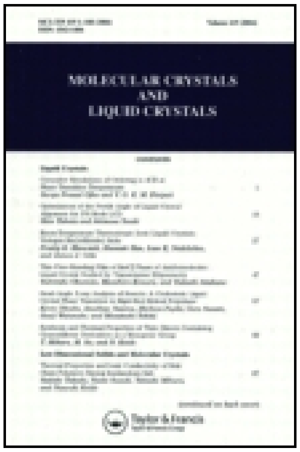

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Exciton Transport and Destruction - Stabilization Processes in Styrene-Based Polymers

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Some variants of using the excitation energy transfer for the stabilization of polymers are examined. Intramolecular photostabilizers acting due to exciton trapping are proposed.

Keywords: energy transfer; photostabilizers

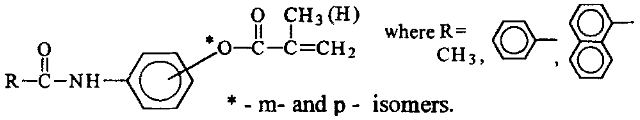
INTRODUCTION

Destruction processes in carbon-chain polymers consist, mainly, in splitting of macrochains under UV-light or heat action (in the presence of water and oxygen). The initiation of these processes can be the consequence of electronic energy transfer from an absorbing center to a photoreactive group or a "weak" linkage in a polymeric chain. The exciton transport is also often responsible for the deactivation of the excited states by stabilizers and in this way it participates in the photostabilization of polymers [1]. Except common methods of photo- and thermostabilization (mechanical addition of antioxidants etc.) there are possibilities of intrachain stabilization of polymer materials by so-called "doping" monomers which can be included in the macromolecular chain by copolymerization - derivatives of aminophenols and aminonaphthols which were found by us.

The esters and secondary amides of unsaturated acids entered a base chaine due to active double bonds of acid residues and may be also converted under the action of light in the outcome of a Fries photorearrangement to derivatives of oxy- or aminoketones, which would protect polymers as UV-absorbers. Besides, it is known that the protective action of series of photostabilizers is based on processes of an excitation energy transfer from units of a basic chain to the units of a stabilizer. A new, perspective approach consists in the development of such photostabilizers, the structure (disposition of energy levels of which) would promote to interception of an exitation energy with stabilizations by them of chains of base polymer, and to acceleration of a photochemical response occurring inside a molecule of a stabilizer [2,3].

RESULTS AND DISCUSSION

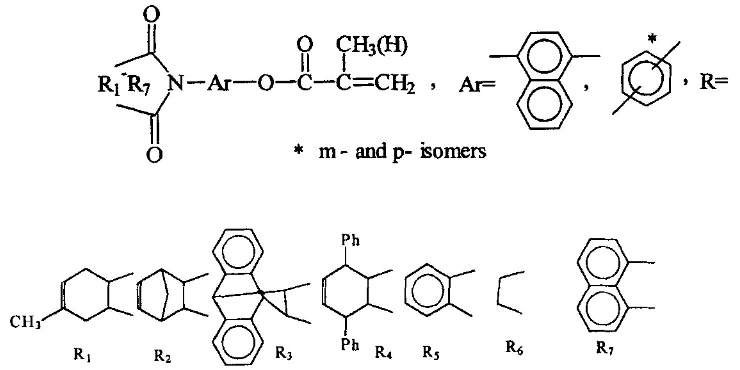
The following monomers-modifiers were developed. Some of them are sufficiently effective. So-called acetylaminophenylmethacrylates are only thermostabilisers as was seen from DTGA data [4].



* - m- and p - isomers.

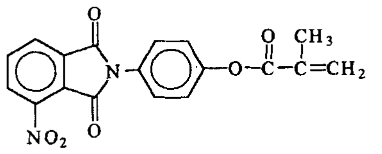
(1)

Imidophenyl(meth)acrylates and imidonaphthyl(meth)acrylates with structures:



(2)

have as a rule photostabilizing activity, too. It can be connected with intramolecular energy transfer in their molecules, which we can observe, 5for example, for oxyphenylphthalimide: according to Form. (2) Ar= C_6H_4, $R=R_5$ and with -OH group in p-position. It consists of two independent aromatic π-electron systems which corresponding energy levels were determined in[2] and singlet-triplet (S-T) energy transfer was proved by phosphorescence spectra.



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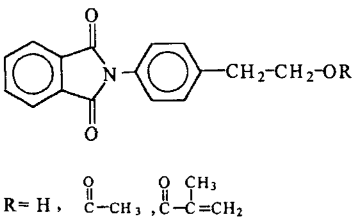

(4)

Both ways were succesful and energy-transfer was observed. More effective photostabilizers are thse that have naphthalene rings, so-called imidonaphthylmethacrylates (Form.(2)). These compounds have higher quantum yields of phosphorescence. The most interesting monomer here is PHTINMA - according to Form. (2) Ar= $C_{10}H_8$, $R=R_5$. First, E-T increases the rate of Fries photorearrangement for it[5].

There are essential differences in rates of a Fries photorearrangement in series of imidonaphthylmethacrylates (where the influence of electronacceptance of the substituents is negligible) and unlike phenylmethacrylates, it becomes possible due to intramolecular energy transfer from independent π-electronic system heterocyclic substituent to naphthylmethacrylates (NMA) reactionary center. It was shown by the research of absorption and luminescence spectra of imidoarylmethacrylates. Finally in a such way we find new UV-absorber units in macromolecules.

Second, such monomer units as PHTINMA are stong energy dissipation and deactivation centers due to a complete S-T convertion. Only phosphorescence exists for such electron systems.

The obtained conclusions are very valuable for studying “doping” monomers with the "programmed" chemical properties, in particularly, as photostabilizers of polymeric materials by a selection of independent π- electronic systems as fragments of a molecule.

For example, three samples of polystyrene (PS) (unstabilized, modified by 5 mass.% of succinimidonaphthylmethacrylate SINMA, R_6 in formula (2) and modified by 5 mass. % of PHTINMA) were irradiated by polychromatyc UV-light with irradiance 610 W/m^2. Fig. 1 shows the changes in UV-absorption spectra of PS (unstabilized and stabilized) after UV-irradiation (0, 60, 120, 180 min). The changes in spectra are continue for 120 min and then photooxidation processes are observed, because PHTINMA units in polymer chains are already destructed (Fig. 1).

The effect of photostabilization is observed only before the complete photodestrunction of PHTINMA units, and then the rates of photooxidation are the same.

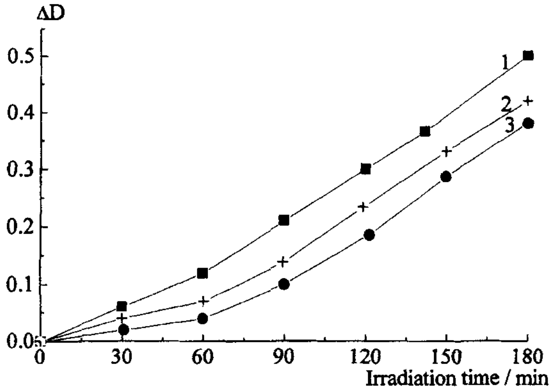

FIGURE 1 The dependence of optical density changes (λ=250 nm) in absorption spectra of polystyrene (1), polystyrene stabilized by SINMA (2) or PHTINMA (3) from UV-irradiation time.

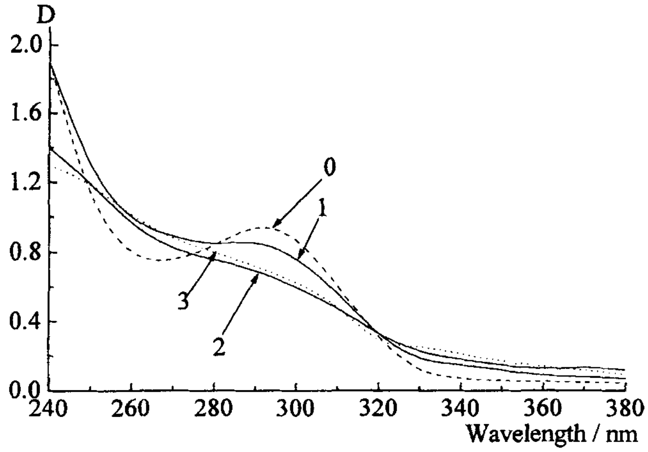

FIGURE 2 Changes in absorption spectra of PHTINMA in polystyrene stabilized by it after such UV-irradiation time: 0 min (0), 60 min (1), 120 min (2), 180 min (3).

It gives us a possibility for the development of materials with a predicted time of life due to the "security-unit" mechanism of photostabilization connected with energy conversion to undangerous for polymer chain by the exciton transport.

Another photostabilization mechanism connected with exitons transport can be realized in PS materials if we increase the distance between styrene units by copolymerization. If it's more than "exciton jump" distance (4-5 units of division) 18 Å [6], exciton migration is finished and energy does not transport to points of contact with photooxidation agent (oxygen). Such materials, which had evident fotostabilization effect, were also obtained by us[7].

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