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Photo-Oxidation Stabilization of Polystyrene by Aromatic Ultraviolet Light Absorbers Forming Charge Transfer Complexes

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Summary

The aim of this work was to investigate the influence of UV light absorbing additives on the rate of ultra violet light initiated degradation of polystyrene (PS) in solutions. Anthracene (ANT), chloranil (CA) nitrobenzene (TNB) which can form charge transfer complexes between each other were used. It was found for illuminated PS-solutions by light of $\lambda=254$ nm that independently of the screening efficiency of these compounds, the formed CT complexes ANT-CA and ANT-TNB cause a decrease of the rate constant of degradation and of the value of the number average of chain scission S. This effect is due to the energy transfer from the excited polymer chain segments to the low energy triplets of these CT-complexes thus hindering the rection of polymer chain segments with oxygen leading to slowing down of photodegradation.

Introduction

Many aromatic compounds are known to be UV-stabilizers for several polymers (RANBY, RABEK 1975), (HELLER 1969). This is due to their filtering action which depends in turn, on their absorption characteristics. When the filtering effect occurs simultaneously with the quenching of excited states of polymer chain elements (HELLER 1969), (GEORGE 1974 a), (KLÖPFFER 1970) thus both processes can be equivalently important.

The efficiency of excited states quenching depends upon the energy levels of excited polymer segments and upon those of aromatic compounds. Especially their triplet states which can act as energy sink, should be taken into consideration. The energy transfer from excited polymer molecules to the triplet states of aromatic compounds can be enhenced by the creation of a favourable situation for lowering the characteristic triplet levels of aromatic additives e.g. by formation of charge transfer complexes (CT-complexes) with a second low molecular weight compound of higher electron affinity (aromatic compounds act usually as donors).

Following this concept it was shown that in solid PS films some additives, formating CT-complexes, can lead to its stabilization against photooxidative degradation (KRYSZEWSKI, NADOLSKI 1978). This effect depends on excited levels created in PS when illuminated with UV-light. The energy diagram of photolysis (REINISCH, GLORIA, ANDROES, 1970) shows that the disappearance of PS excited states leading to photolysis is similar

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for excitation in the wavelength range 190-275 nm. Absorption of light of $\lambda=254$ nm by PS (RABEK, RANBY 1974a) causes the excitation of benzene ring to singlet state which after transition to triplet state can be quenched by molecular oxygen. This in turn results in singlet oxygen production causing effective, photooxidative degradation of PS. Effect of singlet oxygen was evidenced by measurements of activity of effective oxygene quenchers (RABEK, RANBY 1974b). On the other hand the phosphorescence studies of PS (CARSTENSEN 1971) have shown that the initiation of PS photodegradation process is enhenced by the presence of chromophoric carbonyl groups formed during PS synthesis (HELLER 1969, GEORGE 1974b). At the same time it was pointed out that typical UV-absorbers e.g. 2-hydroxybenzophenone and 2-hydroxybenzotriazole are more effective as stabilizers for PS when illuminated by light of $\lambda=290$ nm. It is due to the quenching of triplet states absorbing at 395 nm. The effective energy transfer from these excited triplets to UV-stabilizer molecules is possible due to their low energy triplets at 435 nm and 420 nm respectively.

The aim of this work is to study the photodegradation of PS solution containing aromatic compounds forming CT complexes which can act as PS stabilizers against UV irradiation. The purpose of this investigation is also to reach some conclusions on the filtering or excited states quenching activity taking into consideration the possibility of singlet oxygen formation.

We have used monochromatic light of $\lambda=254$ nm which facilitates the distinction between filtering and quenching effect. It is known that light of this wavelength is very efficient in PS photooxidative degradation.

The studies on the rate of photodegradation of PS films have shown (KRYSZEWSKI, NADOLSKI 1978) that anthracene (ANT), 1,3,5-trinitrobenzene (TNB) and chloranil (CA) in the system allowing for mutual CT-complex formation are active stabilizers in spite of the fact that in two component system with PS (without acceptor) they can act as sensitizers of photodegradation. This stabilization activity can be related to the energy transfer from the PS triplet ($\lambda=335$ nm) (RABEK, RANBY 1974 a) and / or from the triplet states of carbonyl group containing PS (KLÖPFFER 1970) to the triplet states of these CT-complexes: ANT-TNB ($\lambda=465$ nm) and ANT-CA ($\lambda=620$ nm). Fluorescence studies of these systems in solid PS, when excited by $\lambda=361$ nm evidenced the possible energy transfer between different components of the above mentioned solid solution. (DEGORSKI, KRYSZEWSKI 1975).

Experimental

PS, a commercial product was purified by dissolution in chloroform, precipitated by methanol from diluted solution and dried under vacuum to constant mass. The fraction of $M_n=133900$, $M_\eta=250300$ and $M_n/M_\eta=1,86$ were used. All aromatic additives were purified according to method described in our previous works (KRYSZEWSKI, NADOLSKI 1978), (DEGORSKI, KRYSZEWSKI 1975). The solvents used were spectroscopic grade.

Photooxidation studies were carried out on 0.8 g/ml PS solutions were illuminated by low pressure mercury lamp (Phillips 85/40) with a maximum of emission (about 90% $\lambda=254$ nm. The intensity of incident light measured by potassium ferrioxalate actinometer was equal to 1.8×10^{16} quanta/cm^{2}s. The concentrations of stabilizing additives were in the range of 10^{-3} mol/l.

The degradation of PS was followed by viscosity measurements and by quantum yield for chain scission determinations.

Viscosity of solutions was measured using an Ubbelohde viscometer supplied by a quartz window for immediate illumination. All solutions were filtered in order to separate mechanical impurities. Intrinsic viscosity was determined by one-point method (KILP, GUILLET 1977). The protective stabilization efficiency of PS against UV-light illumination was determined as a ratio of quantum yield for chain scission at the same incident light intensity for pure PS-solutions and those with additives according to the relation given by: (NEMZEK, GUILLET 1977a).

$$\frac{\phi_o}{\phi} = \frac{S_o}{S} \; \frac{I_{pa}}{I_{po}} \qquad (1)$$

where S_o and S are the average chain scission number without and in the presence of stabilizers and I_{pa} and I_{po} are the fractions of the absorbed energy by polymer solution in the presence of absorbers given by the relation:

$$\frac{I_{pa}}{I_{po}} = \frac{D_{po}(1-10^{-D_{pa}})}{D_{pa}(1-10^{-D_{po}})} \qquad (2)$$

where D_{pa} and D_{po} are the optical densities of polymer solutions without and with absorbers.

The average chain scission number is given by

$$\frac{S}{\overline{M}_{no}} = \frac{1}{\overline{M}_{nt}} - \frac{1}{\overline{M}_{no}} = kt \qquad (3)$$

where $\overline{M}_{nt}$ and $\overline{M}_{no}$ are the number average molecular weights at time t and t=0 of photodegradation respectively; k is the rate constant.

S values can be estimated from intrinsic viscosity measurements using the relation (KILP, GUILLET 1977a)

$$S = \left\{ \left(\frac{[\eta]_o}{[\eta]} \right)^{1/\alpha} - 1 \right\} \qquad (4)$$

assuming that molecular weight distributions do not change during photodegradation process. This can be ascertained at early stages of this reaction, especially at rather low light intensities and for random chain scission.
In the above given equation α denotes a constant in the Mark-Houvink relation $\eta=KM^{\alpha}$ equal to $\alpha=0.735$ and $K=1.06x10^4$ (DANUSSO, MORAGLIO 1957).

Results and Discussion

All additives used in this work show a high optical density for $\lambda=254$ nm thus their activity towards stabilization of PS against irradiation at this wave length is mostly related to their filtering effect which can be characterized by effective screening ratio I_{pa}/I_{po} according to eq.2. The effective screening ratio, the number average chain scission S as well as the protective efficiency ϕ_o/ϕ in function of concentration of additives are presented in Fig.1,2,3 respectively.

Fig.2 shows that CA acts as a sensitizer for photodegradation of PS under illumination by light of $\lambda=254$ nm, similarly to the observations made earlier when using light of $\lambda=360$ nm (RABEK, RANBY 1974b).
Because sensitizing activity of quinone is observed in PS solution only in the presence of oxygen thus it is possible that quinone is involved in singlet oxygen formation when irradiated (oxygen does not directly take part in hydrogen transfer to quinone). Introducing the screening effect, according to eq. 1, the protective stabilization efficiency ϕ_o/ϕ dependence on concentration of additives can be analysed.

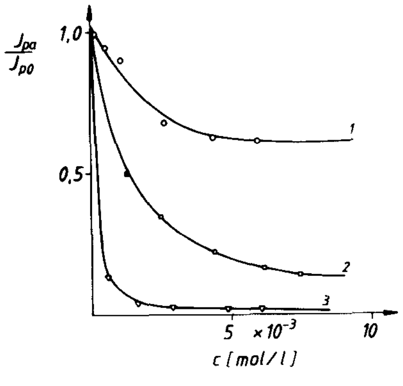

Fig.1. Dependence of effective screening ratio I_{pa}/I_{po} on additive concentration
1--PS-CA; 2--PS-TNB; 3--PS-ANT

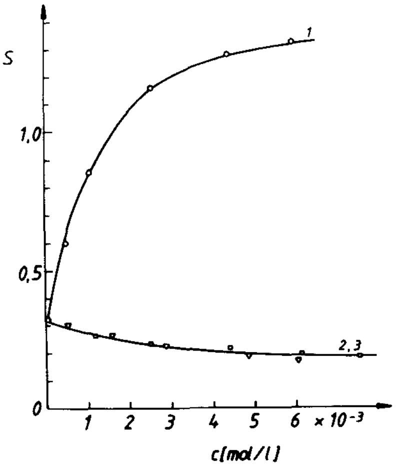

Fig.2. Dependence of number average chain scission S on additive concentration;
1--PS-CA; 2--PS-TNB; 3--PS-ANT

ANT and TNB show a stronger screening effect because of their higher absorption coefficients as compared with CA at $\lambda = 254$nm.

Fig. 3 shows that all low molecular weight substances used exhibit a sensitizing activity because the values ϕ_o/ϕ are smaller than unity (GEORGE 1974).
The most effective from that point of view is ANT inspite of its screening activity. This due to the fact that similarly to the case found when irradiating by light of $\lambda = 360$ nm (COWEL, PITTS 1968), the photooxidation of ANT occurs according to the scheme:

$$\mathrm{ANT} + h\nu \rightarrow \mathrm{ANT} \rightarrow \mathrm{ANT}^{*} \qquad {}^{3}\mathrm{ANT}^{*} + {}^{3}O_2 \rightarrow \mathrm{ANT} + {}^{1}O_2$$

The generated singlet oxygen can participate in the photodegradation of PS.
A different situation is expected when CT-complex can be formed between low molecular weight additives.
Taking into consideration that the concentration of CT-complexes is proportional to the concentration of components (DEGORSKI, KRYSZEWSKI 1978) the studies on complex influence on photodegradation of PS were carried out at constant ANT concentration $C_{ANT} = 6.0\times10^{-3}$ m/l and the other component concentration was varied. The results obtained are presented in Fig.4.

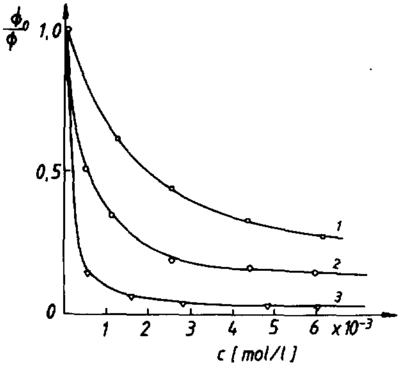

Fig.3. Dependence of protective stabilization efficiency ϕ_o/ϕ on additive concentration 1--PS-CA; 2--PS-TNB; 3--PS-ANT

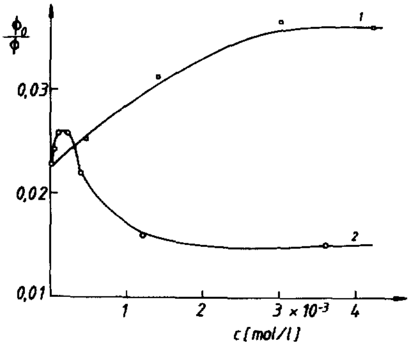

Fig.4. Dependence of protective stabilization efficiency ϕ_o/ϕ on acceptor concentration 1--PS-ANT ($c = 6x10^3$ m/l)-CA; 2--PS-ANT ($c = 6x10^3$ m/l)-TNB

One can see that only in the case of ANT-CA protective efficiency ϕ_o/ϕ is observed (not in the case ANT-TNB). This effect is small because the excess of not complexed component acts still as an sentitizer. Exact estimation of complex concentration is difficult in view of the fact that two complexes are formed simultaneously with the some acceptor. Accordingly, the use of standard method (see FOSTER 1969) consisting of a simultaneous determination of the equilibrium constant K and $\varepsilon_{\text{compl.max}}$ is difficult.

The values of the rate constants k and of quantum yield for PS-chain scission ϕ_{sc} evaluated for different concentrations of additives are gathered in Table I and presented in Fig.5.

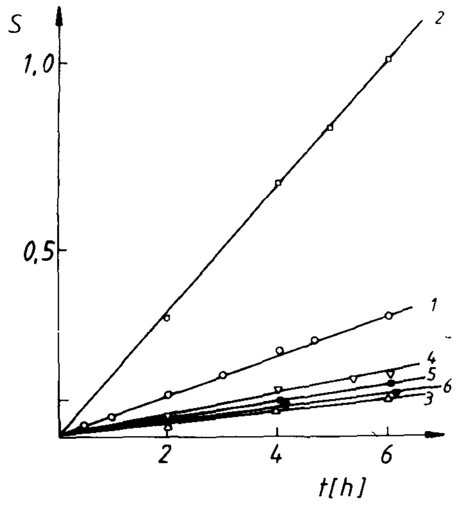

Fig.5. Dependence of average chain scission S on additive concentration and time of illumination; 1--PS; 2--PS-CA ($c=2,64\times10^{-3}$ mol/l); 3--PS-TNB ($c=7.47\times10^{-3}$ mol/l); 4--PS-ANT ($c=6.00\times10^{-3}$ mol/l); 5--PS-ANT($c=6.00\times10^{-3}$ mol/l) CA(0.2×10^{-3} mol/l; 6--PS-ANT ($c=6.00\times10^{-3}$ mol/l); TNB (3.00×10^{-3} mol/l)

Fig.5. shows that all additives, except CA, cause a decrease of k values. Similar conclusion can be drawn on the ϕ_{sc}. It shall be mentioned that this effect is not very important probably due to weak CT-complex formation. Free components of the CT-complexes act individually as filtering agents however the explanation of the k-value decrease cannot be achieved only considering their screening effects (CA is sensitizer and in the presence of ANT the protective activity can be related only to formed CT-complexes). Although the role of singlet oxygen in the reaction under discussion of was considered by several authors (e.g. RABEK, RANBY 1978, KRYSZEWSKI, NADOLSKI 1978) the published results provide only an indirect proof of this mechanism but the influence of excited state quenching by aromatics and CT-complexes is doubtless. This study shows that in the search of UV-stabilizers for PS one

shall also consider the ability of these compounds to form CT-complexes with PS segments thus preventing $^1O_2$ generation or/and to form low energy CT complexes acting as excitation energy sinks. For that reason one has to consider in further studies other compounds, with low ionisation potential and high electron affinity as well as with appropriate absorption characteristics.

TABLE I

Rate constants k and quantum yield ϕ_{cs} of PS photodegradation without and with donor acceptor additives.

System	$k\times10^8 (s^{-1})$	ϕ_{cs}
PS*	1.15	7.66×10^{-4}
PS-CA(2,64x10^{-3} mol/l)	4.18	2.77×10^{-3}
PS-TNB(7.47x10^{-3}mol/l)	0.66	4.34×10^{-4}
PS-ANT(6.0x10^{-3} mol/l)	0.60	4.01×10^{-4}
CA(0.2x10^{-3} mol/l)	0.54	3.60×10^{-4}
PS-ANT(3.0x10^{-3} mol/l)		
TNB(3.0x10^{-3} mol/l)	0.37	2.43×10^{-4}

*PS concentration of PS inirradiated g/l

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