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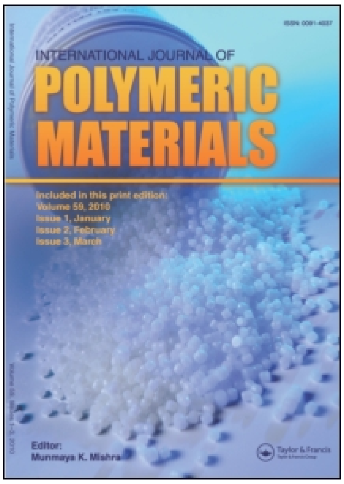

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Belichenko, A. S. , Dyumaev, K. M. , Maslyukov, A. P. , Matyushin, G. A. and Nechitailo, V. S.(1992) 'The Mechanism of Radiation Destruction of Dyes in Polymers: A New Method for Increasing the Stability of Dyed Polymers Based on Oscillative Cross-Relaxation', International Journal of Polymeric Materials, 16: 1, 165 — 169

To link to this Article: DOI: 10.1080/00914039208035419

URL: http://dx.doi.org/10.1080/00914039208035419

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Intern. J. Polymeric Mater., 1992, Vol. 16, pp. 165–169
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Printed in the United Kingdom

The Mechanism of Radiation Destruction of Dyes in Polymers: A New Method for Increasing the Stability of Dyed Polymers Based on Oscillative Cross-Relaxation

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Discussion of the mechanism of radiation destruction of dyes in polymers, which is associated with solid-phase chemical reaction between dye molecules and oxyradicals appearing either on destruction of polymer molecules or on oxidation of macroradicals by the oxygen dissolved in the matrix. Experimental results are given on radiolysis and photolysis of polymethyl methacrylate with a "resonant" low molecular weight additive and dye (nickel dithiobenzil complex and vanadyl phthalocyanine), which demonstrate the decisive role of oscillative cross-relaxation between macromolecules and molecules of the additive in increasing the radiation stability of dyed polymers.

KEY WORDS Dyes, degradation, polymers

RESULTS AND DISCUSSION

The mechanism of radiation destruction of optical polymers of the acrylic and methacrylic series in γ-irradiation with doses 10 kGy and higher has been studied quite thoroughly,[1-5] whereas the study of the mechanism of polymer radiolysis in irradiation with low doses (less than 10 kGy) has been significantly less thorough.[6] This is because experimental methods used in the studies (EPR and optical spectroscopy) have insufficient sensitivity. For instance, the EPR method makes it possible to reliably detect the formation of radical products with concentrations of 10^{-4}–10^{-3} mol/l.[2,6]

In the present work, we propose to increase the sensitivity of the optical method by adding organic dyes to a polymer. These dyes change their spectroscopic characteristics upon interaction with the products of radiation destruction of the polymer matrix. Noting that the extinction coefficients of dyes are in the range of $\varepsilon = 10^4$–10^5 l/mol cm,[7] it may be expected that noticeable changes in the absorption spectra of dyed polymers will already be observed with variations of dye concentrations by 10^{-6}–10^{-7} mol/l.

As such dyes, it is possible to use, for instance, vanadyl phthalocyanine and nickel dithiobenzil complex which possess a high radiation stability and change their optical characteristics as a result of a solid-phase chemical reaction with the oxyradicals appearing in a polymer matrix upon laser irradiation.[7]

Considering the experimental results presented in Reference 7, it might be expected that the mechanism of radiation destruction of dyed polymers upon ultraviolet (uv) and γ-irradiation should also be associated with a chemical reaction between dye molecules and oxyradicals which appear either on destruction of polymer macromolecules or on oxidation of macroradicals by the oxygen dissolved in the matrix. If this is really so, then the radiation stability of dyes should depend substantially on the rate of formation of primary radicals in the polymer under the action of uv and γ-irradiation. As has been demonstrated earlier,[4] this rate can be influenced by "resonant" low molecular weight additives which perform oscillative cross-relaxation.

An object of the present study is to prove experimentally the expressed ideas on the mechanism of radiation destruction of dyes in polymers and on the possibility of the use of dyes in investigating the mechanism of radiolysis of polymers in low-dose irradiation.

As an object of study, we have chosen the well-known optical polymer, poly(methyl methacrylate) (PMMA). Triethyl phosphate (TEP) is used as a "resonant" low-molecular weight additive to PMMA. The latter is dyed with vanadyl phthalocyanine and nickel dithiobenzil complex added in a concentration of 10^{-4}–10^{-5} mol/l.

The experiments are carried out with the use of polymer specimens in the form of optical discs 20 mm in diameter and 6 mm thick; workpieces for discs are obtained by means of block-radical polymerization of the initial monomer compositions with introduced TEP and dye additives, in which the concentration of dissolved oxygen was less than 10^{-7} mol/l.

The specimens are irradiated at 300 K in air by a source of ^{60}Co with a capacity of 1.2 Gy/s in successive doses of 100 Gy up to a total dose of 10 kGy. UV irradiation is carried out by means of a lamp type DKsTV-15000 with exposure time up to 100 h and a flash lamp type IFP-800 with number of pulses up to 1000. The diagnosis of polymer destruction is carried out by the weight of specimens P, vitrification temperature T_v, absorption spectra in the uv, visible and infrared (IR) light, and the threshold of multipulse laser destruction $I_{\min}$.[4] These parameters are controlled before irradiation, during irradiation (between successive doses), and during a year after irradiation.

Figure 1 shows the absorption spectra of PMMA with different concentrations of TEP before and after γ-irradiation with doses of 1.4 kGy and 10 kGy. As may be seen, an addition of TEP to PMMA, like an addition of propyl alcohol,[4] substantially increases the transparency of the polymer in the uv spectrum (see curves 1, 4 and 7).

With due consideration of the results obtained in Reference 4, the observed changes in the spectrum of the initial polymer with increasing concentration of the "resonant" additive can be interpreted in the following way. In the course of block-radical polymerization of the initial monomer composition, destruction of PMMA

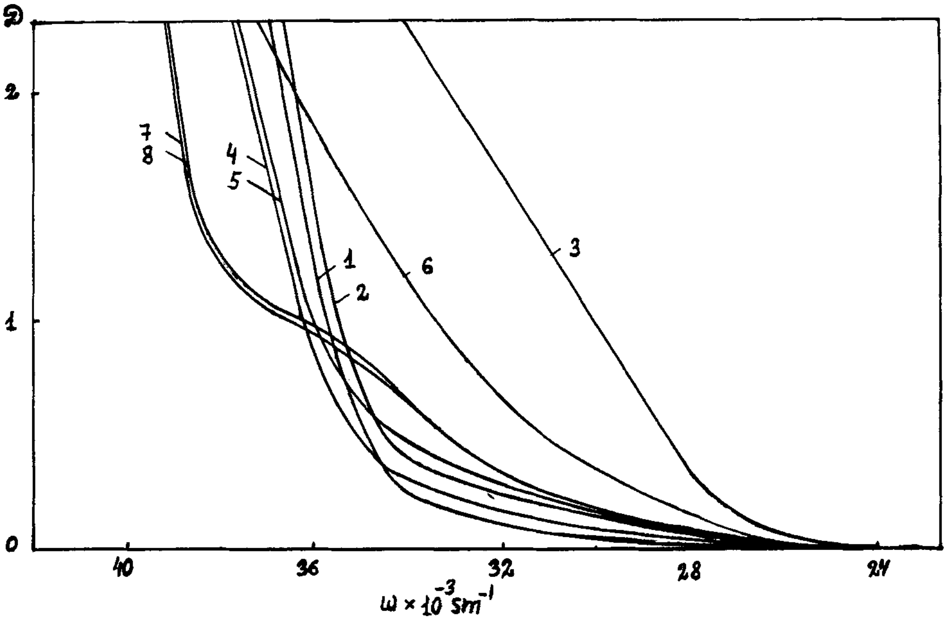

FIGURE 1 Absorption spectra of PMMA (1), (2), (3), PMMA + 10% TEP (4), (5), (6), and PMMA + 20% TEP (7), (8) on γ-irradiation with different dose (kGy): (1), (4), (7) 0; (2), (5) 1.4; (3), (6), (8) 10. D = optical density per 1 cm.

macromolecules takes place at the last conversion stage, which leads to the formation of allyl radicals ($\omega_1 = 39 \times 10^3$ cm^{-1}), ketones ($\omega_2 = 36 \times 10^3$ cm^{-1}), and unsaturated ketones ($\omega_3 = 32 \times 10^3$ cm^{-1}),[4] whereas the introduction of the "resonant" additive, which performs effective energy transfer of oscillatory excitation from macromolecules to molecules of the additive, suppresses the process of destruction of macromolecules and leads to an appreciable decrease of the concentration of allyl radicals and to a certain increase of the concentration of ketones already at the polymerization stage.

As may be seen, the absorption in uv spectrum in all irradiated specimens increases with an increase in the total dose. The intensity of uv absorption in γ-irradiation increases more slowly at a higher concentration of TEP (see curves 3, 6 and 8 in Figure 1). It is found that the parameters P, T_v and $I_{\min}$ are not changed in that case. These results suggest that the products formed on γ-irradiation of PMMA are not of low-molecular weight and that the introduction of the "resonant" additives inhibits the formation of primary radicals.

It may also be seen in Figure 1 that with irradiation doses less than 1 kGy, the changes in the absorption spectra of the specimens are quite insignificant, which involves certain difficulties in interpretation and identification of the products of polymer radiolysis.

As has been indicated earlier, the sensitivity of the optical method can be increased by adding organic dyes to a polymer. Figure 2 shows the dependence of the optical density D of the nickel dithiobenzil complex in PMMA + 10% TEP on the γ-irradiation dose D_γ immediately after preparation of specimens (curve 1)

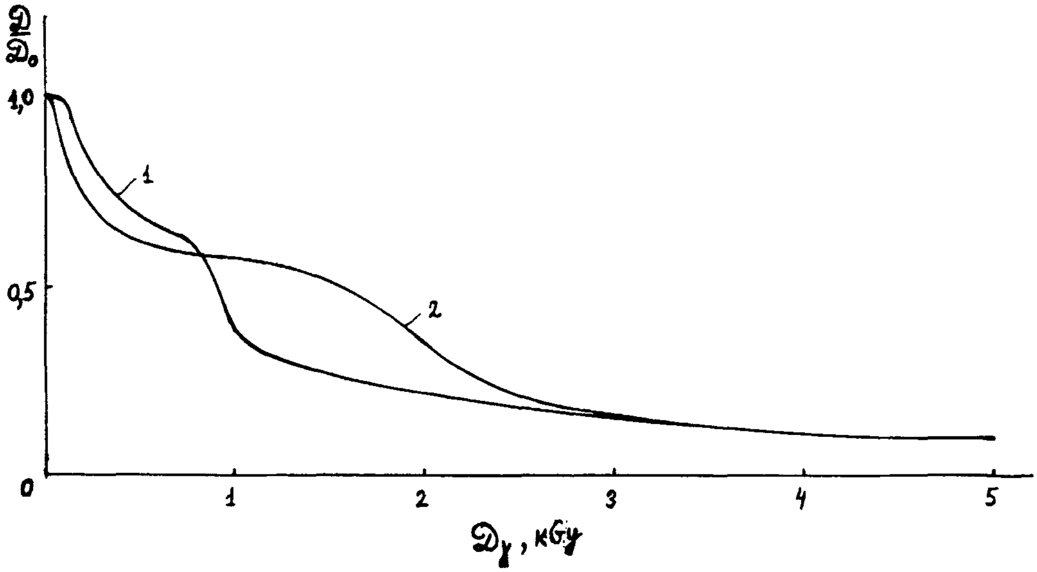

FIGURE 2 Dependence of the optical density D at λ = 1060 nm (related to the initial optical density D_0) of the nickel dithiobenzil complex in PMMA + 10% TEP on γ-irradiation dose D_γ (curve 1). Curve 2 is the dependence of D on D_γ after one year of storage.

and after one year of storage (curve 2). As may be seen, the optical density decreases with an increase in the total dose, with noticeable changes of D being observed already at $D \simeq 0.1$ kGy.

Similar experiments carried out with dyed PMMA specimens without additives show that substantial changes of D are detected at $D_\gamma \lesssim 0.01$ kGy. These results demonstrate that an addition of dye to a polymer really makes it possible to investigate the mechanism of polymer radiolysis at low irradiation doses and that an introduction of a "resonant" additive (TEP) to PMMA leads to an appreciable rise in the radiation stability both of the polymer matrix proper and of the dye.

It should be noted that the dependence of D on D_γ has a clearly pronounced two-stage pattern (see curve 1 in Figure 2). At the first stage with $0.1 < D_\gamma < 0.7$ kGy, a substantial decrease (by 30–40%) in the dye concentration is observed, which is evidence of a high rate of the process of destruction of polymer macromolecules in γ-irradiation. At the second stage with $0.7 < D_\gamma < 10$ kGy, the decrease of D with increasing D_γ occurs much more slowly, which is evidence of a lower rate of polymer destruction.

The results obtained on polymer radiolysis can be interpreted as follows. At the first stage, destruction of macromolecules takes place at the so-called "weak" bonds which form in the process of block-radical polymerization at the last stage of conversion (see earlier); at the second stage, destruction occurs at the "common" bonds.

These concepts agree well with the results of experiments on radiolysis of polymer specimens of the same composition after one year of storage when they have been saturated with oxygen from the ambient air due to diffusion (see curve 2 in Figure 2). At the first stage, destruction of macromolecules at the "weak" bonds occurs even with a higher rate, which is probably due to the chemical interaction of the "weak" bonds with oxygen. At the second stage, destruction initially occurs at $0.7 < D_\gamma < 3$ kGy with participation of the dissolved oxygen and then, at $D_\gamma > 3$ kGy, at the "common" bonds in the absence of oxygen.

In the course of storage of γ-irradiated specimens it has been detected that complete discoloration takes place in the surface layers of the specimens, with the discoloration reaction front moving into the depth of the specimens by the diffusion law during 10–15 days, after which the reaction front is stopped.

This result can easily be explained within the framework of the theory of diffusion with "traps."[8] As a result of γ-irradiation of the initial oxygen-free specimens (or specimens saturated with oxygen and irradiated to a dose of $D_\gamma > 3$ kGy, long-living (lifetime 10–15 days) alkyl radicals are formed in their volume.[2,3,6] With diffusion of oxygen from the air into the polymer, these radicals are oxidized with the formation of peroxide products whose decomposition leads to the appearance of oxyradicals and destruction of dye molecules due to interaction with them.

Similar results have been obtained by us in γ-irradiation of polymers with vanadyl phthalocyanine. It should only be noted that the addition of 20% TEP to PMMA has led to an appreciable rise of the γ-stability of the dye: no changes of D were observed at D_γ up to 1 kGy. In the frames of the proposed mechanism of radiation destruction of dyes in polymers, this result can be explained by the high radiation stability of the polymer matrix containing the "resonant" additive in a substantial concentration (see curves 7 and 8 in Figure 1).

Ultraviolet irradiation of polymer specimens with dyes and additives by means of a continuous-emission lamp for 100 h or a flash lamp with the number of pulses up to 1000 causes no substantial changes: D_0, P, T_v and $I_{\min}$ remain constant. This fact can easily be explained by the high uv stability of the polymer matrix with "resonant" additive.[4] Besides, when dyes having an intensive absorption band in the uv spectrum are added to the polymer, this leads to screening of the polymer volume against the action of uv light.

Thus, the whole combination of the experimental facts on uv and γ-stability of dyed polymers suggests that the introduction of additives which can cause oscillatory cross-relaxation between macromolecules and molecules of the additive is an efficient method for increasing the radiation stability of dyes in polymers. Addition of organic dyes makes it possible to investigate the mechanism of polymer radiolysis at low doses of γ-irradiation.

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