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Photodegradation of High Polymers in Solution

Part 4 – The Effect of Additives on the Photolysis of Poly(methyl methacrylate)

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PREVIOUS REPORTS IN THIS SERIES

"Part 1—Solvent Effects in the Photolysis of Poly(α-methylstyrene)," R. B. Fox and T. R. Price, NRL Report 6120, Aug. 1964

"Part 2—Solvent Effects in the Photolysis of Polystyrene," T. R. Price and R. B. Fox, NRL Report 6328, Oct. 1965

"Part 3—Poly(methyl methacrylate)," R. B. Fox and T. R. Price, NRL Report 6423, Sept. 1966

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ABSTRACT

Poly(methyl methacrylate) has been photolyzed by 2537A radiation at room temperatures in methylene chloride and in dioxane. The quantum yields for random scission in the absence of air in dioxane were 0.168 scission/quantum absorbed at an intensity absorbed by the polymer of 0.30×10^{16} quanta/ml-min; in methylene chloride the corresponding data are 0.149 and 0.27×10^{16}. The quantum yields in the presence of air are about half these yields. A wide variety of chemical additives in the polymer solutions were sensitizers or inhibitors of degradation. The strongest inhibitors were those additives whose lowest excited triplet levels were below about 23,000 cm^{-1}, and the sensitizers were those additives whose lowest excited triplet levels were above 27,000 cm^{-1}. By postulating electronic energy transfer via the lowest excited triplet levels as the mechanism for inhibition or sensitization a triplet is inferred for the polymer between 23,000 and 27,000 cm^{-1}. As further evidence of this postulate a number of nitro compounds which would be expected to form triplets were found to show promise as inhibitors to the poly(methyl methacrylate) photolysis.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C04-04
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where N is Avogadro's number, α is the exponent in the Mark-Houwink equation, and the subscript zero refers to undegraded polymer. Such evaluations were made from plots of $([\eta_0]/[\eta])^{1/\alpha} - 1$ (the number of scissions per polymer molecule) versus $I_a^P t$ (the energy absorbed by the polymer alone); α was taken as 0.79 for methylene chloride and 0.76 for dioxane. It was assumed that the extinction coefficient for poly(methyl methacrylate) at 2537A, 0.0090 1/g-cm in either solvent, did not undergo change during a run; therefore $I_a^P = 0.0090\ I_0 c/A^{soln}$, where A^{soln} is the absorbance of the entire solution at 2537A. In certain instances the ratios of scissions per molecule to quanta absorbed tended to decrease with increasing total absorbed dose. In these instances comparisons of Φ_s^P were arbitrarily made at the point where an average of one scission per molecule was attained, as well as at the beginning of the degradation. To indicate a changing rate, both values of Φ_s^P will be noted; where only one value of Φ_s^P is given, the quantum yield was constant at least to one scission per polymer molecule.

As a measure of protective effectiveness a "protection index" analogous to that used by other workers (6) is employed. The protection index, which is

$$100 \left(\Phi^P_{s(0)} - \Phi_s^P\right) \Big/ \Phi^P_{s(0)}$$

where $\Phi^P_{s(0)}$ is the quantum yield in pure solvent, tends to stress small effects and underemphasize differences among highly effective additives. The protection index is based on the quantum yield at one scission per molecule. In order to maintain initial intensities absorbed by the polymer at the same order of magnitude widely varying concentrations of additives were required; these are reflected in both the concentrations in solution and in the mole ratios of polymer to additive shown in the tables. Comparisons among the protection indexes of the additives should be made with this point in mind.

RESULTS

Tables 1 and 2 show data obtained from the irradiation of poly(methyl methacrylate) solutions in the absence of air. The results from solutions run in the presence of air are shown in Tables 3 and 4. Data in Tables 1 through 4 were obtained with the 88A45 lamp. The tables are organized to the extent that runs with additives of similar chemical type are listed together. Protection indexes in the absence of air were derived from a comparison of quantum yields at the same initial intensity of radiation in the presence and absence of the additive. Data for solutions in the pure solvent at intensities other than that shown are given in Ref. 3. Protection indexes for air runs are calculated from the quantum yield for the corresponding run in air where no additive was used.

The 84A1 lamp was used in the biacetyl concentration study described later in this report and in the investigation of the effects of a variety of nitro compounds on poly(methyl methacrylate) photodegradation. The latter data are shown in Table 5. As noted in the pure solvent study (3), some variation in the results due to the radiation source was observed, as can be seen by comparing Φ_s^P in the first line of Table 5 with Φ_s^P in the first line of Table 2; therefore data from different sources should not be compared quantitatively.

DISCUSSION

In appearance, the data of Tables 1 through 4 show every evidence of chaos. Partly, this can be ascribed to the wide variations of mole ratios of polymer to additive. Intensity differences may also play a role, although the results in pure solvents (3) suggest that this role may be small in most instances. A far more likely cause of variation may be in the photolysis of the additives themselves, with the products in turn exerting their own effects. One obvious instance of this is 1,3-cyclohexadiene, which in either dioxane

Table 1
Photodegradation of Poly(methyl methacrylate) in Degassed Dioxane Solutions

Additive	Conc. of Additive (g/l)	Mole Ratio of Monomer Units to Additive	I_a^P $\left(10^{16} \frac{\text{quanta}}{\text{ml-min}}\right)$	Φ_s^P (scissions/ quantum absorbed)	Protection Index
None	0	--	0.30*	0.168*	--
1,3-Cyclohexadiene	0.05	80	0.096†	0.077	64
				0.039‡	78
Benzene	0.32	12*	0.45*	0.204*	-28*
Naphthalene	0.05	128	0.23	0.146	14
Pyrene	0.11	93	0.037	0.134‡	33
Acetone	1.6	1.8	0.70	0.145	3
Biacetyl	2.14	2.0	0.14	0.113	36
Acetophenone	0.05	120	0.19	0.153	10
Benzoic acid	0.08	76	0.47	0.161	-2

*From Ref. 3.
†A^{soln} changes rapidly during photolysis.
‡At one scission.

Table 2
Photodegradation of Poly(methyl methacrylate) in Degassed Methylene Chloride Solutions

Additive	Conc. of Additive (g/l)	Mole Ratio of Monomer Units to Additive	I_a^P $\left(10^{16} \frac{\text{quanta}}{\text{ml-min}}\right)$	Φ_s^P (scissions/ quantum absorbed)	Protection Index
None	0	--	0.27*	0.149*	--
1,3-Cyclohexadiene	0.05	80	0.10†	0.159	1
				0.018‡	89
2,5-Dimethyl-2,4-hexadiene	0.05	110	0.026	0.121	33
				0.093‡	49
Benzene	0.32	12*	0.34*	0.161*	-10*
Naphthalene	0.05	128	0.23	0.060	60
Pyrene	0.05	202	0.10	0.094	40
Acetone	1.6	1.8	0.52	0.127	9
Acetophenone	0.05	120	0.11	0.119	26
Benzoquinone§	0.05	108	0.08	0.135§	18
Benzoic acid	0.05	122	0.56	0.108	23
Nitromethane	1.0	3	0.42	0.103	27
				0.041‡	71

*From Ref. 3.
†A^{soln} changes rapidly during photolysis.
‡At one scission.
§Posteffect.

Table 3
Photodegradation of Poly(methyl methacrylate) in Dioxane in the Presence of Air

Additive	Conc. of Additive (g/l)	Mole Ratio of Monomer Units to Additive	I_a^P $\left(10^{16} \frac{\text{quanta}}{\text{ml-min}}\right)$	Φ_s^P (scissions/ quantum absorbed)	Protection Index
None*	0	--	0.18	0.067	--
1,3-Cyclohexadiene	0.05	80	0.22	0.055	18
Benzene*	0.32	12	0.24	0.083	-24
Naphthalene	0.05	128	0.18	0.063	6
Acetone	1.6	1.8	0.44	0.070	-4
Biacetyl	2.0	2.1	0.08	0.132	-97

*From Ref. 3.

Table 4
Photodegradation of Poly(methyl methacrylate) in Methylene Chloride in the Presence of Air

Additive	Conc. of Additive (g/l)	Mole Ratio of Monomer Units to Additive	I_a^P $\left(10^{16} \frac{\text{quanta}}{\text{ml-min}}\right)$	Φ_s^P (scissions/ quantum absorbed	Protection Index
None	0	--	1.03*	0.071*	--
1,3-Cyclohexadiene	0.05	80	0.12	0.011	84
Benzene	0.32	12*	0.31*	0.074*	-4*
Benzene	32	0.11*	0.0044*	0.238*	-235*
Naphthalene	0.05	128	0.20	0.047	34
Pyrene	0.05	202	0.095	0.034	51
Acetone	1.6	1.8	0.62	0.055	23
Biacetyl	2.0	2.0	0.52	0.264 0.072†	-272 -1
Nitromethane	1.0	3.0	0.66	0.069	3

*From Ref. 3.
†At one scission.

Table 5
Effect of Nitro Compounds on the Photodegradation of Poly(methyl methacrylate) in Degassed Methylene Chloride Solutions*

Additive	Conc. of Additive (g/l)	Mole Ratio of Monomer Units to Additive	I_a^P $\left(10^{16} \frac{\text{quanta}}{\text{ml-min}}\right)$	Φ_s^P (scissions/ quantum absorbed		Protection Index
				Initial	s = 1	
None	0	--	0.28	0.098	0.098	--
Nitromethane	1.0	3.0	0.19	0.084	0.029	70
Nitroethane	1.0	3.8	0.20	0.093	0.078	20
1-Nitropropane	1.0	4.5	0.21	0.095	0.095	3
4,4,4-Trinitro-butyric acid	1.0	10	0.13	0.042	0.013	87
4,4,4-Trinitro-butyric acid	0.1	100	0.27	0.082	0.044	55
2-Methyl-2-nitro-1,3-propanediol	1.0	6.8	0.20	0.106	0.086	12
Nitrobenzene	0.01	620	0.085	0.097	0.083	15
p-Nitrotoluene	0.01	690	0.15	0.085	0.063	36

*84A1 quartz lamp used, whereas the data in Tables 1 through 4 were obtained using the 88A45 lamp with a Vycor jacket.

or methylene chloride undergoes rapid photolysis as evidenced by large spectral changes in the 230 to 300 nm region. It was also observed that aromatic hydrocarbons in methylene chloride underwent photolytic change to form new compounds with specific ultraviolet absorption bands, but identification of these products is outside the scope of the present report.

The most common explanation for the behavior of polymer systems undergoing photolysis is the interaction of free radicals formed by bond-breaking as the result of the absorption of radiant energy. This might be called a "radical-scavenging mechanism." In a simple example, if a secondary free radical along a polymer chain (such as that formed by homolysis of a C-H bond in polymethylene) is a precursor to a main-chain scission, then anything which could scavenge those radicals would act as a degradation inhibitor, and anything which enhanced radical formation would be an accelerator of degradation. A typical scavenging reaction would be the combination of the polymer radical with a "foreign" free radical. A typical accelerating reaction would be the abstraction of hydrogen atoms from the polymer by a highly reactive "foreign" free radical. Both of these effects require the presence of such radicals.

While such an explanation may be tenable in certain instances, it is difficult to ascribe the major part of the results given in Tables 1 through 4 to free radical scavenging

or attack by additive fragments. For example, as a general rule aromatic hydrocarbons are less prone to photolysis than aliphatic ketones under comparable conditions, yet in the absence of air benzene accelerates the degradation of poly(methyl methacrylate) whereas biacetyl acts as an inhibitor and acetone has almost no effect. At the same time, it might be expected that benzene and its polycyclic homologs would undergo photolysis at qualitatively similar rates, presumably to form radical intermediates. The behavior of benzene, naphthalene, and pyrene in poly(methyl methacrylate) solutions shows no such similarity; on the contrary these hydrocarbons cover nearly the entire range of effectiveness seen in the current study.

In the case of biacetyl more than one mechanism may be operating to provide the effect observed with poly(methyl methacrylate). For example, degradation occurred in the dark in the presence of biacetyl prior to irradiation, and small ultraviolet spectral posteffects were observed after irradiation, It should be added that dioxane and biacetyl form a charge-transfer complex, evident in the spectrum, and this complex breaks down under irradiation; the influence of this complex on the degradation was not assessed. In the absence of air, biacetyl acted as an inhibitor to the photolysis of poly(methyl methacrylate) in either dioxane or methylene chloride. The presence of more than one reaction, at least in methylene chloride, is seen in the effect of increasing biacetyl concentration on the quantum yield for scission of the polymer. This is shown in Fig. 1, from which it is apparent that the protection index reaches a maximum. In part, this effect might be ascribed to the dark reaction or posteffects, but the duration of the experiments was such that a more important effect must be playing a part. A strong possibility is that radical formation from the biacetyl is the explanation.

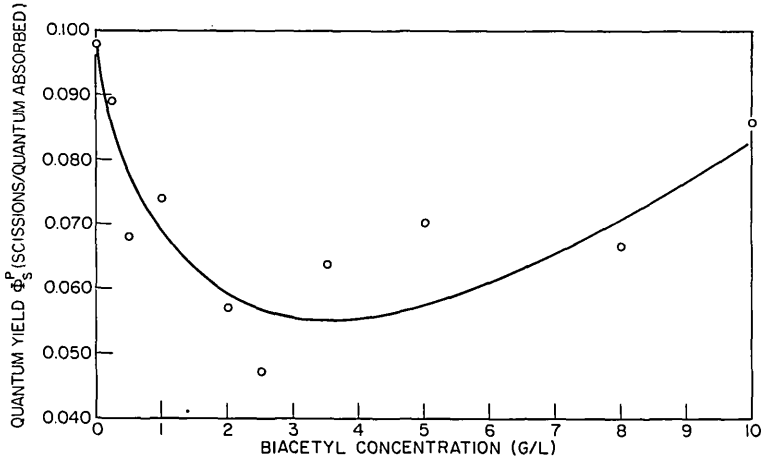


Fig. 1 - Effect of biacetyl concentration on the quantum yield for scission of poly(methyl methacrylate) in degassed methylene chloride solutions (84A1 source)

In air, biacetyl strongly accelerated the photodegradation of poly(methyl methacrylate). That this is a consequence of radical formation from biacetyl is indicated by the high quantum yields for both oxygen consumption and product formation which have been observed for biacetyl-oxygen mixtures subjected to relatively long (4358A) wavelength radiation (7).

The effect of oxygen itself was discussed in the work on pure solvents (3). Although oxygen behaves as an accelerator of photodegradation with some polymers, with poly(methyl methacrylate) oxygen appears to be an inhibitor. It is possible that this

inhibition comes about through the formation of stable peroxides by an oxygen scavenging reaction with secondary polymer free radicals or that a charge-transfer mechanism is operating. Most of the additives used had the same effect in the presence as in the absence of oxygen.

Since such varied chemical entities appear to influence the photodegradation of poly(methyl methacrylate), and since free radical interaction does not offer a complete explanation of the observation, it is reasonable to consider interactions which might occur before bond scission takes place. These are the photophysical processes which have recently been the subject of a number of reviews (8).

"Energy transfer," without specification of states, has been proposed as an explanation of the inhibiting influence of certain scintillators in the photodegradation of poly(methyl methacrylate) films (9). The behavior of "protecting agents" in the degradation of poly(methyl methacrylate) films subjected to ionizing radiation has also been vaguely ascribed to electronic energy transfer between polymer and additive (6,10,11).

It so happens that the maximum of the first absorption band of poly(methyl methacrylate) lies at 213 nm. This is an $n \rightarrow \pi^*$, singlet-singlet transition involving a nonbonding electron at the oxygen atom in the carbonyl group. The transition is to a higher energy level, 47000 cm^{-1}, than the lowest excited singlet levels of any of the additives used in this study. On the basis of energy levels alone, therefore, the transfer of electronic energy is possible from the polymer to any of the additives by way of singlet states.

In Table 6 are given energy levels of the lowest excited singlet states of the additives used in this work. These energy levels are plotted against the corresponding protection indexes in Fig. 2. Any correlation here is minimal, although singlet-singlet transfer in specific cases cannot be ruled out on the basis of the present work.

Table 6
Approximate First Excited Energy Levels

Compound	Triplet* (10^3 cm^{-1})	Singlet† (10^3 cm^{-1})
Poly(methyl methacrylate)	--	47
Benzene	29.7	38.5
Benzoic acid	27.2	35.7
Acetophenone	25.8	30.8
Acetone	24.5	35.8
Naphthalene	21.3	32.0
Biacetyl	19.7	23.0
2,5-Dimethyl-2,4-hexadiene	19	44.2
1,3-Cyclohexadiene	18.7	39.1
Benzoquinone	17.3	23.0
Pyrene	17	27.0
Oxygen‡	36.1	7.9§
Nitromethane	--	37.0

*Generally based on phosphorescence spectra (12); conditions vary.
†Represented by the longest wavelength absorption maxima.
‡The ground state is a triplet.
§From the emission spectrum.

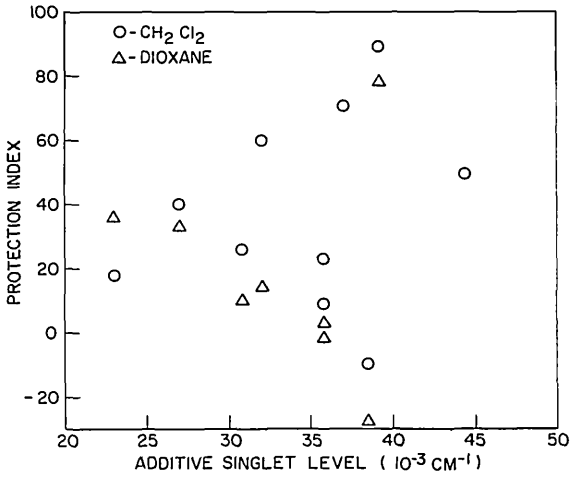


Fig. 2 - Relation between the lowest excited singlet levels of additives and their effect on poly(methyl methacrylate) photolysis in the absence of air

An alternative route for the transfer of electronic energy is available. For every singlet state in which there are no unpaired electrons there is a triplet state in which the members of a pair of electrons have parallel spins. These triplet states are of lower energy and longer life than the corresponding singlet states. As a consequence a molecule in an excited triplet state has an increased probability of returning to the ground state by transfer of its energy on collision with a second molecule. There is also a greater probability that a molecule in a triplet state will undergo dissociation before it can return to the ground state by any of the routes open to it.

It is suggested that the photochemical dissociation process, i.e., photodegradation, observed in poly(methyl methacrylate) involves a triplet intermediate. The degradation process would be analogous to the photochemical reactions involving triplet energy transfer which have been studied by Hammond and coworkers (13). Even though the lowest excited singlet level of the polymer is at a higher energy level than that of any of the additives, the corresponding lowest excited triplet level of the polymer may lie at a point where the triplets of specific additives might be above or below that of the polymer. These energy level relationships are shown in Fig. 3.

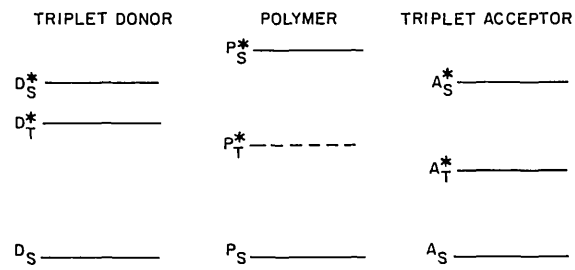


Fig. 3 - Relative electronic energy levels in a polymer and additives

An additive whose excited triplet D_T^* lies above that of the polymer might transfer its energy to the polymer in the process

$$P_S + D_T^* \rightarrow P_T^* + D_S \; ;$$

to the extent that degradation takes place in P_T^*, the process would be effectively accelerated by the presence of the "triplet donor" molecule. Similarly, if a "triplet acceptor" is present, the excited polymer may transfer its energy to such a molecule in the process

$$P_T^* + A_S \rightarrow P_S + A_T^*$$

and degradation from P_T^* would be decreased. Other processes can be envisioned, but these illustrate the general point.

In Fig. 4 the lowest excited triplet energy levels (Table 6) of the additives used in this study have been plotted against the corresponding protection indexes for photodegradation of poly(methyl methacrylate). Protection indexes in methylene chloride were consistently higher than those in dioxane for the same additive, which may be indicative of solvent involvement. Some of the scatter in the data is undoubtedly due to the wide variation in the ratios of polymer to additive as well as to varying efficiencies of transfer.

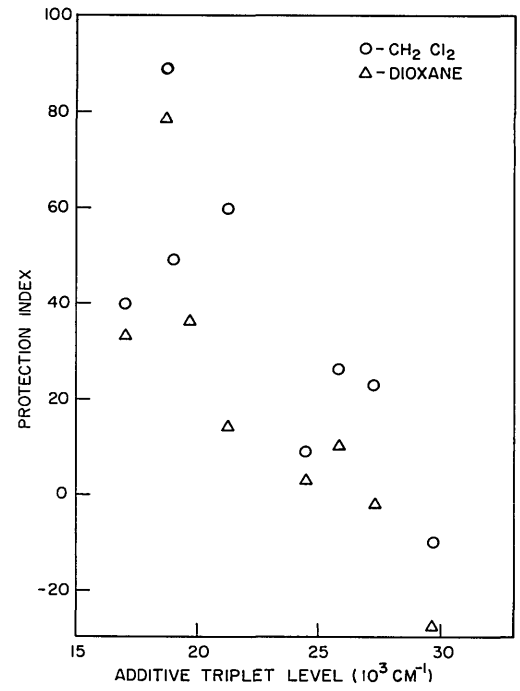


Fig. 4 - Relation between lowest excited triplet levels of additives and their effect on poly(methyl methacrylate) photolysis in the absence of air

It is clear from Fig. 4 that additives having triplet levels below about 23,000 cm would function as inhibitors for the photodegradation of poly(methyl methacrylate). Those in the 23,000 to 27,000 cm^{-1} range appear to have little effect, and those additives having triplet levels above 27,000 cm^{-1} would probably act as sensitizers of photodegradation. This is an empirical observation, and it applies only to poly(methyl methacrylate) under the conditions of these experiments. Inferentially, an excited triplet for poly(methyl methacrylate) might be expected to lie in the 23,000 to 27,000 cm^{-1} region.

Similar plots can be constructed from the more limited data obtained in the presence of air. Such a plot is shown in Fig. 5 (the data for biacetyl have been omitted). It would appear that conclusions may be drawn similar to those for the data in the absence of air, in particular that an exited triplet for poly(methyl methacrylate) in the 23,000 to 27,000 cm^{-1} region is inferred. Oxygen is a well-known quencher for most (but not all) triplets. The effect seen here may be that of two additives - oxygen and a second compound - competing for polymer triplets. In a series of runs oxygen will be present in nearly the same concentration in a given solvent system and will therefore be a constant factor; the effect seen on comparison with a run in air without an additive would then be that of the additive alone. It is possible that oxygen behaves in a manner analogous to the other additives but that the act of energy transfer raises the ground state triplet of oxygen to a low-energy singlet.

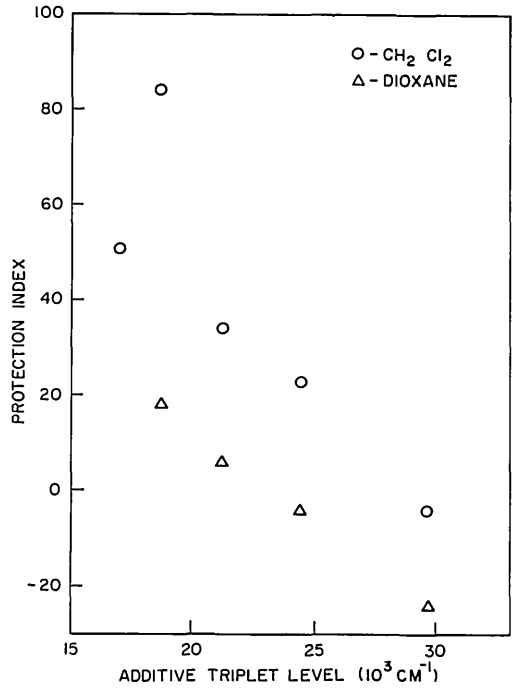


Fig. 5 - Relation between lowest excited triplet levels of additives and their effect on poly(methyl methacrylate) photolysis in the presence of air.

Effect of Nitro Compounds

The nitro group is an example of an arrangement of atoms which should be readily excited to a triplet or diradical state. Phosphorescence has not been observed in nitromethane (14), but the compound does have an $n \rightarrow \pi^*$ transition at 270 nm (37,000 cm^{-1}) and the corresponding triplet may be sufficiently low that it could act as an inhibitor to the photodegradation of poly(methyl methacrylate).

It is evident from the data in Tables 2 and 4 that nitromethane does indeed act as an inhibitor in methylene chloride, although rather high concentrations are required. In the presence of air, nitromethane had little effect. Nitromethane forms a strong charge-transfer complex with dioxane (15), and runs were not made in this solvent.

A number of nitro compounds were run in degassed methylene chloride solutions of poly(methyl methacrylate). The results are shown in Table 5. Most of these compounds show promise as inhibitors, but the photolysis products are apparently more effective than the original materials, since the quantum yields for scission decreased with time of exposure. One of these compounds, 4,4,4-trinitrobutyric acid (TNBA), was selected for future study. The results, compared with runs in the absence of additive (3), are shown in Fig. 6. As with nitromethane, TNBA was ineffective in air, and in the absence of air its effectiveness increased with exposure and with concentration. Pretreatment of the polymer solution with oxygen did not alter the effectiveness of TNBA, so that if peroxides are formed, they do not negate the effect of the nitro compound. A sample of poly(methyl methacrylate) which had been irradiated in the presence of TNBA underwent no change in thermal stability, indicating that recombination of chain ends through the nitro compound diradical is probably not a significant factor in the inhibition process. Nitrogen dioxide, which is an expected photolysis product from nitro compounds, itself acted as an inhibitor of poly(methyl methacrylate) photodegradation in methylene chloride in the absence of air. During photolysis, the nitrogen dioxide was consumed, since the quantum yield for scission tended to increase with total exposure.

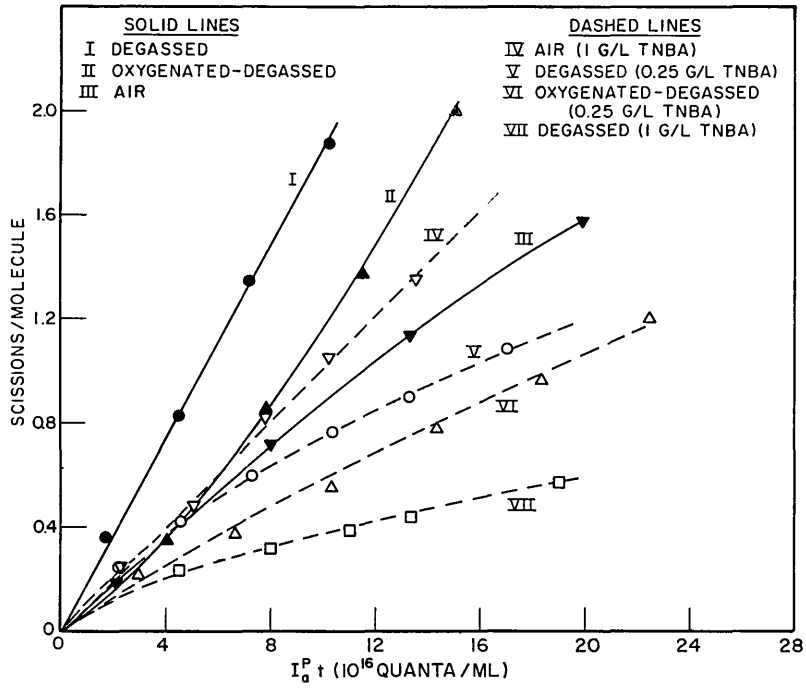
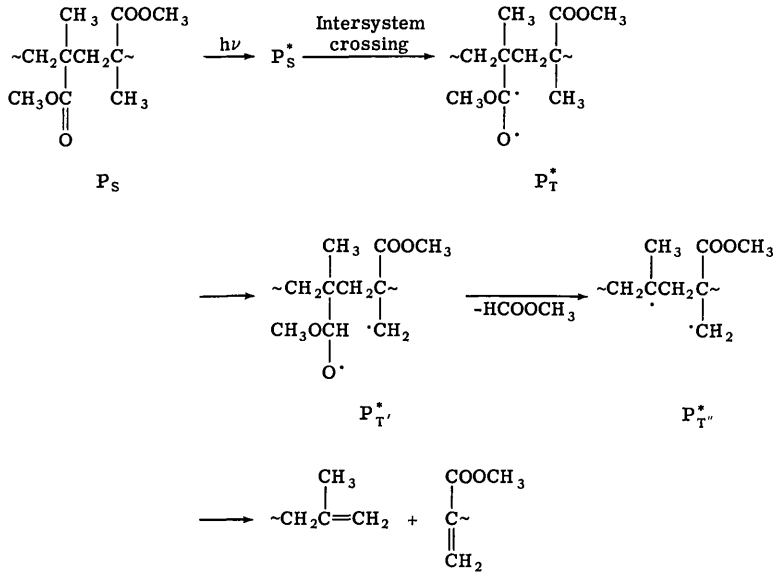


Fig. 6 - Effect of TNBA on the photolysis of poly(methyl methacrylate) in methylene chloride (84Al source)

Mechanism

Photolysis of poly(methyl methacrylate) films yields methyl formate as a major product (4). The actual act of chain scission is therefore probably preceded by the formation of the same diradical which Shultz (16) proposed for the radiolysis of poly(methyl methacrylate). The events leading to this triplet diradical may be



It is evident that anything which changes the rate of formation of $P^*_{T''}$ is going to change the rate of scission of the polymer. Energy transfer, as indicated in the earlier discussion, can involve either P^*_S or P^*_T, but reaction with either $P^*_{T'}$ or $P^*_{T''}$ would result in consumption of the additive.

CONCLUSIONS

It has been shown that not only solvents but other molecules in low concentration, can grossly affect the course of photodegradation of poly(methyl methacrylate) in solution. On an empirical basis the rates of photolysis of the polymer in dioxane and in methylene chloride in the presence of a wide variety of chemical additives can be related to the lowest excited triplet energy levels of the additives. Conversion of the quantum yields for scission to a protection index reveals that additives having triplet levels below 23,000 cm^{-1} behave as degradation inhibitors, whereas those with triplets above 27,000 cm^{-1} sensitize photodegradation. A triplet for the polymer between 23,000 and 27,000 cm^{-1} is inferred. Oxygen also behaves as an inhibitor, but the type of energy transfer involved is different from that of the other substances investigated. Nitro compounds have been shown to constitute a new class of photodegradation inhibitors for poly(methyl methacrylate).

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PHOTODEGRADATION OF HIGH POLYMERS IN SOLUTION, PART 4 — THE EFFECT OF ADDITIVES ON THE PHOTOLYSIS OF POLY(METHYL METHACRYLATE

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13. ABSTRACT

Poly(methyl methacrylate) has been photolyzed by 2537A radiation at room temperatures in methylene chloride and in dioxane. The quantum yields for random scission in the absence of air in dioxane were 0.168 scission/quantum absorbed at an intensity absorbed by the polymer of 0.30×10^{16} quanta/ml-min; in methylene chloride the corresponding data are 0.149 and 0.27×10^{16}. The quantum yields in the presence of air are about half these yields. A wide variety of chemical additives in the polymer solutions were sensitizers or inhibitors of degradation. The strongest inhibitors were those additives whose lowest excited triplet levels were below about 23,000 cm^{-1}, and the sensitizers were those additives whose lowest excited triplet levels were above 27,000 cm^{-1}. By postulating electronic energy transfer via the lowest excited triplet levels as the mechanism for inhibition or sensitization a triplet is inferred for the polymer between 23,000 and 27,000 cm^{-1} As further evidence of this postulate a number of nitro compounds which would be expected to form triplets were found to show promise as inhibitors to the poly(methyl methacrylate) photolysis.

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Security Classification

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Polymer degradation						
Spectra (ultraviolet)						
Excited states						
Energy transfer						
Triplet levels						
Quantum yields						
Singlet levels						
Inhibitors						
Stabilizers						
Sensitizers						