

Photodegradation of Poly(methyl Methacrylate) in Solution and the Effect of Added Solutes

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Synopsis

Poly(methyl methacrylate) has been photolyzed with 2537 Å. radiation in dioxane and in methylene chloride at about 25°C. in the presence and absence of air. In degassed solutions, quantum yields for random scission are only slightly affected by either intensity or polymer concentration. Oxygen is an apparent inhibitor for photodegradation. The inhibiting and sensitizing effects of a variety of added solutes, including aromatic hydrocarbons, aliphatic dienes, and ketones were investigated; the behavior is similar whether or not oxygen is present. The results are best explained on the basis of an electronic energy transfer mechanism involving the lowest excited triplet levels of the polymer and the added solutes.

INTRODUCTION

A number of polymers have been photodegraded in solution, and the dependence of the rate of degradation on the nature of the solvent is well established. It is reasonable to expect that substances other than the solvent in a polymer solution would also influence the course of polymer photolysis. Where main-chain scission is the only photolytic reaction for a polymer in a photochemically inert solvent, a way is opened to the study of the effect and mechanism of the interaction between added solutes and a polymer subjected to ultraviolet radiation.

Poly(methyl methacrylate) has shown no tendency to crosslink in films in the absence of sensitizers¹ and no mention has been made of crosslinking in any reported solution work;²⁻⁷ post-effects appear to be absent. Although poly(methyl methacrylate) is a poor absorber of ultraviolet radiation at wavelengths above 2500 Å., it does undergo chain scission at a sufficiently high rate that its degradation is readily studied with the 2537 Å. radiation from low-pressure mercury lamps. This polymer was therefore chosen as the subject for an empirical study of the influence of solvents and low-concentration solutes on polymer photodegradation.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) was prepared by bulk polymerization of freshly distilled monomer under nitrogen at 50°C. with azobisisobutyro-

nitrile as the initiator; conversions were about 10%. After being twice precipitated from tetrahydrofuran solution with methanol, the polymer was dried several days in vacuum at room temperature. The number-average molecular weight of this material was 5.56×10^5 , based on its intrinsic viscosity in benzene. Dioxane and tetrahydrofuran were distilled from lithium aluminum hydride. Methylene chloride was a spectroscopic grade sample, 1 cm. of which had negligible absorbance at 2537 Å., and which showed no initial inhibition of poly(methyl methacrylate) photodegradation in the absence of air. Other solvents and solutes were spectroscopic grade or were appropriately purified.

Procedure

The general procedure and apparatus have been described.⁸ A Hanovia 88A45 low-pressure mercury lamp with a Vycor jacket was used as the radiation source. For the systems and cells reported here, 2537 Å. is the major photolytically active wavelength of radiation from this source. Ferrioxalate actinometry⁹ corrected for wavelengths above 3000 Å. and monitoring with a photocell were used to determine the energy incident to the cell. Intensities were varied by the use of screens.

Systems to be irradiated were prepared by adding solvents or solutions to the polymer sample in the quartz irradiation cell. Polymer concentrations were within 10% of 5 g./l. except where noted; solution volumes of 20 ml. were used. Mixtures run in the absence of air were degassed through three freeze-thaw cycles to a final pressure over the solid of 10^{-3} torr; no mercury was present in the vacuum system. All exposures were made at laboratory temperatures, approximately 25°C. At the beginning of a run and after each exposure, as appropriate, ultraviolet spectra and relative viscosities at 30°C. were determined.

Evaluation of Quantum Yields

It was assumed that random chain scission was the major photochemical reaction in the solutions studied; this has been shown to be the case with films¹ and with 2-chloroethanol solutions.⁷ The quantum yield for random scission Φ_s^P , based on the energy absorbed by the polymer only $I_a^P t$, where I_a^P is the intensity absorbed by the polymer only and t is exposure time, can then be calculated from

$$\Phi_s^P = (cN/\bar{M}_n) [([\eta_0]/[\eta])^{1/\alpha} - 1] / I_a^P t$$

where c is the concentration of polymer, N is Avogadro's number, $[\eta_0]$ and $[\eta]$ are the intrinsic viscosities of the solutions before and after degradation, and α is the exponent in the Mark-Houwink equation, $[\eta] = K\bar{M}_n^\alpha$. Intrinsic viscosities were calculated from the single-point relative viscosities by the equation¹⁰ $[\eta] = \sqrt{2}/c(\eta_{sp} - \ln \eta_r)^{1/2}$. Exponents α were estimated by the method of Meyerhoff;¹¹ for poly(methyl methacrylate) in dioxane and in methylene chloride, α was found to be 0.76 and 0.79, respectively.

Total exposures were usually sufficient to produce an average of more than one scission per polymer molecule. In most cases, plots of the number of scissions, $([\eta_0]/[\eta])^{1/\alpha} - 1$, against the energy absorbed, $I_a^P t$, were linear; in the few instances where the slopes decreased with time, they are so noted. In absolute terms, the largest error in these calculations arises from the measurement of small absorbances, particularly where the absorbance of the polymer is a small fraction of the total absorbance or where the total absorbance is changing rapidly. At 2537 Å., the extinction coefficient for our sample of poly(methyl methacrylate) was 0.0090 l./cm.-g. in either methylene chloride or dioxane.

To assess the effect of added solutes on the degradation rate, a "protection index"¹² (P.I. = $100(\Phi_s^P(0) - \Phi_s^P)/\Phi_s^P(0)$, where $\Phi_s^P(0)$ is the quantum yield in pure solvent) is used. This index, which is based on quantum yield at one scission, tends to stress small effects. In order to maintain initial intensities absorbed by the polymer within the same order of magnitude, widely varying ratios of polymer to additive were necessary. Comparisons among the additives should be made with this in mind.

RESULTS AND DISCUSSION

Photolysis in Pure Solvents

For this work, solvents as nearly photochemically inert as possible were desired. Jellinek and Wang⁷ observed a strong interaction between poly(methyl methacrylate) and 2-chloroethanol, and chloroform^{2,4} appears to interact with the polymer. Both dioxane^{2,4} and benzene^{2-6,13} have been used without detailed study in poly(methyl methacrylate) photolyses.

TABLE I
Photodegradation of Poly(methyl Methacrylate) in Pure Solvents

Solvent	Atmosphere	$I_a^P \times 10^{-16}$, quanta/ ml.-min.	$\Phi_s(0)$, scission/quantum absorbed
Dioxane	Solvent	0.070	0.188
Dioxane	Solvent	0.30	0.168
Dioxane	Solvent	1.16	0.145
Dioxane	Air	0.71	0.067
Methylene chloride	Solvent	0.27	0.149
Methylene chloride	Solvent	1.03	0.133
Methylene chloride	Air	1.03	0.071

Benzene, however, is a very strong absorber of 2537 Å. radiation; the intensity absorbed by the polymer in a 5 g./l. benzene solution is about 10^{-4} of the I_a^P in a transparent solvent. Qualitatively, we found the Φ_s^P in benzene to be about ten times that in a solvent such as methylene chloride. The requirements of polymer solubility, solvent transparency, and solvent stability eventually narrowed the choices to methylene chloride and dioxane

(tetrahydrofuran, pyran, and similar solvents would undoubtedly serve as well).

In Table I are given the Φ_s^P found in dioxane and methylene chloride in the presence and absence of air; a second poly(methyl methacrylate) sample ($\bar{M}_n = 7.76 \times 10^5$) gave the same results. Changes in the ultraviolet absorption spectrum were negligible, and scission versus dose plots were linear out to 3 scissions. The effect of intensity in degassed solutions is indicated in Table I. In the range given, a tenfold increase in I_a^P caused about a 10% decrease in Φ_s^P . In the presence of air, the effect of intensity variation is even less; a fourfold intensity change in an aerated dioxane produced no change in Φ_s^P within experimental error. The intensity exponent is therefore fairly close to unity, as it was in the film.¹ Over the range of 2.5–10 g./l., polymer concentration changes gave Φ_s^P which corresponded only to the changes in I_a^P .

Polymer-solvent reaction during photolysis of poly(methyl methacrylate) thus appears to be fairly small in methylene chloride and in dioxane. These solvents were therefore used for studies involving additional solutes. It should be recognized, however, that the effect of the solvent may change in the presence of other substances and that further observations are necessarily empirical.

Photolysis in the Presence of Added Solutes

The protection index affords a measure of the influence of an added solute on the rate of degradation over and above its effect as an optical filter. The latter effect reduces the intensity of radiation absorbed by the polymer; an absorbing additive is therefore a degradation inhibitor on a time basis. Additives having negative protection indexes are, in fact, accelerators of degradation, whereas those with the more positive protection indexes are, on this basis, the most effective degradation inhibitors.

Table II shows the protection indexes for a number of substances in the photodegradation of poly(methyl methacrylate) in dioxane and methylene chloride. These indexes are based on $\Phi_s^P(0)$ at the same I_a^P as that for the solution containing the additive; the indexes for aerated solutions are based on $\Phi_s^P(0)$ for solutions in air. Polymer concentrations were maintained at 5 g./l. (0.05 base molar). The wide variation in mole ratios of monomer units to additive ($[M]/[A]$) was necessitated by the need to hold I_a^P within the same order of magnitude for most solutions.

Correlations among these protection indexes are necessarily rough, not only because of concentration variations, but because of secondary effects due to the photolysis products of the additives themselves. Deviations of the scissions versus $I_a^P t$ plots from linearity were taken as evidence of such secondary effects; in most cases, the result was a further reduction of Φ_s^P as $I_a^P t$ increased. Photolysis of the dienes in degassed solutions was readily observed in the rapidly changing ultraviolet absorption spectrum. Relatively slow spectral changes were also observed in methylene chloride solutions containing the aromatic hydrocarbons. Post-effects on the

TABLE II
Photodegradation of Poly(methyl Methacrylate) in Solution
in the Presence of Added Solutes

Solute	[M]/[A] ^a	E_T^b , cm. ⁻¹ × 10 ⁻³	Protection index			
			Degassed		Aerated	
			Dioxane	Methylene chloride	Dioxane	Methylene chloride
Benzene	12	29.7	-28	-10	-24	-4 ^c
Benzoic acid	76	27.2	-2	23 ^d		
Acetophenone	120	25.8	10	26		
Acetone	1.8	24.5	3	9	-4	23
Naphthalene	128	21.3	14	60	6	34
Biacetyl	2.0	19.7	36		°	°
2,5-Dimethyl-2,4- hexadiene	110	19		49 ^f		
1,3-Cyclo- hexadiene	80	18.7	78 ^f	89 ^f	18	84
Pyrene	202	17	33 ^{f,g}	40		51

^a Mole ratio of monomer units to added solute; [M] = 0.05 base molar.

^b Lowest excited triplet energy, generally based on phosphorescence spectra.

^c -235 at [M]/[A] = 0.11.

^d At [M]/[A] = 122.

^e Undergoes dark reaction.

^f At 1 scission; Φ_s^P decreases with dose.

^g At [M]/[A] = 93.

scission rate were evident in solutions containing biacetyl, particularly in air. In spite of these shortcomings, the very fact of great variation in the protection indexes indicates that these substances are behaving as more than optical filters in the photodegradation of poly(methyl methacrylate) in these solutions.

A general explanation of these results on the basis of free radical scavenging is unsuccessful. Aromatic hydrocarbons run the gamut of effectiveness, while ketones, present in higher concentration and more prone to photolysis than the hydrocarbons, are relatively ineffective. Oxygen itself was an inhibitor (see Table I). Peroxides, if formed, behave as photolyzable inhibitors. A sample of polymer which had been recovered after oxygenation in methylene chloride was irradiated in a degassed methylene chloride solution in the usual way; the slope of the scissions versus dose plot initially was similar to that of an aerated solution, but after a short period the slope increased to that for a degassed solution.

Without specification of states, electronic energy transfer has been proposed to explain the behavior of certain substances in the photolysis¹⁴ and radiolysis^{12,15,16} of poly(methyl methacrylate) films. The rates of a number of sensitized photochemical reactions in solution have been related to the relative lowest excited energy levels in the sensitizers and the molecule undergoing dissociation. From an energetic standpoint, singlet-singlet

transfer is possible from poly(methacrylate) to any of the additives used here. Although no correlation was found between the protection indexes and the lowest excited singlet levels of the additives, such a process may be operating in specific instances.

Arrangement of the added solutes in order of their lowest excited triplet levels, as was done in Table II, does indeed reveal a general correlation between the protection indexes and the triplet levels. It would appear that additives having lowest excited triplet levels above about 27 kK. would act as sensitizers and those below about 23 kK. would behave as inhibitors in poly(methyl methacrylate) photolysis. A general similarity of behavior of the additives can be observed in both degassed and aerated solutions, which suggests that the process by which oxygen (a triplet in the ground state) inhibits degradation of the polymer operates independently and in competition with other transfer processes.

These empirical results lend support to the diradical intermediate proposed by Shultz¹⁷ for the radiolysis of poly(methyl methacrylate) if such a diradical can be preceded by a triplet involving the ester carbonyl group. The results also suggest that a knowledge of the spectroscopic states of all of the constituents in a polymer system should contribute greatly to predicting its behavior under photodegrading conditions.

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Résumé

Du polyméthacrylate de méthyle a été photolysé pour une radiation de 2537 Å. dans le dioxane et le chlorure de méthylène à environ 25°C. en présence et en absence d'air. Dans les solutions dégazées, les rendements quantiques pour la rupture statistique ne sont que faiblement affectés par l'intensité et par la concentration en polymères. L'oxygène est un inhibiteur manifeste pour la photodégradation. Les effets inhibiteurs et sensibilisateurs causés par une série de produits dissous, y compris des hydrocarbures aromatiques, des diènes aliphatiques et des cétones ont été étudiés; le comportement est

semblable, que l'oxygène soit présent ou non. Les résultats s'expliquent le mieux sur la base d'un mécanisme de transfert d'énergie électronique faisant intervenir les niveaux triplets excités les plus bas du polymère et des solutés ajoutés.

Zusammenfassung

Polymethylmethacrylat wurde mit einer Strahlung von 2537 Å in Dioxan und Methylenchlorid bei etwa 25°C. in Gegenwart und Abwesenheit von Luft photolysiert. In entgasten Lösungen wird die Quantenausbeute für die statistische Spaltung durch Intensität oder Polymerkonzentration nur schwach beeinflusst. Sauerstoff ist für den photochemischen Abbau offenbar ein Inhibitor. Die inhibierende und sensibilisierende Wirkung einer Reihe von Lösungszusätzen, wie aromatischen Kohlenwasserstoffen, aliphatischen Dienen und Ketonen, wurde untersucht; das Verhalten ist bei Fehlen und Vorhandensein von Sauerstoff ähnlich. Die Ergebnisse können am besten auf Grundlage eines Elektronenenergie-Übertragungsmechanismus unter Beteiligung der niedrigsten angeregten Tripletniveaus des Polymeren und der zugesetzten Stoffe verstanden werden.

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