

Photodegradation of High Polymers in Solution

Part 3 - Poly(methyl methacrylate)

R. B. FOX AND T. R. PRICE

*Organic and Biological Chemistry Branch
Chemistry Division*

September 7, 1966



NAVAL RESEARCH LABORATORY
Washington, D.C.

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

CONTENTS

| | |
|--|----|
| Abstract | ii |
| Problem Status | ii |
| Authorization | ii |
| INTRODUCTION | 1 |
| EXPERIMENTAL PART | 2 |
| Materials | 2 |
| Apparatus | 2 |
| Procedure | 3 |
| Evaluation of Quantum Yields for Random Scission | 3 |
| RESULTS | 5 |
| Variability With Polymer Sample | 5 |
| Dependence on the Solvent | 5 |
| Intensity Effects | 7 |
| Dependence on Polymer Concentration | 7 |
| Effects of Air and Peroxides | 8 |
| Effect of Mixed Solvents | 10 |
| DISCUSSION | 10 |
| ACKNOWLEDGMENT | 13 |
| REFERENCES | 15 |

ABSTRACT

The photodegradation of poly(methyl methacrylate) in solution in the presence and absence of air under 2537A irradiation at about 25°C has been investigated, primarily by means of viscosity measurements. Random scission is confirmed as the major chain-breaking process. Quantum yields for scission in degassed solutions are solvent dependent; for methylene chloride, dioxane, and ethyl acetate, the quantum yields are 0.15, 0.17, and 0.38, respectively. In methylene chloride the quantum yield is nearly independent of polymer concentration and decreases slightly with increasing absorbed radiation intensity. Small amounts of benzene tend to increase the quantum yields, but carbon tetrachloride has relatively small effect and does not sensitize the degradation. In any of the solvents in the presence of air the quantum yields are approximately half of those found in the absence of air. Adventitious peroxides appear not to play a role in the degradation, but an oxygenated sample which probably contains peroxides acts initially as a sample would in air. The results can be interpreted in terms of possible electronic energy transfer processes.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C04-04
Project RR 001-02-43-4801

Manuscript submitted April 26, 1966.

PHOTODEGRADATION OF HIGH POLYMERS IN SOLUTION

PART 3 - POLY(METHYL METHACRYLATE)

INTRODUCTION

In almost every use of organic polymers, stabilization against degrading environmental influences is an important consideration. Where polymeric materials are used in exposed outdoor locations, as in protective coatings, for example, the deleterious effect of light, air, and water, chiefly, must be minimized. Extraterrestrial applications might require stabilization of a plastic to solar radiation in a very high vacuum. Engineering requirements almost invariably make it necessary to use commercially available materials of often unknown purity. These materials are usually mixed with additives which change the physical properties in some useful way; plasticizers, cure accelerators, and stabilizers themselves are examples of such additives. Therefore, it is not a pure polymer but a complex polymer system which must meet the practical stability requirements.

Usually, the problem of stabilizing a polymer system against the effects of light has been met by adding an organic compound which absorbs the offending radiation and converts it to heat without degrading the polymer. Hopefully, such compounds will not adversely affect the physical properties of the system and will only act as optical filters. The compounds themselves are ordinarily selected on an empirical basis.

One purpose of the work for which this report is a part is to put this selection of a radiation-absorbing additive on rational grounds in terms of both the polymer and the other constituents of the system. Such a rationalization requires a knowledge of the interactions occurring among the parts of the system under the degrading influences; in this instance, the influences of interest are those of ultraviolet light and air. Much work has been done on polymer films, both at this Laboratory and elsewhere. Such work suffers, however, because composition, especially where volatile compounds are involved, is difficult to control. It has been necessary to turn to the study of polymer solutions as a means of controlling composition, even though those effects which are due to bulk polymer properties cannot then be assessed. The first problem which arises is to what extent any solvent would affect the degradation of a given polymer. Once this has been established, some insight into the mechanisms of such degradation may be gained; if a solvent proves to be fairly inert, additional constituents can be added and their effects assessed.

An examination of the influence of solvents on the photodegradation of poly(α -methylstyrene) (1) and polystyrene (2) has already been reported. These are polymers which are very strong absorbers of 2537A light, which was the radiation used in this and earlier work. In both cases considerable interaction with the solvents was indicated by the marked dependence of the apparent quantum yields for random scission on the nature of the solvent. If solvents under these conditions can affect polymer photodegradation, it is apparent that under practical conditions similar materials may also exercise a controlling influence on polymer degradation.

It is of considerable interest to extend this work to a polymer which is not a good absorber of 2537A radiation, for then may be studied the specific effect of the nonpolymer constituent, which may absorb much of the radiation. Poly(methyl methacrylate) is such a polymer and is the subject of the present report. This polymer has been studied

extensively in film form (3). Under 2537A irradiation, it undergoes rapid scission and is generally free from crosslinking. As a prototype polymer structure whose properties are well known, and as a useful film-forming material, poly(methyl methacrylate) is well suited to this type of investigation.

As evidence of the suitability of poly(methyl methacrylate), much of the polymer solution degradation research undertaken by other investigators has concerned this polymer. The only detailed study of poly(methyl methacrylate) in solution has been Jellinek and Wang (4), who irradiated solutions in 2-chloroethanol under nitrogen; the work was internally consistent but quantum yields were not reported and quantitative comparisons with work by others cannot therefore be made. The photodegradation was carried out at 25 to 150°C under 2537A irradiation. Random scission was observed, with a small contribution from chain-end initiation at the higher temperatures; depolymerization to monomer also occurred with an energy of activation of about 9 kcal/mole and an intensity exponent of 0.66, which indicates a second-order termination reaction. Of particular interest is that termination was diffusion-controlled in both dilute solution and in the bulk. The rate of scission was nearly independent of temperature but was markedly dependent on the polymer concentration, which implies considerable solvent participation. Mönig and Kriegel (5-8) followed the changes in specific viscosity of poly(methyl methacrylate) solutions in the presence of oxygen and nitrogen at 20°C under irradiation by light having wavelengths below 2950Å. The solvents used were benzene, chloroform, and dioxane, and rates of degradation increased in that order, although no account was taken of the radiation absorbed by the solvent. Degradation was accelerated by oxygen in benzene but inhibited by oxygen in dioxane. Finally, Charlesby and Thomas (9) briefly investigated the photodegradation of poly(methyl methacrylate) in benzene with the radiation from a medium-pressure mercury lamp. The atmosphere was not stated, but the rate of degradation was independent of concentration over a 20-fold range, and it was concluded that benzene was without influence on the photodegradation of this polymer.

EXPERIMENTAL PART

Materials

Two samples of poly(methyl methacrylate) were used in this work; the material designated sample I had an initial number-average molecular weight (\bar{M}_{n_0}) of 7.76×10^5 , while that designated sample II had an \bar{M}_{n_0} of 5.56×10^5 , based on intrinsic viscosities in benzene. Both samples were prepared by bulk polymerization of freshly distilled monomer under nitrogen at 50°C with azodiisobutyronitrile as the initiator; conversions were about 10%. After being twice precipitated from tetrahydrofuran solution with methanol, the polymers were dried several days in vacuum at room temperature. Dioxane and tetrahydrofuran were distilled from lithium aluminum hydride. The methylene chloride was a spectroscopic grade sample selected on the basis of (a) negligible absorbance of 1 cm at 2537Å and (b) lack of any initial inhibition of poly(methyl methacrylate) photodegradation in the absence of air; the identification or means of removal of the consumable inhibitor which was contained in a few methylene chloride samples was not undertaken. Other solvents were spectroscopic grade or highly purified materials.

Apparatus

Irradiations were carried out in a cell similar to that described in an earlier report (1). This apparatus consisted of a 30-ml quartz cell containing a glass-enclosed magnetic stirring bar, surmounted by a filter and capillary viscometer and a quartz cuvette for spectroscopic measurements.

Three low-pressure mercury sources were used: a Hanovia 88A45 lamp with a Vycor jacket and Hanovia 84A1 and 93A1 quartz lamps. Ferrioxalate actinometry (10), corrected

for wavelengths above 3000A, and monitoring with a photocell were used to determine the energy I_0 incident to the cell. Intensities were varied by the use of screens.

Intrinsic viscosities, other than those run in the irradiation apparatus itself, were determined by conventional procedures in Ubbelohde-type dilution viscometers having running times for benzene of about 170 sec at 30°C, the temperature at which all viscometric measurements were made.

Procedure

Most solutions were prepared in situ after weighing the polymer sample directly into the irradiation cell. Experimental runs conducted with solutions in the absence of air were made by degassing the solutions through three freeze-thaw cycles to a final pressure over the solid of about 10^{-3} torr; no mercury was present in the vacuum system. Unless otherwise noted, polymer concentrations were within 10% of 0.5 g/dl (0.05 base molar). Exposures were made at room temperature, approximately 25°C. At the beginning of a run and after each exposure, ultraviolet spectra were run, as appropriate, and relative viscosities determined.

Evaluation of Quantum Yields for Random Scission

Previous film (3) and solution (4) studies have indicated that in the vicinity of 25°C the major photolysis reaction involving the main chain of poly(methyl methacrylate) is random scission. Crosslinking with this polymer has only been observed with solid films in the presence of air and certain sensitizers (11,12). The quantum yield for random scission is therefore simply the number of scissions produced per photon absorbed. This quantum yield may be based on the energy absorbed by any or all parts of the system.

For a stirred solution, in which it is assumed that all constituents are exposed to the same incident radiation intensity I_0 , the intensity absorbed by the solution will be $(1 - T^{\text{sol'n}}) I_0$, where $T^{\text{sol'n}}$ is the fraction of the incident radiation absorbed. In a solution whose constituents have absorbances $A_1, A_2, \dots, A_i, \dots$, where A_i could refer to a combination of constituents as well as a single constituent, the fraction of the total absorbed intensity which is absorbed by any given constituent (or combination of constituents) is $A_i / \sum_i A_i$. The intensity absorbed by the i th constituent(s) is therefore

$$I_a^i = \frac{A_i}{\sum_i A_i} (1 - T^{\text{sol'n}}) I_0.$$

Thus, the intensity absorbed by the polymer alone I_a^p can be determined from a knowledge of the absorbances of the polymer A_p , the absorbance of the entire solution $A_{\text{sol'n}}$ (usually measured in the 1-cm cuvette), the transmittance of the solution in the irradiation cell, and the intensity of incident radiation determined by actinometry.

The number of scissions which have taken place per polymer molecule can be determined viscometrically if a "most probable" molecular weight distribution is assumed before and after irradiation. This number is given by $([\eta_0]/[\eta])^{1/\alpha - 1}$, where the bracketed symbols are the intrinsic viscosities of the polymer before and after degradation, respectively, and α is the exponent in $[\eta] = K\bar{M}_w^\alpha$. This exponent was estimated for each solution by the method of Meyerhoff (13). For poly(methyl methacrylate) in dioxane and in methylene chloride, α was found to be 0.76 and 0.79, respectively. The intrinsic viscosities determined in the irradiation cell were evaluated by means of the equation of Solomon and Ciută (14):

$$[\eta] = (\sqrt{2}/c) \sqrt{\eta_{sp} - \ln \eta_{rel}},$$

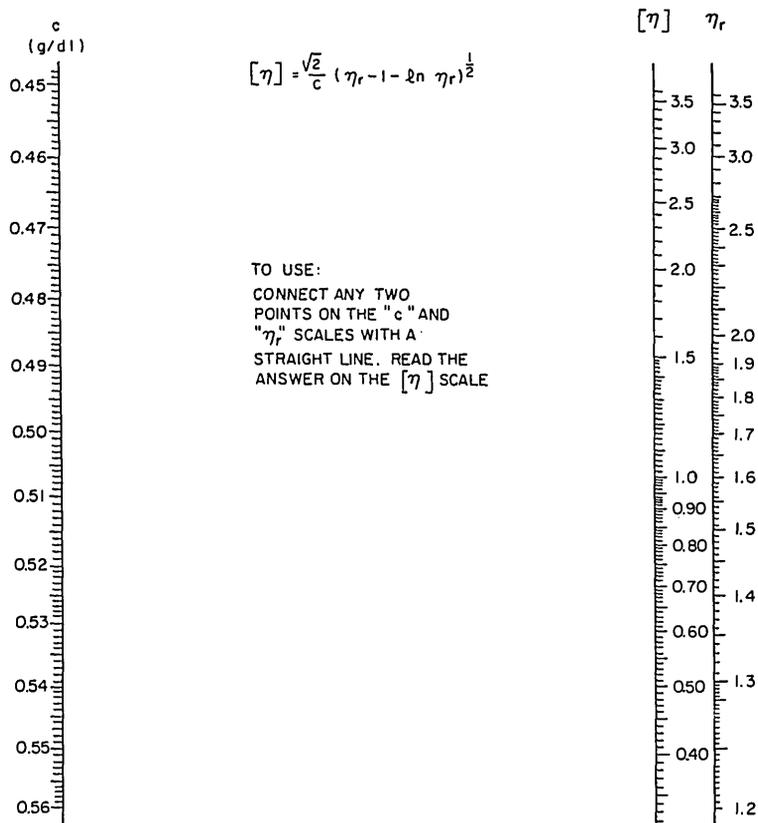


Fig. 1 - Nomograph for $[\eta] = (\sqrt{2}/c) \sqrt{\eta_{sp} - \ln \eta_r}$

where c is the concentration of the polymer solution. A convenient nomograph based on this equation is reproduced in Fig. 1.

In terms of these parameters, the quantum yield for random scission Φ_s^i is given by

$$\Phi_s^i = \left(cN/\bar{M}_{n_0} \right) \left[([\eta_0]/[\eta])^{1/\alpha} - 1 \right] / I_a^i t,$$

where N is Avogadro's number, \bar{M}_{n_0} is the initial number-average molecular weight of the polymer, and t is the time of exposure. These quantum yields are readily evaluated from plots of the number of scissions per polymer molecule against the number of quanta absorbed per unit volume. Such plots will be linear if random scission obtains throughout a run.

The greatest error in the present work is associated with the measurement of small absorbances, particularly in those instances when A_{soln} changes during exposure. At 2537A the extinction coefficient for poly(methyl methacrylate) was found to be 0.090 dl/cm-g in either methylene chloride or in dioxane.

RESULTS

Changes in the ultraviolet spectrum of poly(methyl methacrylate) during ultraviolet irradiation, unlike those in polystyrene and poly(α -methylstyrene), take place very slowly whether the sample is a solid film or is in solution. In most of the solution work reported here, any increases in the absorbance of the solutions were only very slight during prolonged irradiations, and these were of the same order as the increases found for the solvents alone. These increases were general throughout the 250 to 300 $m\mu$ region, and with one exception no hint of a band was seen. The exception was that of degassed solutions containing a small amount of benzene; here, a very broad band appeared to center at about 280 $m\mu$. This band may be due to a photolytic product from benzene itself, but its exact nature was not ascertained. It should be noted that in 2-chloroethanol (4), a solvent in which interaction with poly(methyl methacrylate) was definitely established, the only absorbance increase reported occurred in higher temperature runs at 224 $m\mu$, and this was attributed to the formation of monomer. At the concentrations employed in our work, the solutions were opaque in this region of the spectrum.

Changes in the intrinsic viscosity of solutions of poly(methyl methacrylate) subjected to ultraviolet irradiation provide the clearest and most readily obtained evidence of chain-breaking in the polymer. These changes, in terms of quantum yields for random scission based on energy absorbed by the polymer Φ_s^p , were assessed as a function of the polymer sample, the solvent, the atmosphere above the solution, the polymer concentration, the radiation source, and the intensity of the radiation. It would be expected that under the conditions used in this work the rates of degradation would be sensibly independent of temperature; such was the case with 2-chloroethanol solutions (4).

As indicated in the experimental portion of this report, quantum yields were evaluated from the number of scissions produced by a measured number of quanta absorbed by the polymer. In the case of a random scission process, plots of these two functions against each other should be linear. Typical plots, which cover the gamut of data, are shown in Fig. 2. Generally, these plots were linear out to about one scission per polymer molecule in runs made in the absence of air. As seen in the figure, however, some downward curvature can appear in data from runs made in the presence of air. At the greatest degree of curvature, the slopes represent a change in quantum yield from, for example, about 0.100 initially to about 0.070 at one scission per polymer molecule. While no analysis of errors has been made, the quantum yields appear generally to be reproducible within $\pm 5\%$, with the greatest error involved in the measurement of small absorbances and in the actinometry.

Variability With Polymer Sample

In degassed methylene chloride solutions under the 84A1 source, samples I and II gave the same Φ_s^p within experimental error. These values, 0.095 and 0.097, respectively, were derived from two of the runs shown in Fig. 2. While the range of initial molecular weights encompassed, 5.56×10^5 to 7.76×10^5 , is not large, the similarity of the quantum yields for the two samples and the linearity of the plots are indicative of a random scission process.

Dependence on the Solvent

Not unexpectedly the rate of photodegradation of poly(methyl methacrylate) in solution exhibits a marked dependence on the solvent. Here, single pure solvents are considered; the results are shown in Table 1.

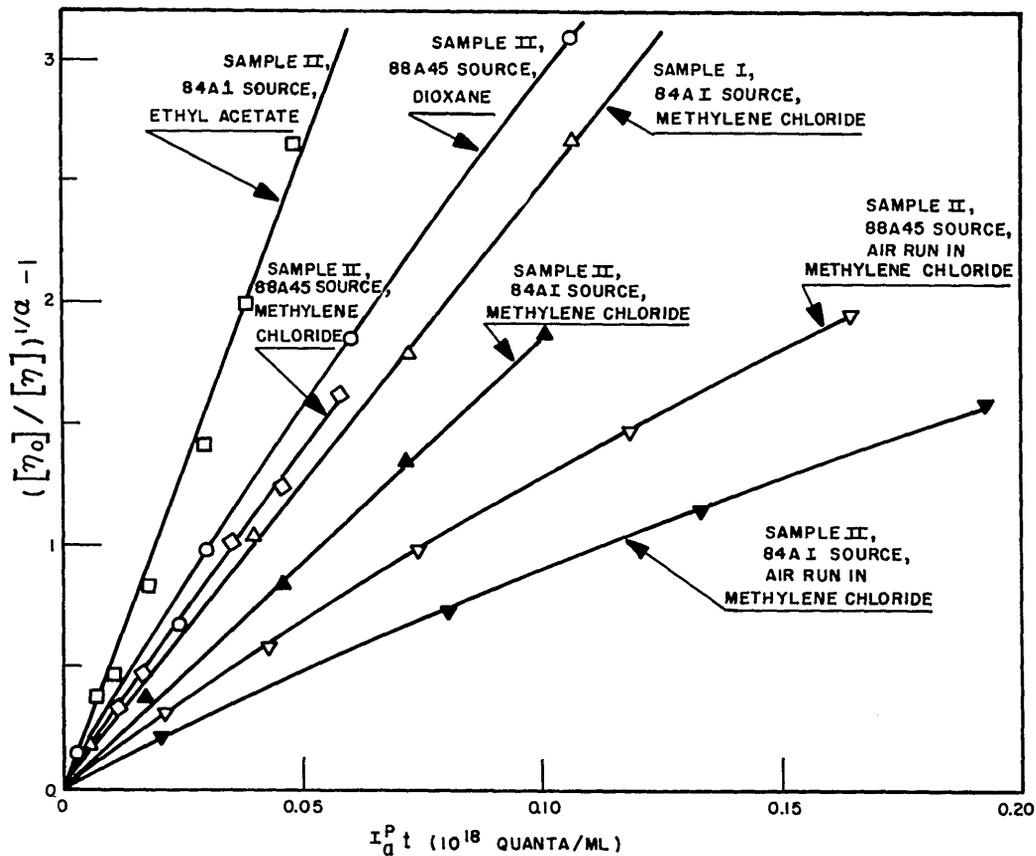


Fig. 2 - Typical experimental data on the photodegradation of poly(methyl methacrylate)

Table 1
Photodegradation of Poly(methyl Methacrylate) in Single Solvents

| Sample | Source | Solvent | Atmosphere | I_a^p (10^{16} quanta/ ml-min) | Φ_s^p (scissions/ quantum absorbed) |
|--------|--------|--------------------|------------|---|--|
| I | 84A1 | Methylene chloride | Solvent | 0.34 | 0.095 |
| I | 84A1 | Benzene | Solvent | 0.000034 | 3.100 |
| II | 88A45 | Methylene chloride | Solvent | 0.27 | 0.149 |
| II | 88A45 | Dioxane | Solvent | 0.30 | 0.168 |
| II | 88A45 | Ethyl acetate | Solvent | 0.038 | 0.380 |
| II | 88A45 | Methylene chloride | Air | 1.03 | 0.071 |
| II | 88A45 | Dioxane | Air | 0.71 | 0.066 |

In the benzene solution the calculated proportion of the incident radiation absorbed by the polymer was extremely small (2.2×10^{-5}), and at these very low intensities the resulting Φ_s^p may be disproportionately high. Comparisons between neat benzene solutions and the less absorbing solutions therefore may not be valid. In addition, long exposures were required to obtain significant amounts of degradation; side effects from photolysis of the solvent or even of trace impurities may then become important.

The remaining solvents, methylene chloride, dioxane, and ethyl acetate, are relatively transparent to 2537A radiation. Polymer sample II in either of the first two solvents had an absorption coefficient of 0.090 dl/g-cm or a base molar extinction coefficient of 0.9 l/base mole-cm; the two solvents, degassed, have absorbances of about 0.04 or less at this wavelength for a 1-cm path length. Ethyl acetate, not rigorously purified, and dioxane in air have absorbances of about 0.7 for 1 cm at 2537A. Thus, the intensities absorbed by the polymer will vary from solution to solution, and this can result in small differences in the results, as shown in the next subsection.

Intensity Effects

A small but nonetheless significant intensity effect was observed in degassed methylene chloride and dioxane solutions (Fig. 3). In the intensity ranges used in this work, a tenfold increase in intensity gives about a 10% decrease in the Φ_s^p . For practical purposes, the scissions produced by 2537A radiation in these solutions depends primarily on the number of quanta absorbed and not on the rate at which they are absorbed by the polymer; the intensity exponent is essentially one.

In dioxane solutions in air, a fourfold change in intensity gave the same Φ_s^p within experimental error.

Dependence on Polymer Concentration

With polymer sample I in degassed methylene chloride solutions irradiated by the 84A1 source the Φ_s^p appeared to be nearly the same over a tenfold change in polymer

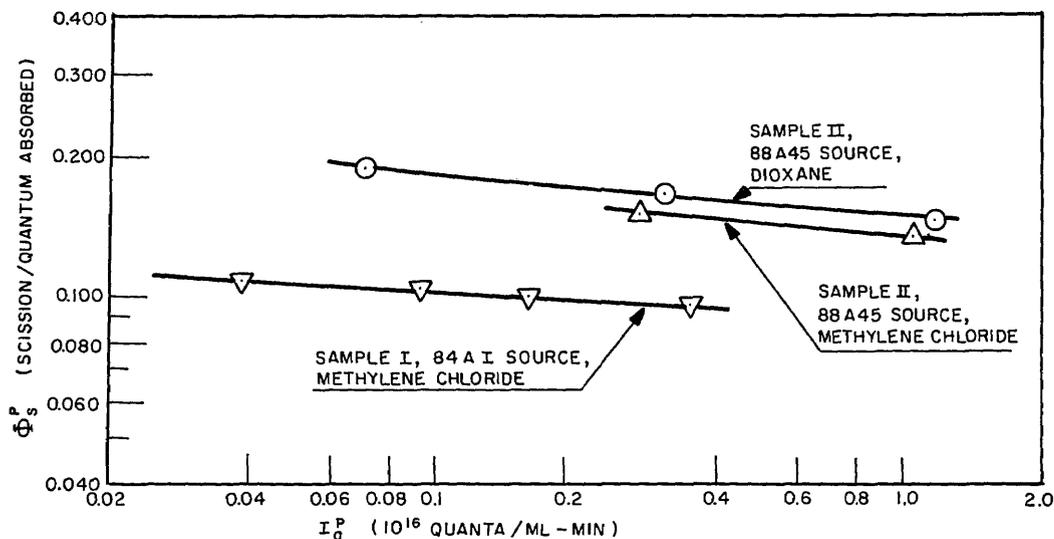


Fig. 3 - Effect of intensity on the quantum yield for scission of poly(methyl methacrylate) in solution in the absence of air

Table 2
Concentration Effects (Sample I, 84A1 Source,
Degassed Methylene Chloride Solutions)

| Concentration (g/dl) | η_{r0} | I_a^p (10^{16} quanta/ ml-min) | Φ_s^p (scissions/ quantum absorbed) |
|-------------------------|-------------|---|--|
| 0.11 | 1.32 | 0.087 | 0.087 |
| 0.236 | 1.84 | 0.17 | 0.098 |
| 0.489 | 3.17 | 0.34 | 0.095 |
| 1.009 | 7.14 | 0.61 | 0.093 |

concentration, as seen in Table 2. The result at the lowest concentration is subject to considerable error from the standpoint of both absorbance and viscosity measurements. Discounting the lowest concentration, then, there seems to be a slight trend downward in Φ_s^p with increasing polymer concentration. In solid poly(methyl methacrylate) in vacuum under a medium-pressure mercury source, Φ_s^p was about 0.040 (3). As concentration increases, so does the rate of radiation absorption I_a^p , and this increase in rate operates to decrease the quantum yields. Concentrations in the other work reported here were maintained within 10% of 0.5 g/dl, and this effect of concentration is considered to be negligible within this range.

Effects of Air and Peroxides

Oxygen, in air, has a very pronounced effect on the rate of photodegradation of poly(methyl methacrylate) measured by viscosity changes. This was true with solid films (3), and it has proved to be the case with the solvents investigated in the present work. Unlike the degassed solutions, runs made in the presence of air gave data which, when plotted as in Fig. 2, produced curves with a slight downward trend. This means that the apparent quantum yields decreased as exposure time increased. In such cases, initial Φ_s^p values were used to make comparisons. These data are given in Table 3. In the solid film, the ratio $\Phi_s^p(\text{Air})/\Phi_s^p(\text{Vacuum})$ was about 0.41 (3).

It is apparent that oxygen plays a most important role in the photodegradation of poly(methyl methacrylate). The possibility of electronic energy transfer to oxygen in its triplet state will be elaborated in a report to follow. At this point, it was necessary to determine the part, if any, which might be played by peroxides in the system. To decompose residual peroxides which might be present, portions of sample II were preheated at 115°C for 24 hours in vacuum under continuous pumping. Preheating this or the original sample in the dark in vacuum at 150°C for three days did not result in a reduction in molecular weight. A methylene chloride solution of a portion of sample II was "peroxidized" by vigorous bubbling with a stream of oxygen; the material was recovered by precipitation with methanol and dried at room temperature in vacuum. These materials were photolyzed in methylene chloride with the 84A1 source; the results are shown in Table 4.

Evidently, from comparison of the values for the samples before and after preheating at 115°C to remove any peroxides, adventitious peroxides are not important in the overall photodegradation of poly(methyl methacrylate) in either the presence or absence of air at room temperature. The supposed removal of peroxides by preheating may have actually resulted in a slight increase in the Φ_s^p in the absence of air, but the preheating may also have decomposed some trace inhibitor.

The curve of scissions versus exposure for the "peroxidized" sample run in the absence of air was unlike that of any other run. Here, the course of the degradation was

Table 3
Effect of Air on Poly(methyl Methacrylate) Photodegradation (Sample II)

| Source | Solvent | Atmo- sphere | I_a^p (10^{16} quanta/ ml-min) | Φ_s^p (scissions/ quantum absorbed) | $\frac{\Phi_s^p(\text{Air})}{\Phi_s^p(\text{Solvent})}$ |
|--------|--|-----------------|---|--|---|
| 84A1 | Methylene chloride | Solvent | 0.29 | 0.097 | 0.54 |
| 84A1 | Methylene chloride | Air | 0.33 | 0.052 | |
| 88A45 | Methylene chloride | Solvent | 1.04 | 0.138 | 0.52 |
| 88A45 | Methylene chloride | Air | 1.03 | 0.071 | |
| 88A45 | 0.0045M benzene in methylene chloride | Solvent | 0.34 | 0.161 | 0.46 |
| 88A45 | 0.0045M benzene in methylene chloride | Air | 0.31 | 0.074 | |
| 88A45 | Dioxane | Solvent | 0.71* | 0.150* | 0.41 |
| 88A45 | Dioxane | Air | 0.71 | 0.066 | |
| 88A45 | 0.0045M benzene in dioxane | Solvent | 0.45 | 0.204 | 0.40 |
| 88A45 | 0.0045M benzene in dioxane | Air | 0.24 | 0.083 | |

*Taken from Fig. 3.

Table 4
"Peroxide" Effects (Methylene Chloride Solutions, 84A1 Source)

| Sample | Atmosphere | I_a^p (10^{16} quanta/ ml-min) | Φ_s^p (scissions/ quantum absorbed) |
|---------------------|------------|---|--|
| Untreated Sample II | Solvent | 0.29 | 97 |
| Preheated at 115°C | Solvent | 0.37 | 108 |
| "Peroxidized" | Solvent | 0.34 | 48* |
| Untreated Sample II | Air | 0.33 | 52 |
| Preheated at 115°C | Air | 0.31 | 53 |

*Initial Φ_s^p ; see text.

initially similar to an ordinary air run. After a short period, however, the curve turned upward, and eventually the slope became identical with that of a run made in the absence of air. If peroxides are formed during the oxygenation, they must be consumed during the photolysis, and their overt effect must be the same as that of oxygen itself; examination of the ultraviolet spectra did not reveal the presence of charge-transfer complexes between oxygen and the polymer.

Effect of Mixed Solvents

If methylene chloride and dioxane can be considered photolytically inert solvents for poly(methyl methacrylate), then it is useful to use these solvents as "diluent" when it is desired to examine the effect of other solvents on the course of the degradation. These solvents are not completely inert, of course, and the effect seen in a mixed solvent system is actually the combined effect of all of the constituents.

As second solvents, benzene, ethanol, and carbon tetrachloride were investigated. The results for benzene and ethanol are summarized in Table 5. While ethanol exerted almost no effect in methylene chloride, benzene acted as a weak sensitizer of the degradation, particularly in dioxane solutions, although this effect is partially obscured by any intensity effect which may exist. Carbon tetrachloride is well known for its facile photolysis to form free radicals, at least as indicated by the products of its photolytic reactions, and it might therefore also be expected to act as a sensitizer. The results of a series of experiments in mixed methylene chloride and carbon tetrachloride solutions are given in Table 6. The expected did not occur. While the apparent ϕ_s^p value in the 80% carbon tetrachloride solution was more than twice that in methylene chloride, in mixtures of the two solvents the ϕ_s^p values were roughly those expected on the basis of dilution. At low concentrations of carbon tetrachloride, there is certainly no sensitization, and there may actually be a slight inhibiting effect over that expected from dilution; up to about 10% carbon tetrachloride, the ϕ_s^p were unchanged within experimental error.

DISCUSSION

Random scission appears to be well established as the major mechanism for the photodegradation of the main chain of poly(methyl methacrylate) at room temperatures, whether the degradation be carried out with solutions or with solid films, and whether or not oxygen is present. This is borne out by the linearity of the plots of scissions produced against the number of quanta absorbed by the polymer in the solvents used in this work. The same linearity has been observed with more photoreactive solvents (4) and with films (3). Random scission is, in fact, the result of photodegradation of most polymers at room temperatures (15), and there is no reason to think it would be otherwise unless there is a preferential absorption of energy at the end groups or there is a specific chemical reaction between the end groups and some other constituent in the system.

There should be no illusions concerning the photolytic "inertness" of dioxane or methylene chloride. To the extent that these substances absorb the incident radiation, photolytic reactions may occur, and if they do, they can involve other substances which are present. The hope here was that by virtue of the low absorption coefficients of the solvents at 2537A the competing solvent photolysis would be small compared to the direct photolysis of dissolved poly(methyl methacrylate). Some interaction may take place, since the quantum yields for scission are slightly different in the two solvents and are about five times greater in solution than in the film. The lower scission rate in the film may be due to the higher viscosity, which would tend to make recombination of polymer chain ends more likely, or it may be due to the higher absorbed intensity of the radiation in the solid film.

An indication of the "inertness" of methylene chloride can be seen in the very small effect of polymer concentration. In a photolytically active solvent, 2-chloroethanol, it has been shown (4) that a fivefold increase in polymer concentration results in fourfold decrease in experimental rate constants; these constants are directly proportional to the quantum yields for scission of the polymer. Chloroform, a solvent which might be expected to be reactive, showed a similar concentration dependence (5). Charlesby and Thomas (9), using benzene solutions, did not find a concentration dependence and concluded that this solvent was inert. In our work, small concentrations of benzene in methylene chloride or,

Table 5
Photodegradation of Poly(methyl Methacrylate) in Mixed Solvents

| Sample* | Second Solvent | Atmosphere | I_a^p (10^{16} quanta/ ml-min) | Φ_s^p (scissions/ quantum absorbed) |
|------------------------------|-----------------|------------|---|--|
| Methylene Chloride Solutions | | | | |
| I | None | Solvent | 0.34 | 95 |
| I | 0.0045M benzene | Solvent | 0.12 | 113 |
| I | 0.45M benzene | Solvent | 0.0012 | 300 |
| I | 0.7M ethanol | Solvent | 0.33 | 91 |
| II | None | Solvent | 0.27 | 149 |
| II | 0.0045M benzene | Solvent | 0.34 | 161 |
| II | None | Air | 1.03 | 71 |
| II | 0.0045M benzene | Air | 0.31 | 74 |
| II | 0.45M benzene | Air | 0.0044 | 238 |
| Dioxane Solutions | | | | |
| II | None | Solvent | 0.45† | 157† |
| II | 0.0045M benzene | Solvent | 0.45 | 204 |
| II | None | Air | 0.71 | 66 |
| II | 0.0045M benzene | Air | 0.24 | 83 |

*Sample I: 84A1 source; Sample II: 88A45 source.

†From Fig. 3.

Table 6
Methylene Chloride and Carbon Tetrachloride Mixtures
(Sample I, 84A1 Source, Degassed Solutions)

| CCl ₄ Concentration | | I_a^p (10^{16} quanta/ ml-min) | Φ_s^p (scissions/ quantum absorbed) |
|--------------------------------|---------------|---|--|
| Vol-% | Mole Fraction | | |
| 0 | 0 | 0.34 | 0.095 |
| 4 | 0.027 | 0.21 | 0.098 |
| 8 | 0.054 | 0.15 | 0.100 |
| 12 | 0.083 | 0.12 | 0.104 |
| 24 | 0.17 | 0.063 | 0.146 |
| 40 | 0.31 | 0.040 | 0.225 |
| 80 | 0.73 | 0.019 | 0.238 |

especially, in dioxane tended to increase the quantum yields for scission of the polymer. We therefore conclude that benzene is not inert; either a radical reaction between benzene and the polymer is taking place, or energy absorbed by the benzene is being transferred to the polymer.

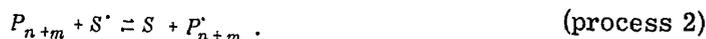
That the quantum yields vary with the solvent indicates solvent involvement. The important questions revolve around how the solvent is involved; for most polymer systems consist of more than one constituent, and the nonpolymer constituents may very well control the rate at which the polymer degrades.

Degradation of poly(methyl methacrylate) in solution under ionizing radiation (16) and in films under ultraviolet radiation (17) have been discussed in terms of what has been called the "direct" and "indirect" action of radiation. In the presence of other molecules a polymer may photolyze by any or all of three general processes. The first process depends only on the polymer and is a consequence of the direct absorption of energy followed by homolytic dissociation of some bond. If the bond broken is in the main chain, the result is readily seen in a change in the number-average molecular weight:



where the asterisk denotes an electronically excited state. Main chain dissociation may be preceded by "side-bond" dissociation, leading to a polymer free radical P_{n+m}^{\cdot} , which in turn undergoes fragmentation. Process 1 would be the major one in a perfectly pure polymer film.

The second and third processes require the presence of molecules, denoted by S , other than the polymer or possibly could involve an interaction among electronically different and independent parts of the polymer molecule itself. A process often used to describe the mechanism of photodegradation depends on the formation of free radicals from the S molecules:



The forward reaction here represents an acceleration of degradation and the reverse reaction an inhibition of the degradation. These, of course, are not the only free radical reactions which might occur. For example the combination of a polymer radical and a solvent radical would also amount to an inhibition of degradation, although the polymer product would be chemically altered.

The rate of the ultimate process of bond-breaking may also be affected by transfers of excitation energy among the species in the system:



Again, the forward reaction represents an acceleration and the reverse reaction an inhibition of degradation. The ease with which this process occurs could be affected by the formation of complexes and by other means by which activation energies might be reduced.

It is the relative contribution of processes 1, 2, and 3 which are of interest. Generally, process 2 has been invoked to explain the overt degradation of polymers in the presence of extraneous substances. In our work with poly(α -methylstyrene) (1), however, certain features of the degradation were difficult to explain on this basis. A comparison of the results of solution degradation of poly(α -methylstyrene) with those of poly(methyl methacrylate) elicits discrepancies not explainable by process 2.

Not only do the rates of photolytic chain breaking in solution depend markedly on the solvent in each of the two polymers, but the relative rates for the two polymers in the various solvents are quite different. For example, comparing the rates in degassed dioxane and methylene chloride solutions, the ratio of quantum yields Φ_s^p for poly(methyl methacrylate) was about 1.05, while for poly(α -methylstyrene) it was 0.08. Of course, there is no reason to suppose that the reactions of process 2 must be identical for the two polymers, and with poly(α -methylstyrene) most of the incident radiation is absorbed by the polymer.

Dioxane and methylene chloride have been shown to be relatively inactive solvents with polymers. What of an active solvent? Such a case is carbon tetrachloride, which would be expected to photolyze to Cl^\cdot and $\text{Cl}_3\text{C}^\cdot$ radicals; with both polymers, absorption by the solvent was significant. Ultraviolet irradiation of polymer-carbon tetrachloride solutions containing chlorine, a situation which should readily generation Cl^\cdot radicals, results in a very rapid degradation with both poly(α -methylstyrene) (1) and with poly(methyl methacrylate) (18). Thus, it might be expected that the addition of carbon tetrachloride to solutions of either polymer in a photolytically inert solvent would result in greatly increased rates of degradation. While this was the case with poly(α -methylstyrene), it is most decidedly not with poly(methyl methacrylate); the behavior of the two polymers is shown graphically in Fig. 4. These results indicate that the attack of Cl^\cdot radicals on the polymer is not the rate-controlling step in the degradation under these conditions.

If solvent radical attacks are not always responsible for the solvent-dependency of the degradation rates, some form of energy transfer seems to be the only reasonable alternative. Attempts have been made to correlate the ultraviolet cutoffs of the solvents with rates of degradation (16), but this is not successful in the present instance. Singlet-singlet energy transfer might be invoked to explain the behavior of carbon tetrachloride solutions of the two polymers. The lowest excited singlet levels of the molecules involved are shown in Fig. 5. Essentially, singlet-singlet energy transfer requires a coupling between the fluorescence emission of the donor and the absorption of the acceptor; reabsorption is not necessarily involved (19). If the 0-0 band corresponding to carbon tetrachloride fluorescence is relatively weak, it may be that a greater overlap will occur between the energy corresponding to the difference between the excited singlet and some high vibrational level in the ground state and the 0-0 absorption band in poly(α -methylstyrene) than in poly(methyl methacrylate). This type of overlap might also be used to explain the relatively high rate of degradation of poly(methyl methacrylate) in methylene chloride but is not helpful with the dioxane solutions or with mixtures containing benzene. In dioxane, charge-transfer complexes may be involved, but attempts to observe such complexes were not successful with poly(methyl methacrylate).

An explanation of the effect of oxygen on the two polymers is not readily made on the basis of present data. It may be noted that oxygen exists as a triplet in the ground state; therefore triplet energy transfer between poly(methyl methacrylate)-carbonyls in an excited triplet level may occur with a resultant decrease in the rate of degradation. This kind of argument is, of course, strictly speculation at this time.

ACKNOWLEDGMENT

The authors are indebted to Mr. Peter Ryan of the Applied Mathematics Staff for constructing the nomograph shown in Fig. 1.

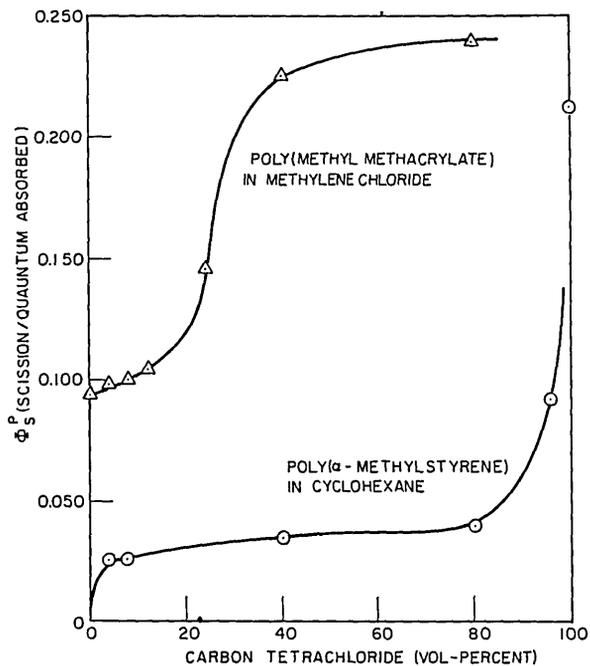


Fig. 4 - Photolysis of poly(α -methylstyrene) (data from Ref. 1) and poly(methyl methacrylate) in solutions containing carbon tetrachloride in the absence of air

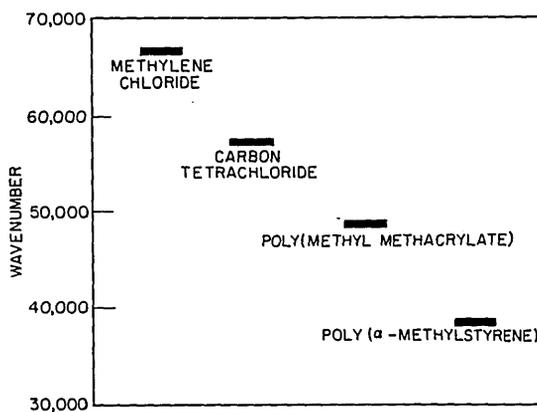


Fig. 5 - Lowest excited singlet levels

REFERENCES

1. Fox, R.B., and Price, T.R., *J. Polymer Sci.* A3:2303 (1965); also "Photodegradation of High Polymers in Solution, Part 1 - Solvent Effects in the Photolysis of Poly(α -methylstyrene), NRL Report 6120, Aug. 1964
2. Price, T.R., and Fox, R.B., "Photodegradation of High Polymers in Solution, Part 2 - Solvent Effects in the Photolysis of Polystyrene," NRL Report 6328, Oct. 1965
3. Fox, R.B., Isaacs, L.G., and Stokes, S., *J. Polymer Sci.* A1:1079 (1963)
4. Jellinek, H.H.G., and Wang, I.C., *Kolloid-Z.* 202:1 (1965)
5. Mönig, H., *Naturwiss.* 45:12 (1958)
6. Mönig, H., and Kriegel, H., *Z. Naturforsch.* 15b:333 (1960)
7. Mönig, H., and Kriegel, H., *Proc. 3rd Internatl. Congress on Photobiol., Copenhagen, 1960*, p. 618, 1961
8. Mönig, H., and Kriegel, H., *Biophysik* 2:22 (1964)
9. Charlesby, A., and Thomas, D.K., *Proc. Roy. Soc. (London)* A269:104 (1962)
10. Hatchard, C.G., and Parker, C.A., *Proc. Roy. Soc. (London)* A235:518 (1956)
11. Bevington, J.C., *J. Polymer Sci.* 34:680 (1959)
12. Oster, G., Oster, G.K., and Moroson, H., *J. Polymer Sci.* 34:671 (1959)
13. Meyerhoff, G., *Makromol. Chem.* 37:97 (1960)
14. Solomon, O.F., and Ciută, I.Z., *J. Applied Polymer Sci.* 6:683 (1962)
15. Fox, R.B., in "Progress in Polymer Science," vol. 1, Oxford:Pergamon (in press)
16. Henglein, A., Schneider, C., and Schnabel, W., *Z. Phys. Chem.* 12:339 (1957)
17. Gardner, D.G., and Epstein, L.M., *J. Chem. Phys.* 34:1653 (1961)
18. Hahn, W., and Grafmüller, F., *Makromol. Chem.* 21:121 (1956)
19. Förster, T., *Radiation Res. Suppl.* 2:243 (1960)

| DOCUMENT CONTROL DATA - R&D | | |
|--|--|-------------------------------|
| <small>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</small> | | |
| 1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390 | 2 a. REPORT SECURITY CLASSIFICATION Unclassified | |
| | 2 b. GROUP | |
| 3. REPORT TITLE PHOTODEGRADATION OF HIGH POLYMERS IN SOLUTION. PART 3 - POLY(METHYL METHACRYLATE) | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) An interim report on the problem. | | |
| 5. AUTHOR(S) (Last name, first name, initial) Fox, R.B. and Price, T.R. | | |
| 6. REPORT DATE September 7, 1966 | 7 a. TOTAL NO. OF PAGES 20 | 7 b. NO. OF REFS 19 |
| 8 a. CONTRACT OR GRANT NO. NRL Problem C04-04 | 9 a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6423 | |
| b. PROJECT NO. RR 001-02-43-4801 | | |
| c. | 9 b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | |
| d. | | |
| 10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited. | | |
| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research), Washington, D.C. 20360 | |
| 13. ABSTRACT <p>The photodegradation of poly(methyl methacrylate) in solution in the presence and absence of air under 2537A irradiation at about 25°C has been investigated, primarily by means of viscosity measurements. Random scission is confirmed as the major chain-breaking process. Quantum yields for scission in degassed solutions are solvent dependent; for methylene chloride, dioxane, and ethyl acetate, the quantum yields are 0.15, 0.17, and 0.38, respectively. In methylene chloride the quantum yield is nearly independent of polymer concentration and decreases slightly with increasing absorbed radiation intensity. Small amounts of benzene tend to increase the quantum yields, but carbon tetrachloride has relatively small effect and does not sensitize the degradation. In any of the solvents in the presence of air the quantum yields are approximately half of those found in the absence of air. Adventitious peroxides appear not to play a role in the degradation, but an oxygenated sample which probably contains peroxides acts initially as a sample would in air. The results can be interpreted in terms of possible electronic energy transfer processes.</p> | | |

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Poly(methyl methacrylate) Acrylic resins Polymers Photochemistry Ultraviolet radiation Viscosity Molecular weight Spectra (ultraviolet) Radiation chemistry Air Scission Polymer degradation Photodegradation in solution | | | | | | |
| Quantum yields Electronic Energy transfer | | | | | | |

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.