Table III
Interaction Radii

Polymer series	Solvent	Interaction radius
PNLA	DCE	5.9 Å $< R <$ 8.9 Å
PNLA	MS[a]	5.9 Å $< R <$ 8.9 Å
PNLG	DCE	5.8 Å $< R <$ 8.8 Å
PNLA	DCE	5.8 Å $< R <$ 8.8 Å[b]

[a] MS = mixed solvent of DCE and HFIP (1:1 by volume). [b] Interaction range for excimer quenching. The range was obtained by using the mean p value 0.66 of the values from eq 10.

greater than for an isolated excited chromophore. The localization of the π orbitals in the excimer might be the reason for this observation.

References and Notes

(1) (a) Tohoku University; (b) Tokyo University.
(2) S. S. Yanari, F. A. Bovey, and R. Lumry, *Nature (London)*, **200**, 242 (1963).
(3) M. T. Vala, J. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).
(4) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
(5) A. I. Lashkov and V. L. Ermolaev, *Opt. Spektrosk.*, **22**, 462 (1967).
(6) R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1969).
(7) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).
(8) F. Heisel and G. Laustriat, *J. Chim. Phys. Phys.-Chim. Biol.*, **66**, 1881 (1969).
(9) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 537 (1970).
(10) C. David, W. Demarteau, and Geuskens, *Eur. Polym. J.*, **6**, 1405 (1970).
(11) R. B. Fox, T. R. Price, and R. F. Cozzens, *J. Chem. Phys.*, **54**, 79 (1971).
(12) R. C. Powell, *J. Chem. Phys.*, **55**, 1871 (1971).
(13) R. C. Johnson and H. W. Offen, *J. Chem. Phys.*, **55**, 2945 (1971).
(14) A. C. Somersall and J. E. Guillet, *Macromolecules*, **5**, 410 (1972).
(15) C. David, M. Piens, and G. Geuskens, *Eur. Polym. J.*, **9**, 533 (1973).
(16) A. C. Somersall and J. E. Guillet, *Macromolecules*, **6**, 218 (1973).
(17) F. Heitz, G. Spach, C. Helene, and J. L. Dimicoli, *Macromolecules*, **6**, 845 (1973).
(18) E. Leroy, C. F. Lapp, and G. Laustriat, *Biopolymers*, **13**, 507 (1974).
(19) A. M. North, D. A. Ross, and M. F. Treadaway, *Eur. Polym. J.*, **10**, 411 (1974).
(20) C. David, N. P. Lavareille, and G. Geuskens, *Eur. Polym. J.*, **10**, 617 (1974).
(21) A. Ueno, F. Toda, and Y. Iwakura, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1841 (1974).
(22) A. Ueno, F. Toda, and Y. Iwakura, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 287 (1974).
(23) A. Ueno, F. Toda, and Y. Iwakura, *Biopolymers*, **13**, 1213 (1974).
(24) A. Ueno, T. Ishiguro, F. Toda, K. Uno, and Y. Iwakura, *Biopolymers*, **14**, 353 (1975).
(25) A. Ueno, M. Nohara, F. Toda, K. Uno, and Y. Iwakura, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2751 (1975).
(26) A. Ueno, T. Osa, and F. Toda, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 521 (1976).
(27) J. B. Birks, D. J. Dyson, and I. H. Munro, *Proc. R. Soc. London, Ser. A*, **275**, 575 (1963).
(28) E. J. Bowen and W. S. Metcalf, *Proc. R. Soc. London, Ser. A*, **206**, 437 (1951).
(29) W. R. Ware and J. S. Novros, *J. Phys. Chem.*, **70**, 3246 (1966).
(30) R. Voltz, J. Klein, F. Heisel, H. Lami, G. Laustriat, and A. Coche, *J. Chim. Phys. Phys.-Chim. Biol.*, **63**, 1259 (1966).
(31) D. Gerald, G. Laustriat, and H. Lami, *Biochim. Biophys. Acta*, **263**, 482 (1972).
(32) M. Heskins and J. E. Guillet, *Macromolecules*, **3**, 224 (1970).
(33) A. D. Osborne and A. Porter, *Proc. R. Soc. London, Ser. A*, **284**, 9 (1965).
(34) H. J. V. Tyrell, "Diffusion and Flow in Liquids", Butterworths, London, 1961, p 127.
(35) J. T. Dubois and M. Cox, *J. Chem. Phys.*, **38**, 2536 (1963).
(36) J. B. Birks "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1964, p 518.
(37) J. B. Birks, M. Salete, and S. C. P. Leite, *J. Phys. B*, **3**, 417 (1970).
(38) J. H. Gorrell and J. T. Dubois, *Trans. Faraday Soc.*, **63**, 347 (1967).
(39) A. M. North and M. F. Treadaway, *Eur. Polym. J.*, **9**, 609 (1973).

On the Kinetics of Polymer Degradation in Solution. 5.[1,2] Pulse Radiolysis of PMMA Using the Light Scattering Detection Method

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ABSTRACT: The time dependence of the change of the light scattering intensity (LSI) of PMMA solutions after irradiation with a 2-μs pulse of 15-MeV electrons was monitored. Evidence for the existence of two intermediates causing main chain scission was obtained. The LSI decays in two modes: (1) a fast decay with a lifetime of ca. 20 μs probably corresponding to the diffusion of fragments which are generated by main chain ruptures occurring via electronically excited or ionic intermediates; (2) a slow decay with a lifetime τ (slow) $\approx$ 6 ms ($k_2 = 170\ \mathrm{s}^{-1}$) corresponding presumably to a lateral macroradical. τ(slow) decreases with increasing concentrations of O_2 and C_2H_5SH. The degree of degradation also decreases with increasing concentration of these two additives. The following rate constants for the reaction of O_2 and C_2H_5SH with the transient causing the slow main chain ruptures were determined in acetone (at room temperature): $k_{O_2} = 1 \times 10^7\ M^{-1}\ s^{-1}$ and $k_{C_2H_5SH} = 2.5 \times 10^4\ M^{-1}\ s^{-1}$. Solvents used were acetone, n-hexanone-2, and acetonitrile.

Preliminary experiments[3] led to the conclusion that the radiation-induced main-chain degradation of poly(methyl methacrylate) (PMMA) in solution proceeds via two different intermediates. Evidence for these was obtained by monitoring the time dependence of decrease of light scattering intensity (LSI) after the irradiation of a dilute solution of PMMA with a 2-μs pulse of 15-MeV electrons. Immediately after the pulse the LSI decreased rapidly with a lifetime of less than 150μs. Subsequently a slow decrease with a lifetime of about 6 ms ($k = 170\ \mathrm{s}^{-1}$) was observed. It was suggested that the rapid decay is due to main chain scissions caused by an electronically excited or an ionic transient. The slow decay, on the other hand, was thought to be due to main chain ruptures caused by free radicals.

In order to substantiate these suggestions experiments were carried out with acetone solutions containing oxygen or ethanethiol. In additional experiments acetonitrile and n-hexanone-2 were used as solvents instead of acetone. The results of these experiments are described in this paper. They affirm the suggestion that the slow LSI decay is correlated to the lifetime of free PMMA radicals. Thus, it appears that the system under investigation provides a good example to demonstrate the applicability of the light scattering detection method for the investigations of the kinetics of chemical reactions of short-lived intermediates.

The Influence of Radical Scavengers on the LSI Decay. In the following a working hypothesis is developed which is based on the postulate that two intermediates P^*_{n+m} and $\mathrm{P}\cdot_{n+m}$ are involved in the process of main chain degradation. P^*_{n+m} designates an excited or ionic species decaying relatively fast, i.e., with a lifetime much shorter than the diffusion time of the fragments originating from main chain scissions. $\mathrm{P}\cdot_{n+m}$ denotes a lateral macroradical which is rather long lived.

$$\mathrm{P}^*_{n+m} \xrightarrow{k_1} \mathrm{P}_n + \mathrm{P}_m \tag{1}$$

$$\mathrm{P}\cdot_{n+m} \xrightarrow{k_2} \mathrm{P}_n + \mathrm{P}\cdot_m \tag{2}$$

$$\mathrm{P}_{n+m} + \mathrm{S} \begin{cases} \xrightarrow{k_\mathrm{S}} \mathrm{P}_{n+m}\cdots\mathrm{S}\cdot & (3) \\ \xrightarrow{k_{\mathrm{S}'}} \mathrm{P}_{n+m} + \mathrm{S}\cdot & (3') \end{cases}$$

Whereas by the transfer reaction 3′ macroradicals are repaired, the addition of scavenger molecules to macroradicals (reaction 3) leads to another type of free macroradicals which may stabilize by hydrogen abstraction:

$$\mathrm{P}_{n+m}\text{- - -}\mathrm{S}\cdot + \mathrm{RH} \rightarrow \mathrm{P}_{n+m}\text{- - -}\mathrm{SH} + \mathrm{R}\cdot \tag{4}$$

The product thus formed is probably not very stable and may undergo main chain scission under the influence of further irradiation or heat. It may, however, be emphasized that reaction 3 as well as reaction 3′ prevent main chain ruptures of the type described in reaction 2. That means, upon irradiation of a polymer solution with a single pulse of fast electrons, those macroradicals undergoing reactions 3 or 3′ will not contribute to the decrease of LSI. Therefore, in the presence of a radical scavenger the degree of degradation will be reduced, i.e., the extent of LSI decrease will become smaller. A correlation between the degree of degradation α (number of main chain scissions per base unit of the macromolecule) and the rate constant $\Sigma k_\mathrm{S} = (k_\mathrm{s} + k_\mathrm{s}')$ can be derived in the following way:

The final degree of degradation α_∞ observed a long time after the absorption of the electron pulse is

$$\alpha_\infty = \alpha_\infty^\mathrm{R} + \alpha_\infty^\mathrm{E} \tag{5}$$

α_∞^R and α_∞^E denote the numbers of main chain ruptures per base unit due to radical reaction 2 or due to reaction 1, respectively. Reaction 1 is not influenced by the presence of a radical scavenger, i.e., α_∞^E is considered to be constant. α_∞^R depends on the scavenger concentration according to eq 6 (in this case $\alpha_\infty^\mathrm{R} \equiv \alpha_{\infty,\mathrm{S}}^\mathrm{R}$):

$$\alpha_{\infty,\mathrm{S}}^\mathrm{R} = \alpha_{\infty,0}^\mathrm{R} \frac{k_2}{k_2 + \Sigma k_\mathrm{S}[\mathrm{S}]} \tag{6}$$

Combining eq 5 and 6 one obtains:

$$\frac{\alpha_{\infty,0}^\mathrm{R}}{\alpha_{\infty,\mathrm{S}} - \alpha_\infty^\mathrm{E}} = 1 + \frac{\Sigma k_\mathrm{S}[\mathrm{S}]}{k_2} \tag{7}$$

Σk_S can be evaluated by measuring α_∞ as a function of the scavenger concentration [S] if k_2 is known and if α_∞^E can be obtained experimentally. The latter condition meets the experimental findings described below.

Another mode of evaluating Σk_S derives from the measurements of the rate of LSI change for solutions containing different amounts of scavenger. A prerequisite is that the rate of LSI change is proportional to the rate of decrease of the macroradical concentration. This holds for the case where the average lifetime of the macroradicals is relatively long. In other words, reaction 2 is considered to be a process consisting of two consecutive steps. During the first step chemical bonds are broken causing main chain cleavage. The second step comprises the separation of the fragments by diffusion:

$$\mathrm{P}\cdot_{n+m} \xrightarrow{k_2'} [\mathrm{P}\cdot_n \cdots \mathrm{P}_m] \xrightarrow{k_2''} \mathrm{P}\cdot_n + \mathrm{P}_m \tag{2'}$$

The observed change of the LSI signal is related to the separation of the fragments.[3] If $k_2'' \gg k_2'$, the rate of LSI change is entirely determined by the rate of the first step, i.e., by the rate constant $k_2' = (\tau_2')^{-1}$. The rate constant k_2' can be evaluated by application of the rate law

$$[\mathrm{P}\cdot]_t = [\mathrm{P}\cdot]_0 e^{-k_2't} \tag{8}$$

Since $[\mathrm{P}\cdot]_0 \propto \alpha_\infty^\mathrm{R}$ and $[\mathrm{P}\cdot]_t \propto \alpha_\infty^\mathrm{R} - \alpha_t^\mathrm{R}$, k_2' is obtained from plots according to eq 9

$$\ln \frac{\alpha_\infty - \alpha_t}{\alpha_\infty} = -k_2't \tag{9}$$

In the presence of a scavenger S reactions 3 and 3′ compete with reaction 2. Thus, one obtains the following pseudo-first-order expression:

$$[\mathrm{P}\cdot]_t = [\mathrm{P}]_0 e^{-(k_2' + \Sigma k_\mathrm{S}[\mathrm{S}])t} \tag{10}$$

Equation 10 holds for the case where the scavenger concentration is practically not changed during the reaction. This condition is met by using relatively high scavenger concentration. By measuring the lifetime of the LSI decay as a function of the scavenger concentration Σk_S can be obtained according to eq 11:

$$(\tau)^{-1} = k_2' + \Sigma k_\mathrm{S}[\mathrm{S}] \tag{11}$$

For the evaluation of values of τ reported in one of the following sections, the change of the light scattering signal voltage was plotted according to eq 12, which was derived from eq 9 and 10 as reported earlier.[3]

$$\ln \frac{(U_\infty - U_\mathrm{L})^{-1} - (U_t - U_\mathrm{L})^{-1}}{(U_\infty - U_\mathrm{L})^{-1} - (U_0 - U_\mathrm{L})^{-1}} = -(k_2' + \Sigma k_\mathrm{S}[\mathrm{S}])t$$

The subscripts to the signal voltages U designate: ∞, a long time after the pulse; t, time t; 0, $t = 0$; L, solvent.

Experimental Section

(a) Polymer Samples and Solvents. Two poly(methyl methacrylate) samples were used which were obtained by polymerization of methyl methacrylate (Ferak, Berlin) in bulk in the absence of additives with the aid of the field emission technique described earlier.[4]

The molecular weights were determined by the light scattering method using a Sofica apparatus: sample 1, $M_\mathrm{w} = 3.8 \times 10^6$; sample 2, $M_\mathrm{w} = 4.6 \times 10^6$. The polymer samples were reprecipitated three times from acetone solutions with methanol.

Acetone (Merck, p.a.) and *n*-hexanone-2 (Ega-Chemie, 99%) used for the irradiations were fractionated using a splitting tube column (Fischer, Bonn).

(b) Refractive Index Increments. The refractive index increment of PMMA in *n*-hexanone-2 was measured with the aid of an Brice-Phoenix differential refractometer at 25 °C: $(\mathrm{d}n/\mathrm{d}c) = 0.098$ ml/g, $\mathrm{d}n/\mathrm{d}c = 0.134$ ml/g for PMMA in acetone, and $(\mathrm{d}n/\mathrm{d}c) = 0.137$ ml/g for PMMA in acetonitrile was taken from the literature.[11]

(c) Sample Preparation. In order to carry out irradiations in the absence of oxygen polymer solutions were bubbled with Ar containing 1 ppm $\mathrm{O_2}$. In order to establish well-defined $\mathrm{O_2}$ concentrations, samples were bubbled with argon-oxygen mixtures which were obtained by combining the two gases in a mixing device containing an "endOmess" instrument (Friedrichsfeld) in front of the exit for continuous $\mathrm{O_2}$ analysis. $\mathrm{O_2}$ concentrations were calculated on the basis of 1.14×10^{-2} M $\mathrm{O_2}$ being equivalent to a pressure of 1 atm at 25 °C.[5]

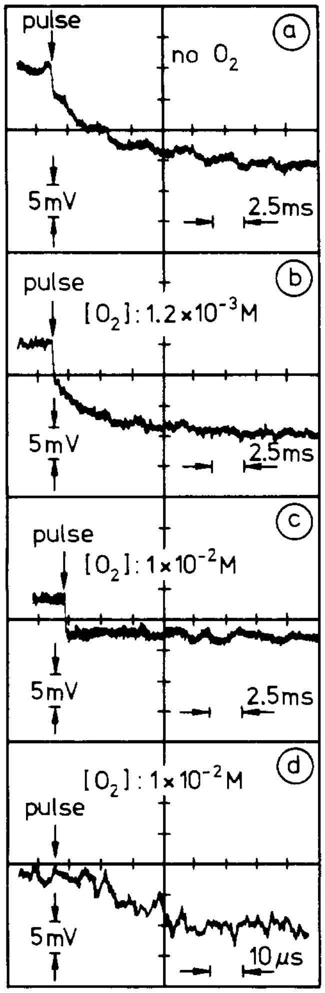

Figure 1. Oscilloscope traces obtained with acetone solutions at 24 °C demonstrating the fast and the slow decrease of light scattering intensity. [PMMA] = 1.4 × 10^{-2} base mol/l; absorbed dose per pulse = 4.8 × 10^4 rad; signal voltages = U_0 = 595 mV, U_L = 25 mV. (a) Solution saturated with purified argon; (b) $[O_2]$ = 1.2 × 10^{-3} M; (c) $[O_2]$ = 1.0 × 10^{-2} M; (d) fast LSI decrease, time-resolved, $[O_2]$ = 1.0 × 10^{-2} M.

(d) Irradiation of Samples. The irradiations were performed with an L-band linear accelerator (Vickers). The sample cell was attached to a flow system. Details of the light scattering measurements have been reported elsewhere.[1-3] An argon-ion laser from Spectraphysics was used as the light source. The LSI was measured at an angle of 90° with respect to the primary light beam. The signal of the photomultiplier was fed into a Tektronix plug-in 7A22 and displayed on a Tektronix storage oscilloscope 7613. A Tektronix time base 7B53A was used.

(e) Dosimetry. The dose absorbed per pulse was determined with the Fricke dosimeter using O_2-saturated dosimeter solutions ($G(Fe^{3+})$ = 13.0[6]). The dose per pulse was varied between 2 × 10^4 and 4 × 10^4 rad. The average number of scissions per macromolecule based on G(S) = 2.0 was in all cases smaller than 0.5.

Results

(a) Influence of Oxygen. Figure 1 shows oscilloscope traces obtained during typical experiments in acetone solution.

The traces shown in Figure 1a–c demonstrate that two modes of LSI change exist. The slower decaying component can be seen to be influenced by oxygen. If the oxygen concentration was sufficiently high the slow LSI decrease was completely suppressed and the LSI decreased only by the fast mode as shown in Figure 1c. In Figure 1d the time resolved LSI decrease according to the fast mode is presented. The lifetime of the fast decrease is about 20 µs. The lifetime of the slow mode became shorter upon increasing the oxygen concentration.

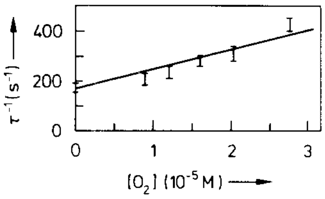

Figure 2. Reciprocal lifetime of the slow LSI decrease as a function of oxygen concentration. PMMA in acetone solution (1.4 × 10^{-2} base mol/l.). T = 24 °C. Absorbed dose per pulse 4.8 × 10^4 rad.

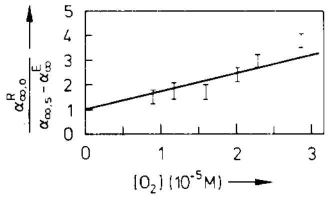

Figure 3. The influence of oxygen on the degree of degradation. Plot according to eq 7. Same experimental conditions as during experiments demonstrated in Figures 1 and 2.

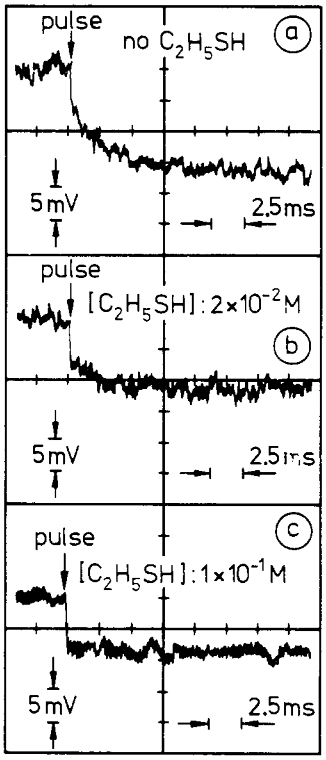

Figure 4. Oscilloscope traces obtained with oxygen-free acetone solutions at 22 °C demonstrating the influence of C_2H_5SH on the change on LSI. [PMMA] = 1.25 × 10^{-2} base mol/l; absorbed dose per pulse = 4.8 × 10^4 rad; signal voltages = U_0 = 855 mV, U_L = 43 mV. (a) No additive; (b) $[C_2H_5SH]$ = 2 × 10^{-2} M; (c) $[C_2H_5SH]$ = 1 × 10^{-1} M.

Figure 2 shows the reciprocal lifetime of the slow LSI decay plotted as a function of the oxygen concentration. From the slope of the straight line in Figure 2 the quenching rate constant k_{O_2} = 8 × 10^6 M^{-1} s^{-1} was obtained.

From the change in the degree of degradation with increasing oxygen concentration k_{O_2} = 1.2 × 10^7 M^{-1} s^{-1} was estimated by plotting $\alpha_{\infty,S}$ as a function of oxygen concentration according to eq 7. The respective plot is shown in Figure 3. The slope of the straight line amounts to 7.1 × 10^4

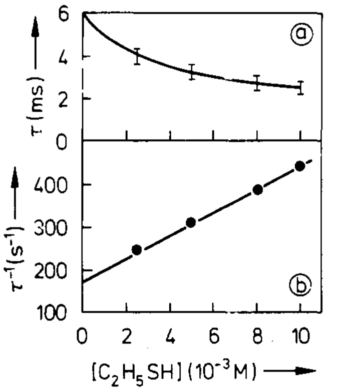

Figure 5. The dependence of the lifetime on the concentration of C_2H_5SH. Same experimental conditions as in experiments demonstrated in Figure 4.

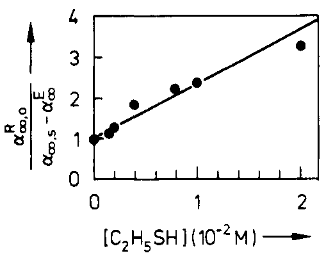

Figure 6. The influence of C_2H_5SH on the degree of degradation. Plot according to eq 7. Same experimental conditions as in experiments demonstrated in Figure 4.

M^{-1}. $k_2 = 170$ s^{-1} was used for the evaluation of k_{O_2}. The two values of k_{O_2} agree fairly well within the error limit.

(b) Influence of Thiol. The addition of small concentrations of ethanethiol to solutions of PMMA in acetone leads to a suppression of the slow LSI decay leaving the fast decay unchanged. Typical oscilloscope traces are shown in Figure 4. The decrease of the lifetime τ with increasing thiol concentration is presented in Figure 5a. From the plot of τ^{-1} vs. the thiol concentration (Figure 5b), the quenching rate constant, $k_{C_2H_5SH} = 2.7 \times 10^4$ M^{-1} s^{-1}, was obtained. A similar value ($k_{C_2H_5SH} = 2.3 \times 10^4$ M^{-1} s^{-1}) was evaluated by plotting the degree of degradation as a function of thiol concentration according to eq 7 as shown in Figure 6.

(c) Experiments in *n*-Hexanone-2 and Acetonitrile. Several experiments were carried out in hexanone solution. The viscosity of *n*-hexanone-2 (0.73 cP at 26 °C) is significantly greater than that of acetone (0.31 cP at 26 °C). Therefore a diminution of the lifetime of the slow LSI decrease was expected if the respective process would correspond to diffusion. However, it was found that the lifetime of the slow decay was the same (within the error limit) for both solvents. Thus, it is concluded that the slow LSI decay is correlated to the lifetime of an intermediate whose decay leads to bond scission in the main chain of the macromolecule.

Due to the relatively low refractive index increment in hexanone-2 the signal-to-noise ratio was not as good as in the case of acetone solutions. Therefore, the fast decaying portion of the LSI decrease could not be resolved sufficiently well in order to recognize a dependence of the lifetime of the fast LSI decay on microviscosity.

For solutions of PMMA in acetonitrile ($\eta = 0.345$ cP at 25 °C) the decay constant determined for the slow decay was $k = 160$ s^{-1}. This is about the same value as found in acetone solutions.

Discussion

The results demonstrate that the slow LSI decay is influenced by oxygen and ethanethiol. The lifetime of the slow LSI decay decreases with increasing concentration of the additive in a way expected if the additive reacts with the intermediate whose decay is leading to main chain rupture. An analogous conclusion is arrived at by considering the dependence of the degree of degradation on the additive concentration. Thus, it is concluded that the observed slow mode of LSI decay corresponds to the lifetime of an intermediate. It is assumed that this intermediate is a lateral macroradical. The rate constant $k_{O_2} \approx 1 \times 10^7$ M^{-1} s^{-1} found in this work is of the same magnitude as the value estimated by Schulz and Henrici[7] for the reaction of oxygen with end group macroradicals of PMMA formed during the polymerization of MMA ($k_{O_2} \approx 10^7$ M^{-1} s^{-1} at 50 °C).

Rate constants k_S for the reaction of thiols with macroradicals have been determined by investigating the polymerization of monomers at various thiol concentrations.[8] k_S was derived from the ratio k_S/k_p (k_p being the rate constant of propagation). Values reported for the reaction of macroradicals of different monomers with *n*-butylmercaptan range from 5×10^2 to 2×10^5 M^{-1} s^{-1}.[8] Those results demonstrate that there is no simple universal order of reactivity. The radical reactivity depends strongly on the substrate and probably also on the structure of the thiol. More recent investigations employing the method of pulse radiolysis (optical detection method) yielded rate constants in aqueous solutions of 10^7 to 10^8 M^{-1} s^{-1} for the reaction of low molecular weight radicals ($\cdot CH_2OH$, etc.) with simple thiols (cysteamine, $H_2NCH_2CH_2$-SH,[9] $HOCH_2CH_2SH$[10]). Radicals of polyethylene oxide (M_w = 20 000) react with cysteamine in aqueous solution with $k_S = 5 \times 10^6$ M^{-1} s^{-1}.[8] It turns out that it is not possible to compare in a straightway manner the value found in this work (1×10^4 M^{-1} s^{-1}) with literature data.

In conclusion it can be seen that pulse radiolysis in connection with the light scattering detection method allows in principal the following of the kinetics of the decay of macroradicals (or other intermediates) whose decay leads to mean chain rupture. It has been pointed out that this holds for all cases where the lifetime of the intermediate is significantly longer than the diffusion time of macromolecular fragments.

References and Notes

(1) Part 3: G. Beck, D. Lindenau, and W. Schnabel, *Eur. Polym. J.*, **11**, 761 (1975).
(2) Part 4: G. Dobrowolski, J. Kiwi, and W. Schnabel, *Eur. Polym. J.*, **12**, 657 (1976).
(3) G. Beck, J. Kiwi, D. Lindenau, and W. Schnabel, *Eur. Polym. J.*, **10**, 1069 (1974).
(4) W. F. Schmidt and W. Schnabel, *Ber. Bunsenges. Phys. Chem.*, **75**, 654 (1971); *J. Polym. Sci., Polym. Symp.*, **No. 42**, 273 (1973); W. Wablat, W. F. Schmidt, and W. Schnabel, *Eur. Polym. J.*, **11**, 113 (1975).
(5) E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973).
(6) A. K. Pikaev, "Pulse Radiolysis of Water and Aqueous Solutions", Indiana University Press, 1967.
(7) G. V. Schulz and G. Henrici, *Makromol. Chem.*, **18/19**, 437 (1956).
(8) A. D. Jenkins, "Advances in Free-Radical Chemistry", Vol. II, G. H. Williams, Ed., Logos Press, London, 1967, p 151.
(9) G. E. Adams, R. C. Armstrong, A. Charlesby, B. D. Michael, and R. L. Wilson, *Trans. Faraday Soc.*, **65**, 732 (1969).
(10) W. Karmann, A. Granzow, G. Meissner, and A. Henglein, *Int. J. Radiat. Phys. Chem.*, **1**, 395 (1969).
(11) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", Wiley, London, 1975, IV-277.