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Real-Time Determination of Ultraviolet Degradation Kinetics of Polymers in Solution

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Real time monitoring of ultraviolet degradation of polystyrene with varying degrees of methylvinyl ketone (MVK) substitutions was carried out. This automated technique is demonstrated to be rapid, accurate and quantitative, yielding the absolute degradation rate constant in terms of number of bonds broken per second per initial g/mol of polymer mass. The MVK substituted heteropolymers yielded degradation rates around two orders of magnitude higher than pure polystyrene, which varied linearly with the percentage of MVK substitution. By the use of an actinometric determination of absorbed flux in the sample, approximate degradation quantum efficiencies of 0.00169, 0.0965, 0.159 and 0.194 were obtained for pure polystyrene and the 5, 10 and 15% MVK substituted copolymers, respectively.

Keywords: Polymer degradation kinetics, light scattering, copolymers, polystyrene

INTRODUCTION

We have found time-dependent static light scattering (TDSLS) to be a useful and efficient means of making real-time determinations of absolute degradation rate constants, and also for making mechanistic and structural deductions about the polymers themselves. Information on degradation

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rates, mechanisms and associated polymer structure is of fundamental importance in such areas as developing degradable materials, extracting and processing biological molecules, testing the durability of new polymers, etc. The mechanisms, chemistry, stabilization and other aspects of polymer degradation have been extensively reported.^[1-3]

While many types of degradation are nonrandom, such as exocyclic enzymatic cleavage and shear degradation, the depolymerization of polymers may often be approximated as random when they are subjected to such agents as acids, bases, enzymes, heat, radiation, etc. The focus in this work is the ultraviolet-induced random degradation of modified polystyrene polymers.

The problem of determining fragment distributions for random and degradation of long-chain polymers was treated by Charlesby^[4] and Kuhn,^[5] and later extended to finite single chains by Montroll and Simha.^[6] The basic theory for angular dependent light scattering intensity as a function of random degradation of an initially monodisperse population of single stranded coils was presented in ref.,^[7] and extensions to include non-ideal effects and polydispersity were given in ref..^[8] Under assumptions of ideality it was possible, in ref.,^[9] to find a polydispersity-independent degradation rate constant. Ref.^[10] developed the characteristic time-dependent scattering 'signatures' for simply branched ('comb') polymers undergoing various types of degradation; sidechain stripping, sidechain random degradation, backbone degradation, and combinations of these. Most recently, a general formalism was presented for determining kinetic rates and making structural determinations about multiply stranded polymers.^[11] An early attempt at monitoring UV degradation of poly(methacrylic acid) with light scattering was made by McDonald and Jellinek.^[12] They were able to make single measurements at 1 h intervals, but were unable to obtain quantitative rate constants and concluded that the complexities of the light scattering technique outweighed its advantages over the standard intrinsic viscosity technique. While the latter technique lends itself well to automation, considerable *a priori* knowledge about the degrading polymer's hydrodynamic properties is needed for quantitative interpretation.

Several commercially available biodegradable polymers rely on a photo-oxidative process to start full biological recycling to carbon dioxide and water. Some widely known trade names like E/CO[®], Ecolyte[®], PolyGrade[®], Plastor[®], etc., are polyethylene or polystyrene, modified

either by copolymerization with a carbonyl derivative, such as carbon monoxide and vinyl ketones, or by addition of photosensitizers, such as ferric salts.^[13] For certain applications, however, addition of photoantioxidants, like metal thiolates^[14] is used to retard the initial phase of degradation. The serviceable lifetime of these materials for a given application will depend on fine tuning the amount of photodegradation. Moreover, these modifications must preserve the mechanical characteristics of the unmodified materials.

Our long-range program involves the development of fine control over the serviceable lifetime of certain types of modified plastics. Specifically, the synthesis of copolymers of styrene and vinyl ketones and the study of its photodegradation in the presence of metal oxidants and stabilizers are being carried out. Of interest are the effects of the percent of vinyl ketone co-monomer, amount and type of added metal complexes on degradability parameters like rate of degradation and size of fragments at long irradiation times. Although the rate at which the molecular weight of such materials is reduced is of prime importance, the final mass of the fragments must also be a parameter of control, since microorganism action is inversely proportional to molecular weight.

Background on TDSLS

When a polymer is broken into two or more fragments, the light scattered from the fragments will, in general, be less than from the intact polymer. The central theoretical problem of TDSLS is to determine how the intensity of light scattered is related to the number of cuts made on a polymer, to how the cuts are made (e.g., randomly), and to the structure of the polymer. The quantity that is needed to find this relationship is the polymer scattering form factor $P(q,r)$, which is a function of both scattering vector q and the average number of cuts r made per original polymer. Once $P(q,r)$ is found from a suitable model then, the scattering can be found for an *initially polydisperse* population, using the well known Zimm equation for the total scattering, with explicit r dependence $I(q,r)$ (expressed as the absolute Rayleigh ratio, which in the CGS system is in cm^{-1}).^[15] In the case of a polydisperse initial population of polymers, with initial concentration distribution $C_0(M)$

$$Kc_o / I(q,r) = c_o / \int_0^\infty MC_0(M)P(q,r(M))dM + 2A_2c_o \quad (1)$$

where c_0 is the total initial polymer concentration in g/cm^3 , and $C_0(M)dM$ is the initial concentration of polymer within the mass interval M to $M + dM$. Here q is the usual scattering wave vector amplitude, given by

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2) \quad (2)$$

where n is the pure solvent refractive index, λ the wavelength in vacuum, and θ the scattering angle. K is an optical constant given, for vertically polarized light, as

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A} \quad (3)$$

where dn/dc is the differential refractive index and N_A is Avogadro's number. It does not change during the course of degradation. A_2 is the second virial coefficient ($\text{cm}^3\text{-mole}/\text{g}^2$). In principle, A_2 is a function of polymer mass, and hence can change in a complicated way in time. The effects of a changing A_2 on light scattering by single strand polymers were considered in ref.^[8] It was found experimentally in this work, that the $Kc/I(q,t)$ vs. t curves for different c_0 superpose to within an additive constant of $2A_2c_0$, and multiplicative transformation of the time axis (see Results and Discussion) which justifies taking this latter term as time-independent.

Ref.^[11] provides a general formalism for finding $P(q,r)$: Consider r average cuts, which are introduced into a linear polymer in any fashion at all. The monomers on the polymer are labeled from 1 to N . The probability that the polymer segment between monomers i and j is still intact can be represented by $W(r,i,j)$,^[11] and then $P(q,r)$ is found by

$$P(q,r) = (1/N^2) \sum_{i=1}^N \sum_{j=1}^N W(r,i,j) \ll \exp(-i\vec{q} \cdot \vec{r}_{ij}) \gg \quad (4)$$

This procedure weights the double sum over all polymers by the probability that monomers i and j are still connected after r cuts. If they are no longer connected, the resulting fragments are presumed to diffuse away from each other, leaving no phase correlation between monomers on separate fragments.

For random degradation of random coil polymers, as can occur, for example, with ultraviolet radiation, $P(q,r)$ turns out to be the Debye function $D(u)$ whose traditional argument of $u = q^2 \langle S^2 \rangle_0$ is translated by r ,

$$P(q, r) = D(u) = \frac{2}{u^2} [e^{-u} - 1 + u], \quad u = q \langle S^2 \rangle_0 + r \quad (5)$$

where $\langle S^2 \rangle_0$ is the initial mean square radius of gyration of the undegraded polymer of any initial mass M .

The result that $P(q, r)$ is the Debye function leads to two immediately interesting limiting cases. Namely, if $u > 3$, $P(q, r)$ reaches a linear asymptote such that for random degradation of a single strand ideal coil of any initial polydispersity and initial number average mass $M_{n,0}$

$$Kc_o / I(q, \beta) = 1/2 M_{n,0} + \beta/2 + \gamma q^2 / 2 + 2A_2 c_o \quad u > 3 \quad (6)$$

where β is the number of cuts per original g/mol of polymer mass, and γ is a constant for a given type of ideal coil polymer which relates $\langle S^2 \rangle$ to M via $\langle S^2 \rangle = \gamma M$. We focus on the determination of β and its time derivative $\dot{\beta} (\equiv \partial \beta(t) / \partial t)$, for characterizing degradation rates. β and $\dot{\beta}$ have the virtue of being independent of polydispersity so that for any given polymer initial mass M , the average number of cuts made on it is

$$r = \beta M \quad (7)$$

For many degradation reactions the reaction rate and $\dot{\beta}$ will be constant as long as the number of scissile bonds is large compared to r . Then

$$\beta = \dot{\beta} t \quad (8)$$

This means that as long as $\dot{\beta}$ is constant, $Kc/I(q, t)$ vs. t will be linear. $\dot{\beta}$ is determined simply by the asymptotically linear portion of $Kc/I(q, t)$ according to

$$\dot{\beta} = 2 \frac{\partial (Kc_o / I(q, t))}{\partial t} \quad u > 3 \quad (9)$$

Significantly, in this limit, $\dot{\beta}$ is independent of initial polydispersity, the virial coefficient and any of the initial mass averages.^[9] This limit is reached for random coils for any combination of $q^2 \langle S^2 \rangle$ and r such that $u > 3$, whereas this limit will apply to *any* linear polymer in the $q = 0$ limit, regardless of shape, excluded volume, etc.; that is, it suffices to run the reaction until $r > 3$ to reach the limit in this case. This result for the $q = 0$ limit was pointed out by Thomas and Doty.^[16] While Equation (6) without the β dependence is known as the 'high q -limit' for classical scattering

from random coils, it is interesting to point out that even for very small random coils, and/or at $q = 0$ the Debye function will be traced out in *time* as degradation proceeds, rather than in q^2 as is classically the case.

The second limiting case is when $u < 1$, which will apply for early degradation times near $q = 0$ for all linear polymers of any size and shape, or at early times at any accessible value of q for small molecules where $q^2 \langle S^2 \rangle \ll 1$. This limiting case was termed the 'kinetic Guinier regime',^[11] because it parallels in time what the low-angle Guinier approximation follows in q^2 .

$$\frac{Kc_0}{I(q,t)} = \frac{1}{M_{w,0}} \left[1 + \frac{q^2 \langle S^2 \rangle_{z,0}}{3} + \frac{M_{z,0}}{3} \beta(t) \right] + 2A_2c_0 \quad (10)$$

where $M_{w,0}$ and $M_{z,0}$ are the initial weight and z-averages of the polymer population and $\langle S^2 \rangle_{z,0}$ is the initial z-average mean square radius of gyration. Hence, in this limit the initial reaction rate $\dot{\beta}(0)$ is computed by the initial slope of $Kc_0/I(q,t)$ by

$$\dot{\beta}(0) = \frac{3M_{w,0}}{M_{z,0}} \frac{\partial [Kc_0 / I(q,t)]_{t=0}}{\partial t} \quad u \ll 1 \quad (11)$$

Again, $\dot{\beta}(0)$ is independent of A_2 , and polymer conformation and excluded volume effects, and is itself independent of initial polydispersity, although there is a (simple) dependence on the initial polydispersity.

Since $\dot{\beta}$ is not constant in the case where the number of bonds broken is not much smaller than the total number of scissile bonds, the time dependence of $\dot{\beta}$ must be considered. For the case of random degradation by UV, the polymer bonds will be cut in a first-order reaction dependent on the incident light intensity, so that the total number of intact, scissile bonds B , on an original polymer decreases according to,

$$\frac{dB}{dt} = -kB \quad (12)$$

where k is a degradation rate constant per scissile bond which depends on the rate of absorption of UV photons and the quantum efficiency for photolysis. Then,

$$B(t) = B_0 e^{-kt} \quad (13)$$

where B_0 is the initial total number of uncut bonds. The average number of cuts per initial polymer is simply

$$r(t) = B_0[1 - e^{-kt}] \quad (14)$$

where B_0 is the original number of scissile bonds in a polymer. Hence, when a degradation reaction is measured over long enough times for non-linearity (downwards curvature) in $Kc_0/I(q,t)$ vs. t to become apparent, Equation (14) will be appropriate for fitting in conjunction with Equation (1) for $Kc_0/I(q,r)$.

Finally, it is important to point out that in most previous cases the final fragment sizes of the degradation product were much smaller than the initial polymers themselves, so that the final scattering due to endproducts was negligible. This amounts to neglecting the $j = i$ (self) terms in Equation (4). In this work, however, because the final fragment distribution is governed by the amount of scissile linker (methyl vinyl ketone in this case), the final fragments may still scatter significantly. Under the assumption of equal final fragments small enough that $P(q) = 1$, the following approximation is derivable from Equation (5)

$$P(q, r) = \frac{\delta + D(u)}{1 + \delta} \quad (15)$$

where the Debye function $D(u)$ and the relation of u to q and r are given in Equation (5). Here δ is the reciprocal of the number of final fragments, given by

$$\delta = \frac{1}{fN + 1} \quad (16)$$

where f is the fraction of scissile monomers in the heteropolymer of N total monomers. In this case, determining $\dot{\beta}(0)$ from the initial slope gives

$$\dot{\beta}(0) = \frac{3M_{w,0}}{M_{z,0}(1 + \delta)} \frac{\partial[Kc_0 / I(q, t)]_{t=0}}{\partial t} \quad (17)$$

$\dot{\beta}(0)$ can also be used to estimate the quantum efficiency of bond cleavage ϕ . In comparing the degradability of a polymer ϕ is of central importance. The quantum efficiency of bond scission is defined as

$$\phi = \# \text{ of bonds broken / photon absorbed.} \quad (18)$$

This given by

$$\phi = \dot{\beta}(0) V c_0 N_A / \Phi \quad (19)$$

where V is the volume of polymer solution being irradiated and Φ is the number of photons absorbed per second.

Materials and Methods

TDSLS measurements were made with a Wyatt Technology Dawn-F DSP light scattering photometer (Santa Barbara, CA). The flow cell was used, permitting the scattering to be measured simultaneously from 16 angles, ranging from 26° to 145° . Data were transferred via an RS-232c line to a microcomputer. One of the authors (WR) wrote software for data acquisition and analysis.

Raw scattering voltages at each angle q and time point t $V(q,t)$ were transformed to absolute time-dependent Rayleigh ratios $I(q,t)$ according to

$$I(q,t) = \frac{V(q,t) - V_s(q)}{V_a(q_r) - V_d(q_r)} N(q) I_a F \quad (20)$$

where $V_s(q)$ is the solvent scattering voltage at wave vector q , $V_d(q_r)$ is the voltage at a reference wavevector q_r (here taken as that corresponding to $\theta = 90^\circ$) of the absolute calibration solvent, which in this case was toluene, with a known absolute Rayleigh scattering ratio at $T = 25^\circ\text{C}$ of $I_a = 0.00001408 \text{ cm}^{-1}$. $V_d(q_r)$ is the photodetector dark count at the reference wavevector. F is a geometrical correction factor which, for longitudinal, cylindrical flow cell of the Dawn F , amounts to the ratio of the refractive index of the sample solvent to that of toluene (and approximately to this factor squared for upright cylindrical 'batch' cells), divided by the total Fresnel reflection losses at the glass/solvent interface. $N(q)$ is the normalization factor for each photodiode which is computed according to

$$N(q) = \frac{V_n(q_r) - V_s(q_r)}{V_n(q) - V_s(q)} \quad (21)$$

where $V_n(q_r)$ is the scattering voltage of the normalization solution in the sample solvent at the reference wavevector. The normalization solution is composed of an isotropic scatterer in the sample solvent. In this case a solution of PS of $M_w = 4,000$ at 15 mg/mL in THF was used as the normalizing solution.

Toluene, tetrahydrofuran (THF) and methanol were of HPLC grade (Merck). Styrene (Dow Chemical Co., Milwaukee, WI) and methyl-

vinylketone (MVK; Aldrich Chemical Co., Milwaukee, WI) were freshly distilled prior to use. 2,2'-azobis-isobutyronitrile (AIBN) was recrystallized from methanol. The copolymers of styrene and MVK were prepared by radical polymerization,^[17,18] starting with 5, 10 and 15% in molar fraction of the ketone to yield respectively, MVK5, MVK10 and MVK15 copolymers, as referred to in this work. The procedure for the polymerizations was, typically, 12.5 g (0.24 mols) of styrene, 0.42 g (0.012 mols; 5% in molar fraction) of MVK and 0.16 g of AIBN were added to 12.5 g of distilled toluene. The solution was degassed by four freeze-pump-thaw cycles, the ampoule was sealed under vacuum and heated at 70°C for 48 h. The product was isolated by addition of methanol, redissolved in toluene and, again, precipitated with methanol, dried under vacuum to give yields of approximately 90% of MVK5.

The incorporation of MVK in the polymers were evidenced by the carbonyl absorption at 1712 cm^{-1} in the infrared spectra (Perkin Elmer FT-IR 1750 and Nicolet FT-IR 510) using KBr pellets for the intact heteropolymers and in NaCl pellets for the photoproducts. Elemental analysis of the products (12 samples of each product) showed distinct proportions for MVK incorporation, as shown in Table I. These measurements were made with Perkin Elmer Elemental Analyzer 2400 CHN, in which the sample is heated to 925°C in presence of pure oxygen, with production of CO_2 , H_2O and NO_2 , after which these products pass through a separation column and are detected by thermal conductivity. The level of carbon was obtained from CO_2 and the level of oxygen from the H_2O .

M_w and A_2 values were obtained by 'batch' light scattering in upright, cylindrical cells, using the standard Zimm plot method, with concentrations ranging from 1–15 mg/mL. The angular variation of the heteropolymers was too slight for accurate determination of mean square radius of gyration. This latter quantity, at any rate, is not important for the degradation kinetics of interest. The value of dn/dc was taken as 0.21 mL/g for polystyrene homopolymer in THF at 20°C and used for all polymers.^[19] Table I sum-

TABLE I Characteristics of the PS homopolymer and PS/MVK heteropolymers.

Polymer	MVK%	$M_{w,0}$	A_2 ($\text{cm}^3\text{-mol/g}^2$)	ϵ (mL/mg-cm)*	# of fragments
PS	0	107,700	7.96e-4	1.73	xx
MVK5	6.1 ± 0.7	42,700	1.1e-3	2.01	26
MVK10	11.5 ± 1.2	45,200	1.2e-3	1.89	51
MVK15	13.7 ± 0.9	42,100	1.2e-3	2.11	56

*at $\lambda=254\text{nm}$.

marizes the main features of the polymers used, including the extinction coefficient at $\lambda = 254\text{nm}$ and the number of final fragments due to MVK substitution, considering a monomer mass of 104 g/mol . Unfortunately, no chromatography data were available for assessing the degree of initial polydispersity of the material.

A quartz reaction vessel containing 50mL of the polymer solution, filtered through $0.22\text{-}\mu\text{m}$ Teflon membrane (Millipore Corp., Bedford, MA) with magnetic stirring was set inside of three 4 w circular low-pressure mercury lamps (99.5% of emission at 254 nm) set inside a cylinder with silvered walls. An HPLC pump (600E gradient module, Waters Corp., Milford, MA) provided a continuous pumping rate of 1mL/min through a closed loop; from the reaction cell the solution was led through a dust filter (2-cm precolumn for GPC, $25\text{-}\mu\text{m}$ of porosity, Phenogel-5 guard column, $50 \times 7.8\text{mm}$) to the Wyatt Dawn-F flow cell and back. The amount of solution circulating through the system exterior to the reaction cell was about 17 mL giving an initial dead time of close to 1000 s before photolyzed material entered the scattering detector. The solution was kept at room temperature by forced ventilation.

The photon flux in this irradiation system was determined for actinometry using malachite green leucocyanide, according to Johns^[20] and the malachite green cation formation was monitored by measuring light absorption at 618 nm .

RESULTS AND DISCUSSION

Figure 1 shows typical ultraviolet degradation curves for the four polymers used. Concentrations for all were 0.010 g/cm^3 . The data shown are raw scattering voltages from $\theta = 90^\circ$ transformed into Rayleigh scattering ratios via Equation (20), and represented as $Kc_\theta/I(t)$. No data smoothing was used, and the individual points shown are noise-free enough that they appear as virtually solid lines. The initial 840 s of dead time, the period it takes for degrading polymer to first reach the scattering cell from the reaction vessel, has been eliminated in each.

It is immediately striking that the PS/MVK copolymers degrade extremely rapidly compared to pure PS, which is almost a flat line at the bottom of the figure. Furthermore, the initial slopes, which by Equation (11) (and Eq. (17)) are proportional to the initial scission rates, are seen to

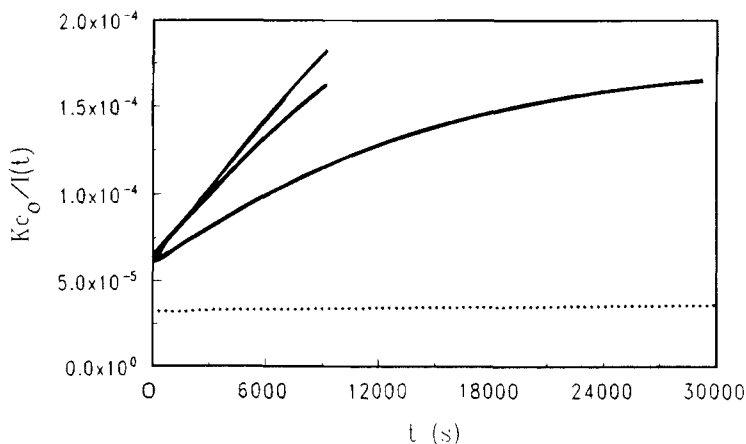


FIGURE 1 $Kc_0/I(q,t)$ vs. t for the ultraviolet degradation of PS, MVK5, MVK10 and MVK15, shown from bottom to top, respectively. All data are from $\theta = 90^\circ$ and for $c_0 = 0.010 \text{ g/cm}^3$.

increase in the order of increasing MVK substitution. The data for MVK5 were collected over a long enough period that significant curvature is seen. The origin of this is discussed below. For the shorter time scale over which they were measured, MVK10 shows little curvature, and MVK15 is virtually a straight line.

Figure 2a shows the initial, linear portion of each curve in Figure 1. The initial dead-time has not been eliminated in these curves. Also, individual data points can be discerned, which show how little noise is present. This stands in contrast to similar experiments in aqueous solution, in which noise levels are typically pronounced.

From the initial linear portions of the curves in Fig. 2a the rate constants $\dot{\beta}(t=0)$ are computed according to Equation (17). We note that the factor δ in $1/(1 + \delta)$ is quite small, amounting to 0.038, 0.02 and 0.018, for MVK5, MVK10 and MVK15, respectively. Since no polydispersity data were available, the rates shown are uncorrected for the polydispersity factor $M_{w,0}/M_{z,0}$ in Equation (17). For a typical polymerization with a most probable distribution, the correction factor would be $2/3$ times the uncorrected values. These uncorrected rates, averaged over the 16 detection angles, are shown in Table II. There being no angular dependence to the scattering, the rate constant was virtually the same at each angle, and the standard deviation from averaging rates over 16 angles was always less than 1%. It can

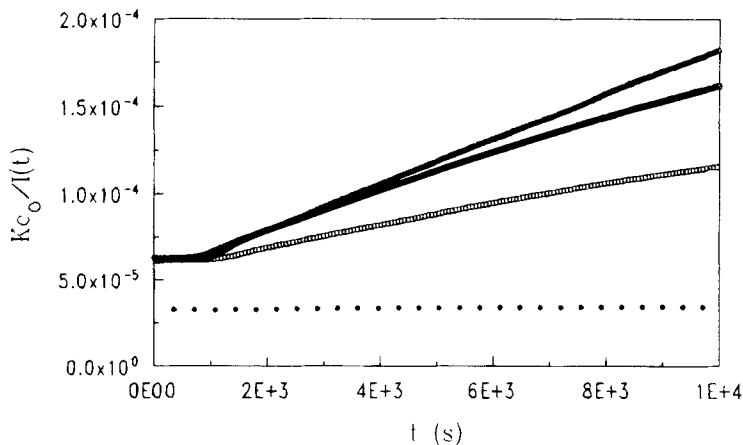


FIGURE 2a Short-time behavior of $Kc_0/I(t)$ for the data from Figure 1, from which the initial degradation rates $\beta(0)$ in Table II are determined. In this graph individual data points can be discerned.

be seen in these short time curves that there is a short, initial transient curvature which follows the dead time period, probably due to mixing, before each curve becomes unambiguously linear.

Figure 2b shows the long-term degradation behavior of PS, from which the rate constant in Table II was determined. Strikingly, the rate constant

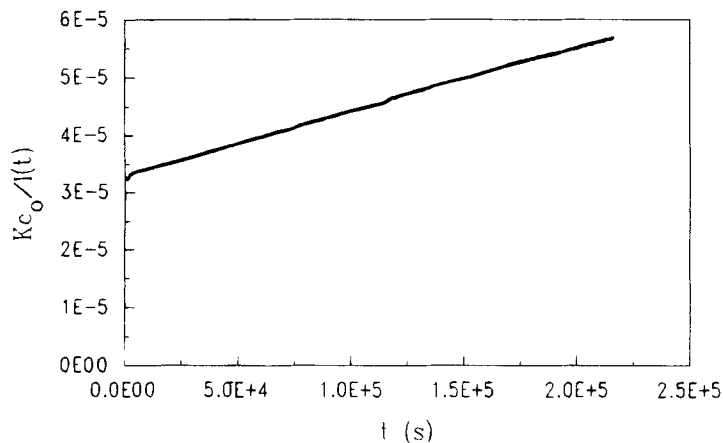


FIGURE 2b Long-term degradation behavior of PS, from which the degradation rate in Table II is determined.

TABLE II Initial degradation rate constants and quantum efficiencies from linear and non-linear fits, uncorrected for polydispersity (see Eq. (17)).

Polymer	PS	MVK5	MVK10	MVK15
$\dot{\beta}(0)$ (cuts/(g/mol)-s), from initial slope, Equation (17)	3.37×10^{-10}	1.93×10^{-8}	3.18×10^{-8}	3.88×10^{-8}
$\dot{\beta}(0)$ from nonlinear fit and Equation (22)	*	1.88×10^{-8}	2.58×10^{-8}	2.80×10^{-8}
ϕ (quantum efficiency of bond scission)	0.00169	0.0965	0.159	0.194

*nonapplicable, data is linear.

for the PS/MVK polymers range from about 60 to over 100 times higher than pure PS. Hence, in these fits and the following, the degradation rate of the pure PS portions of the copolymers was neglected compared to the MVK portion degradation rate.

As mentioned, the downwards curvature in $Kc_0/I(t)$ for MVK5 is quite pronounced, and would undoubtedly have shown up more clearly if the runs for MVK10 and MVK15 had been extended in time. The main reason for the curvature is an exponentially diminishing first order rate constant in time (Eq. (14)). The existence of finite end products rather than monomers can also contribute to the curvature according to Equation (15). For the polymers in this study, however, this latter effect is expected to be small.

In principle, an increasing A_2 with decreasing fragment sizes could also lead to downwards curvature in $Kc_0/I(t)$. To investigate this possibility a kinetic run with MVK15 at five times less concentration ($c_{2,0} = 0.002$ g/cm³) than the usual ($c_{1,0} = 0.010$ g/cm³) was made. The $\dot{\beta}(0)$ computed from this run was about five times higher than that for the high concentration run. This is reasonable since at these relatively low concentrations the quantum efficiency of bond scission should be at least approximately independent of concentration, so that $\dot{\beta}(0) c_0$ should be a constant (Eq. (19)). Furthermore, $Kc_{1,0}/I(q,t)$ was completely superposable on $Kc_{2,0}/I(q,t') + b$, where $b = 2A_2(c_1 - c_2)$ and $t' = c_1/c_2$. It can be shown (author's notes) that for a constant quantum efficiency, $\partial A_2(t) / \partial t$ must be zero in order for the superposability of this transformation to obtain. Hence an increasing A_2 as degradation proceeds is excluded as the cause of the curvature.

Nonlinear least-squares fits for the three heteropolymer curves of Figure 1 were made to Equation (1) using the $P(q,r)$ of Equation (15) and the exponential time-dependence of $r(t)$ from Equation (14). The adjustable parameters taken were k and B_0 , although, in principle, this latter is known.

The fits are included in Figure 1, but run so closely through the points that they can't be seen. Because nonlinear fits with several parameters usually will closely match the data to be fit, we do take the extremely close match of the fits in Figure 1 as good evidence for the model, but not as a proof of it. Table II includes the initial rate constants from these fits, which are obtained from the fitting parameters according to

$$\dot{\beta}(0) = kB_o / M_o \quad (22)$$

with $M_o = M_{w,o}$ taken from Table I. This latter step introduces additional error since the experimental Zimm plot values for $M_{w,o}$ are used. Additionally, initial polydispersity considerations are not taken into account. The agreement for $\dot{\beta}(0)$ for MVK5 between the linear and nonlinear fits is excellent, but is less good for MVK10 and MVK15, probably due in part to the fact that these latter curves have very little nonlinearity to fit to. Besides the use of multiple parameters in a non-linear fit, it is also necessary to use the value of $2A_2c_o$ in Equation (1), which adds further error. Hence, the preferred method of obtaining the rate constants is by the initial slope of $Kc_0/I(q,t)$ vs. t , for which the $2A_2c_o$ factor is irrelevant, and for which the only fitting parameter is the slope.

Figure 3 shows a plot of the initial rate constants $\dot{\beta}(0)$ from both the linear fits and the full nonlinear model fit vs. the percentage of MVK substi-

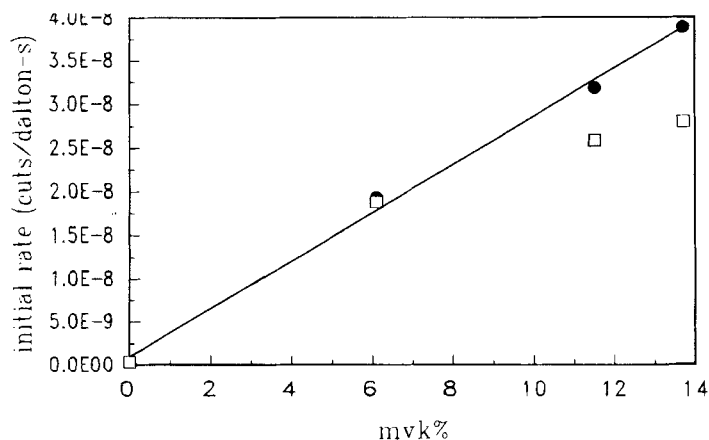


FIGURE 3 Initial degradation rates, $\dot{\beta}(0)$ vs. percentage of MVK substitution, from both initial fits linear fits (●) and full non-linear model (□).

The rate constants are quite linear in percentage of MVK substitution, as expected. Under the experimental conditions used, these rates yield, for a starting polymer of $M = 50,000$ g/mol, 0.06, 3.47, 5.72 and 6.98 cuts per h for PS, MVK5, MVK10, and MVK15, respectively.

Figure 4 shows a direct plot M_w vs. t for each of the degradations, obtained from averaging the 18 angular $Kc_0/I(q,t)$ points, since there was no angular dependence and using

$$1/M_w(t) = Kc_0/I(\text{ave. over all } q, t) - 2A_2c_0 \quad (23)$$

Although this is a useful, and perhaps more familiar representation for seeing the progress of the degradation, we prefer the $Kc_0/I(q,t)$ representation since it immediately yields the rate constants.

An estimate of the number of cuts per absorbed photon (quantum efficiency) was made on the basis of actinometric data. The photon flux was found to be 1.0×10^{-7} Einsteins/s within the volume of the irradiation cell. This gives a flux of $\Phi = 6 \times 10^{16}$ photons absorbed per s. With $E = hc/\lambda$, where h is Planck's constant and c the speed of light, this corresponds to 0.047 W absorbed by the sample. The three lamps had a combined, nominal (manufacturer's) power of about 4.2 W. Approximating the cylinder containing the lamps as a cavity of uniform power density, and taking the ratio of the irradiation cell volume (8.83×10^4 mL, this being a cylindrical sleeve of height 45 mm and diameter 50mm, containing the 33mL of solu-

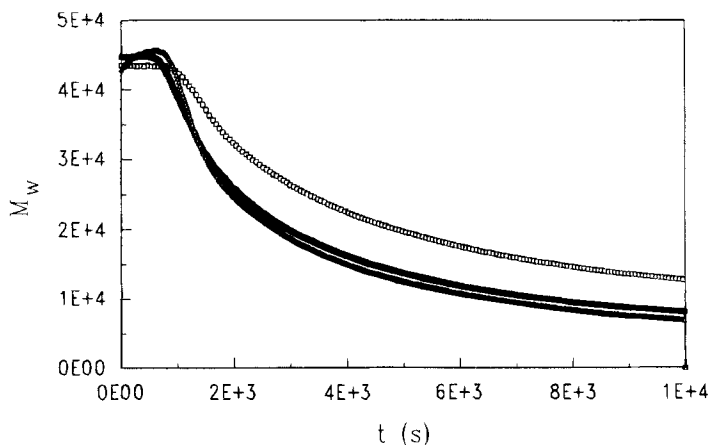


FIGURE 4 Corresponding polymer mass profile vs. t for the same experiments as in Figure 1.

tion in it at any given time.) to the volume of the cavity (1.5×10^6 mL) yields a hypothetical absorbed flux in the sample of 0.247 W. The measured value is 5 times lower, but this is probably reasonable considering decay of the lamps from original specifications, cavity losses through the open bottom and top of the cylinder and reflection losses at the irradiation cell surface.

For the extinction coefficients in Table I, and polymer concentration of 0.010 g/mL, it is clear that all the incident UV flux is absorbed in a very thin layer of solution in the reaction vessel. For MVK5, for example, 99% of the incident flux is absorbed in the first 1mm of the solution. Constant stirring of the solution in the irradiation vessel was hence essential. With these parameters and $V = 50 \text{ cm}^3$, this leads to the values of ϕ (using Eq. (19)) given in Table II. These values are intended as estimates only, the major sources of error in them being the polydispersity correction factor and the value of Φ used in Equation (19). They compare quite favorably to quantum efficiencies of 0.15 and 0.20 for similar MVK polymers reported in ref.^[21]

SUMMARY

The feasibility of making real-time determinations of absolute degradation kinetics for polymers in solution subjected to ultraviolet has been demonstrated. The technique is automated and rapid, and requires no intervention while measurements are being made. Because the theory predicts, within the approximations discussed, and the data show that there is no angular dependence in computing the rate constants, it would be sufficient to measure the time-dependent scattering intensity at a single angle. Thus, a full multirange scattering instrument such as the Dawn-F is not a critical requirement, and much simpler systems, such as a single fixed detector, or even a spectrofluorimeter, could be used.

Although a plausible explanation for the curvature in $Kc_0/I(t)$ is presented and successfully fitted, the linear fits to the initial slope of $Kc_0/I(t)$ provide the simplest and most accurate means of determining initial degradation rates. Degradation rates for the MVK containing copolymers were increased by a factors of 60 to over 100 compared to pure PS, and varied linearly with the percentage of MVK substitution. An actinometric determination of the photon flux absorbed by the sample allowed computation of the quantum

efficiencies of degradation for each polymer (bonds broken per absorbed photon). Future use will include determination of degradation rates for different percentages and sequences of the methylvinyl ketone monomers, and in the presence of catalysts such as oxygen and heavy metals.

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