elasticity has been assumed together with a single relaxation time instead of a relaxation spectrum in each of the two time scale regions. However, it shows that the essential features correspond to a model in which the contributions of trapped and untrapped entanglements are represented.

The first time constant, τ_1, is 3×10^2 s at 0 °C. This is nearly 10^2 larger than the longest relaxation time in the transition zone, corresponding to configurational rearrangement of an average strand between two entanglement loci; the latter can be estimated by applying the Rouse–Mooney theory[12] to viscoelastic measurements of Sanders[13] on a polybutadiene with 91.5% vinyl and correcting for the difference in microstructure by the free volume equation used by Rhee and Ferry,[14] and finally applying an experimentally determined shift factor from 25 to 0 °C. The difference may be partly due to the cyclization of vinyl groups which occurs in irradiation[15] and presumably stiffens the molecule as well as altering the free volume. It seems reasonable that the time scale of the first stage of the retraction is set by configurational rearrangements of strands between entanglements, whether trapped or untrapped (for low R_0', the cross-links are greatly outnumbered). The second time constant, 10^6 s, is reasonable compared with the very slow relaxation times observed in lightly cross-linked conventional networks and attributed to untrapped entanglements of branched structures.

Another 1,2-polybutadiene with 88% vinyl, number-average molecular weight 236 000, T_g −18 °C (polymer B[3]), was studied similarly over a range of R_0' from 0.013 to 0.200. The retraction curves were similar in shape to the bottom curve in Figure 1, but with no reversal. The retraction at 0 °C was more rapid than that of polymer C at similar R_0', because of the lower T_g, but the rate diminished rapidly with decreasing R_0'. Because of the higher molecular weight, a lower ν_x is required to correspond to a given γ which determines T_e, upon which in turn the presence of dangling branched structures depends. But a small ν_x means a small R_0' and λ_s is only slightly larger than 1, so a minimum below λ_s would be difficult to detect.

The result of relaxation of untrapped entanglements is somewhat analogous to that of a sequence of operations discussed by Flory,[16] in which two stages of chemical cross-links are introduced, first in the unstrained state and then in a state of strain, and some of the first-stage cross-links are subsequently removed. The predictions of Flory for λ_s under these circumstances (corresponding to neo-Hookean stress–strain relations) have been numerically evaluated for some specific cases.[5] Comparison with the bottom curve of Figure 1 is not successful, however; given the known total concentration of entanglements, the correct λ_s is predicted by the Flory theory only for much larger values of ν_N and ν_x than are actually found. The discrepancy probably arises from the assumption in the theory that the initial molecular weight is infinite; i.e., molecular ends are not taken into account.

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Determination of Radiation Damage in Isotactic Poly(methyl methacrylate) by X-ray Diffraction

R. P. KUSY* and A. R. GREENBERG

Dental Research Center, University of North Carolina, Chapel Hill, North Carolina 27514. *Received May 30, 1978*

When a polymer is exposed to ionizing radiation, both chemical and physical changes occur. Previously chemical changes have been monitored via quantitative gas analyses,[1] sol–gel partition,[2] free-radical scavenging techniques,[3] or intrinsic viscosity determinations,[4,5] while the total damage has been measured by cryoscopy.[6,8] This note presents X-ray diffraction data on semicrystalline isotactic poly(methyl methacrylate) (PMMA) that verify the magnitude of radiation damage observed previously by the melting point depression technique.[7,8] On the assumption that the probability of radiation-induced changes are equivalent in both crystalline (x_c) and amorphous fractions, a value for G(–units) $\approx$ 15 results from the relative decrease in crystallinity as a function of dose.

Two batches (A and B) of amorphous stereoregular PMMA were crystallized from 4-heptanone and outgassed under vacuum.[9,10] Additionally batch B, which had been heat treated for 2.5 h at 120 °C, was subdivided and heated for 48 h at 100 °C (designated batch B-1). All powders were irradiated *in air* at 30 °C using a Cs-137 γ-ray source at a dose rate of 0.80 Mrad/h. Crystallinity of all powders was measured with a Philips Norelco diffractometer in the reflection mode with stabilized Cu Kα radiation at 35 kV and 20 mA. As reported earlier,[8] several precautions were taken to insure an invariant baseline over the range, 2θ = 5–25°. All data were analyzed by a modified method of Hermans and Weidinger[11,12] whereby a correction was employed for any shifts that might occur to the amorphous halo as a function of dose.[13]

Table I summarizes the results of the present experiments. As was done on isotactic PMMA previously,[8] the heights of three crystalline reflections were scaled off the X-ray scans: 2θ = 8.8, 14.5, and 17.2°. Rather than analyzing these peaks individually, however, they were summed since a more reliable data base resulted by accumulating the crystalline (I_c) and amorphous (I_a) intensities on a per scan basis. Results of the regression of I_c on I_a are illustrated in Figure 1. From the intercept, which represents x_c = 1.0 ($\sum I_c$ = 302; cf. Table II), the x_c of each sample was determined, the maximum of which equalled 0.69 (cf. Table I). When x_c was plotted against dose (D) for each batch (Figure 2), three regression lines resulted having slopes of -1.09×10^{-3}, -3.16×10^{-4}, and

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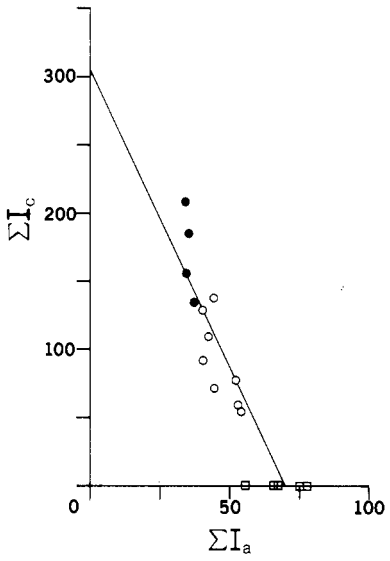

Figure 1. Regression of $\sum I_c$ on $\sum I_a$ for 2θ = (8.8°, 14.5°, 17.2°): ●, ○, and □ represent batches A, B, and the amorphous material, respectively.

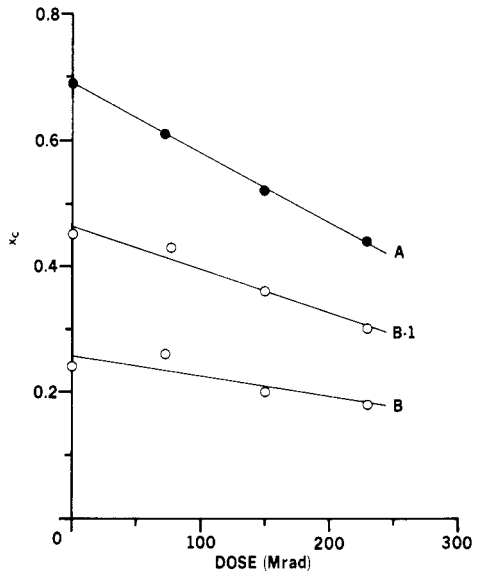

Figure 2. Influence of radiation exposure on the crystalline fraction for three semicrystalline preparations: x_c = 0.24, 0.45, and 0.69.

Table I
Summary of Experimental Results

batch	dose, Mrad[a]	ΣI_a	ΣI_c	x_c	$(1 - X)$
A	0	34.4	208.1	0.69	
	72	36.0	185.5	0.61	0.12
	150	34.9	156.1	0.52	0.25
	230	37.4	134.1	0.44	0.36
B	0	44.0	71.5	0.24	
	72	52.2	77.8	0.26	−0.08
	150	53.3	59.2	0.20	0.17
	230	54.2	55.3	0.18	0.25
B-1	0	43.5	137.0	0.45	
	77	40.6	129.4	0.43	0.04
	150	42.4	108.6	0.36	0.20
	230	40.5	90.5	0.30	0.33
amorphous	0	56.5	0	0	
	58	66.7	0	0	
	150	67.8	0	0	
	230	76.3	0	0	
	290	78.0	0	0	

[a] 1 Mrad = 10^6 rad.

-6.81×10^{-4}, respectively (cf. Table II). Since these slopes are only proportional to the damage in the crystalline regions, account of the amorphous regions must be made. On the assumption that the damage is independent of the degree of long-range ordering, normalization to $x_c = 1.0$ can be made:

$$|\text{slope}|/\text{intercept} = \left(\frac{x_{c_0} - x_{c_F}}{D}\right) \Big/ x_{c_0} = \frac{1 - X}{D} \quad (1)$$

where x_{c_F}/x_{c_0} equals the fraction of undamaged units, X. By inspection eq 1 is easily related to the definition of

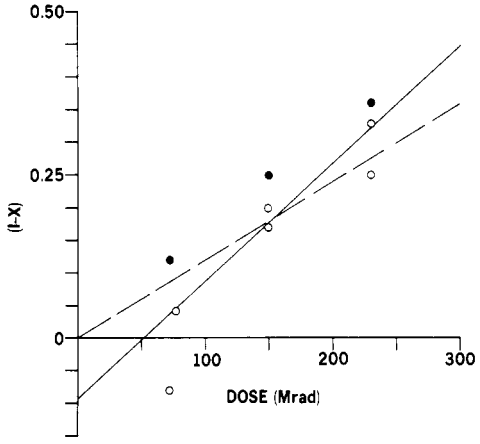

Figure 3. Relationship between radiation exposure and the mole fraction of units damaged.

G(−units), i.e., the number of units of polymer damaged per 100 eV of energy, or

$$G(\text{-units}) = \frac{(1 - X)}{D} \frac{N}{M} \frac{10^2}{6 \times 10^{19}} \quad (2)$$

where N, M, and 6×10^{19} are Avogadro's number, the molecular weight of the repeat unit, and the conversion factor from Mrad to eV/g, respectively. For the present polymer,

$$G(\text{-units}) = (1 - X)10^4/D \quad (2a)$$

Substitution of the appropriate values into eq 2a yields G(−units) = 15.8, 12.3, and 14.7 for batches A, B, and B-1. Corresponding correlation coefficients and levels of significance are shown in Table II. For such small sample

Table II
Statistical Analyses of Results

figure	linear regression analysis	sample correl coeff, r	no. of data points, N	level of significance, P
1	$\Sigma I_c = 302 - 4.34\Sigma I_a$	0.90	17	0.001
2, batch A	$x_c = 0.689 - 0.00109D$	0.99	4	0.001
2, batch B	$x_c = 0.256 - 0.000316D$	0.86	4	0.1
2, batch B-1	$x_c = 0.463 - 0.000681D$	0.98	4	0.05
3, solid line	$(1 - X) = -0.0946 + 0.00183D$	0.89	9	0.01
3, dashed line	$(1 - X) = -0.0232 + 0.00148D$	0.91	8	0.01

populations ($N = 4$), it would be advantageous to increase the data base, e.g., by compounding the batches. Figure 3 illustrates these results when $(1 - X)$ is computed for each batch/dose combination (cf. Table I). The regression plot for this case (solid line) has a slope which equals 18.3×10^{-4} such that $G(-\text{units}) = 18.3$ (eq 2a). Discarding the wild point at (−0.08, 72) yields $G(-\text{units}) = 14.8$ for an $r = 0.91$ and a $P = 0.01$ (Table II).

These experiments indicate that $G(-\text{units}) \approx 15$, in good agreement with a cryoscopic technique[7,8] in which $G(-\text{units}) = 12$ (cf. dashed line, Figure 3). Both G values differ from $G(\text{fractures}) = 1.7$, obtained either by gas analysis[14] or by molecular weight measurements.[4,5,7,15] The present viewpoint is that both sets of results are correct, the former measuring both the chemical and physical damage while the latter measuring only chemical changes. In the case of isotactic PMMA, the difference in $G(-\text{units})$ is attributed to physical damage associated with radiation-induced racemization.[15] Thus the present case graphically shows that significant damage can result in the solid state, which by more established methods might otherwise go undetected. These preliminary X-ray data verify the magnitude of that damage.

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Some Comments on the Kinetics of Cationic Polymerization of Tetrahydrofuran

M. SZWARC

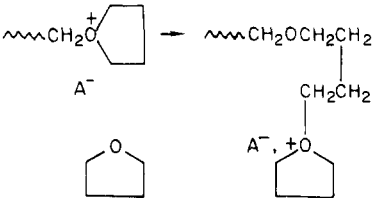
Department of Chemistry, State University of New York, College of Environmental and Science, Syracuse, New York 13210. *Received June 8, 1978*

The kinetics of cationic polymerization of tetrahydrofuran was studied by numerous workers[1–10] in the bulk and in various solvents. The polymerization is reversible, and under proper conditions its termination may be avoided, at least within the period of the experiments. Hence, the resulting polymers are living and the system tetrahydrofuran–(monomer THF) living poly(tetrahydrofuran) attains a state of equilibrium when the concentration of the monomer reaches the equilibrium value $[\text{THF}]_e$ that depends on temperature and the composition of the system.

For a rapid and quantitative initiation only the propagation contributes to the monomer's consumption at later stages of polymerization. Indeed, all the investigators found the rate of the reaction, $-\text{d}[\text{THF}]_t/\text{d}t$ to be given by $k_p I_0\{[\text{THF}]_t - [\text{THF}]_e\}$, at that stage of the process, where k_p is the bimolecular propagation constant, I_0 denotes the initial concentration of the initiator eventually quantitatively converted into living polymers, and $[\text{THF}]_t$ and $[\text{THF}]_e$ are the monomer concentrations at time t and at its equilibrium with the polymer, respectively.

None of the students of THF polymerization commented on this simple relation $-\text{d}[\text{THF}]_t/\text{d}t = k_p I_0([\text{THF}]_t - [\text{THF}]_e)$. It appeared obvious. The problem of how k_p is affected by the composition of the reacting mixture was dealt with by some investigators, notably by Penczek's group.[11] They found the propagation constant of the oxonium pairs, i.e., $k_{p\pm}$ briefly denoted by k_p, to *decrease* with *increasing initial* concentration of THF in the mixture of carbon tetrachloride and the monomer and attributed this result to change of the bulk dielectric constant of the medium. In fact, a linear relation was claimed for $\ln k_{p,\pm}$ with the reciprocal of bulk dielectric constant. The seemingly obvious relation $-\text{d}[\text{THF}]_t/\text{d}t = k_p I_0([\text{THF}]_t - [\text{THF}]_e)$ and the dependence of k_p on the composition of the medium calls for comments, and I wish to examine closer this subject in this note. The composition of the medium may affect the ratio of ion pairs to macroesters and thus the overall k_p. However, I will be concerned here only with the variation of $k_{p\pm}$, the rate of propagation due to oxonium counterion pairs.

Cationic polymerization of THF is propagated by the oxonium ion pairs. (The following discussion applies to



propagation by oxonium ion pairs and not by macroesters.) The composition of the medium around the ionic pairs is, on the whole, different from its nominal composition. The fact that the relation $-\text{d}[\text{THF}]_t/\text{d}t \sim ([\text{THF}]_t - [\text{THF}]_e)$ applies to the polymerization initiated in pure tetrahydrofuran suggests that the solvating power of a THF molecule is comparable to the solvation power of a monomeric segment of poly(tetrahydrofuran). Only then is the probability of finding oxygen atoms of THF molecules neighboring an oxonium ion given by the volume fraction of THF in the monomer–polymer mixture, or approximately by its mole fraction, $\alpha = [\text{THF}]_t/[\text{THF}]_{\text{bulk},0}$.[12]

Addition of a neighboring THF molecule to a growing oxonium ion is the rate-determining step of propagation. In bulk polymerization this forward process is governed by a unimolecular rate constant k_u multiplied by α. The replacement of the added THF molecule by another one arriving from the interior of the solution is diffusion controlled and therefore it does not affect the rate of the forward reaction. In these terms one gets for bulk polymerization of THF the relation

$$-\text{d}[\text{THF}]_t/\text{d}t = k_u(\alpha - \alpha_e)I_0$$

where $\alpha_e = [\text{THF}]_e/[\text{THF}]_{\text{bulk},0}$.

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