

Radiation Degradation of α -Substituted Acrylate Polymers and Copolymers

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Synopsis

Radiation degradation is observed in poly(methyl α -chloroacrylate), poly(methyl α -cyanoacrylate), and poly(α -chloroacrylonitrile) homopolymers and their respective MMA copolymers when γ -irradiated in vacuo. Polymer degradation susceptibilities are quantified in terms of G (scission radicals) and G (scission) - G (crosslinks), measured by EPR and membrane osmometry, respectively; values by these two methods are compared. Higher G (rads) values ranging from 2 to 6 and [G (s) - G (x)] values ranging from 2 to 11 are obtained for the substituted polymers and copolymers relative to the values for PMMA (1.6; 1.9), a standard e -beam positive resist, which suggests that these modified polymers are more sensitive e -beam resists than PMMA.

INTRODUCTION

The radiation chemistry of polymers has received renewed interest of late stemming from the widespread use of radiation-degrading and radiation-crosslinking polymers by the electronics industry.¹ Additional interest is found in the textile industry,² where polymers that degrade and graft are potentially important to electron-beam prototype dry processing. The use of poly(methyl methacrylate) (PMMA) as an electron-beam resist in the production stages of microelectronic circuits is an important example.¹ Although PMMA resist has established technique feasibility, its radiation sensitivity is relatively low, and more sensitive resist polymers are in demand.³ Of particular interest to applications and basic researchers is the determination of the chemical (and possibly steric) configurations which are conducive to polymer degradation.

In the present work, we explore further⁴ the effects of polar and electronegative substituents on the quaternary carbon of vinyl polymers, polymers with repeating units $[\text{CH}_2\text{—C}(\text{X})\text{Y}]$ (where neither X nor Y are H). The general repeating unit is known to be the structural unit of vinyl polymers which degrade when subjected to ionizing radiation.⁵ We use molecular weight and free-radical formation as indices of degradation susceptibility. Our immediate objective is a useful delineation of certain chemical factors which favor higher e -beam radiation sensitivity, rather than a complete study of scission and crosslinking in the degraded polymers.

EXPERIMENTAL

Polymer Preparations

Polymerizations were carried out as prescribed by Sorenson and Campbell⁶ using freshly distilled monomers obtained from Polysciences, Inc., Goodyear Chemicals, or Eastman Kodak. The polymers were reprecipitated twice and chemically analyzed. Polymers investigated, which were prepared by methods described by Sorenson and Campbell, are poly(α -chloroacrylonitrile) (P α CAN), 20% α -CAN/MMA copolymer, poly(methyl α -chloroacrylate) (PMCA), 20% MCA/MMA copolymer, 20% methyl α -cyanoacrylate (MCyA)/MMA copolymer, 20% diethyl ethylidene malonate (DEMAL)/MMA copolymer, and 8% uranyl methacrylate (UO₂MMA)/MMA copolymer. Some samples were polymerized in bulk by heating *in vacuo* at 80–90°C in sealed tubes using azodiisobutyronitrile as initiator.⁴ Polymer samples made by the bulk polymerization method are PMMA, poly(methyl α -cyanoacrylate) (PMCyA), 20% MCyA/MMA, PMCA, 20% MCA/MMA, poly(2-bromo-ethyl methacrylate) (PBrEMA), 20% α -CAN/MMA (see Table I), 4% UO₂MMA/MMA copolymer, 30% diethyl fumarate (DIF)/MMA, and 20% diethyl ethoxymethylene malonate (DEM)/MMA copolymer. The final products of both types of polymerizations were reasonably free of initiators and inhibitors.

EXAMPLE ANAL. Calcd for 20% MCA/MMA copolymer: C, 56.01; H, 7.22; Cl, 5.88. Found: C, 55.80; H, 7.32; Cl, 5.99.

Poly(vinylidene chloride) and polyisobutylene polymers were obtained from Polysciences, Inc., while the poly(vinyl ferrocenyl methacrylate)–methyl methacrylate copolymer was made by Dr. Charles U. Pittman of the University of Alabama.

Polymer Irradiation

Samples were prepared for γ irradiation and subsequent EPR observation at 77°K as described previously.^{4,7} Samples prepared for irradiation and subsequent molecular weight analysis by membrane osmometry or viscometry were sealed in 5-mm O.D. Pyrex tubes at $P < 10^{-4}$ mm Hg and irradiated at 298°K.

TABLE I
G(radicals), G(scission), and Electron-Beam Sensitivities Q for Several Polymers
in the Literature

Polymer	G(rads)	G(s)	Q, coul/cm ²
Poly(α -methylstyrene)	0.05 ¹³	0.25 ¹⁶	1×10^{-4a}
PMMA	1.6 ^a	1.9 ¹⁵	5×10^{-5a}
Polyisobutylene	2.5	3.0 ^b	$2-3 \times 10^{-5a}$
Poly(butene-1 sulfone)	3 ^c	11.0 ^c	2×10^{-6a}

^a L. F. Thompson and M. J. Bowden, *J. Electrochem. Soc.*, **120**, 1722 (1973).

^b A. Chapiro, taken from *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., Interscience, New York, 1966, V-26.

^c J. R. Brown and J. H. O'Donnell, *Macromolecules*, **5**, 109 (1972).

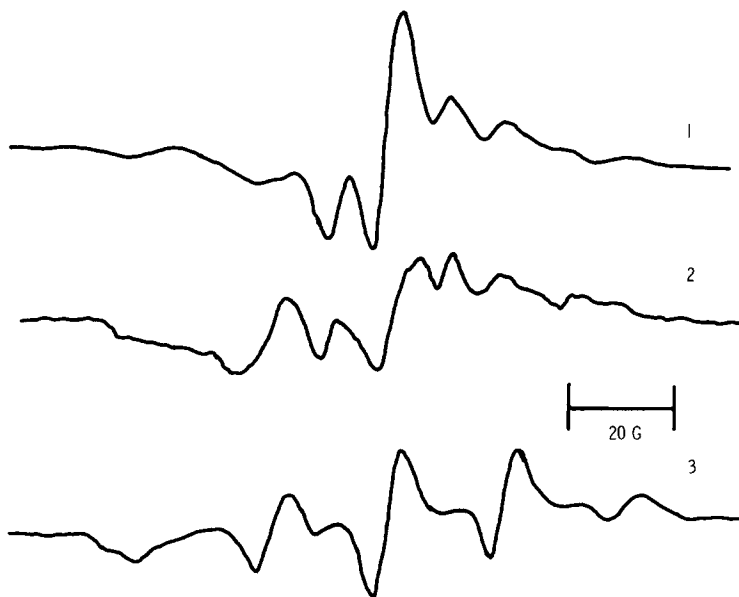


Fig. 1. EPR spectra at 77°K of (1) PMMA, (2) 8% UO₂MMA/MMA synthesized by method from ref. 6 and reprecipitated twice from MEK/methanol, and (3) 4% UO₂MMA/MMA prepared by bulk polymerization (see experimental section). $G(\text{rads}) = 4$ for spectrum 3 vs. PMMA, while $G(\text{rads}) = 0.7$ for spectrum 2.

Analytical Methods

The radical yield per 100 eV absorbed, $G(\text{rads})$, was obtained from a double integration of spectra recorded on a Varian Model 4500 EPR spectrometer equipped with a dual cavity. Molecular weights were derived from polymer solution osmotic pressures obtained on a Hewlett-Packard Model 502 membrane osmometer at 310° or 298°K.

RESULTS

EPR Results

Many of the EPR spectra at 77° and 298°K ascribed to degradation radicals in the polymers and copolymers investigated have been described elsewhere.^{4,8} The EPR results described below are results not previously reported.

The EPR spectra of γ -irradiated 8% UO₂MMA/MMA copolymer at 77°K consists of an anisotropic triplet very similar to the spectrum of PMMA radical (see Fig. 1); the average $G(\text{rads})$ from several recorded spectra was determined to be 0.8 versus irradiated PMMA standard radical; at 298°K, the spectrum is identical to the 298°K γ -irradiated PMMA spectrum. The EPR spectrum of irradiated 2-bromoethyl methacrylate (BrEMA) homopolymer at 77°K consists of a broad anisotropic quartet powder spectrum. Upon warming, the relative radical intensity versus PMMA falls off appreciably and the spectrum becomes the same as the nine-line spectrum of PMMA.⁹ The average $G(\text{rads})$ obtained

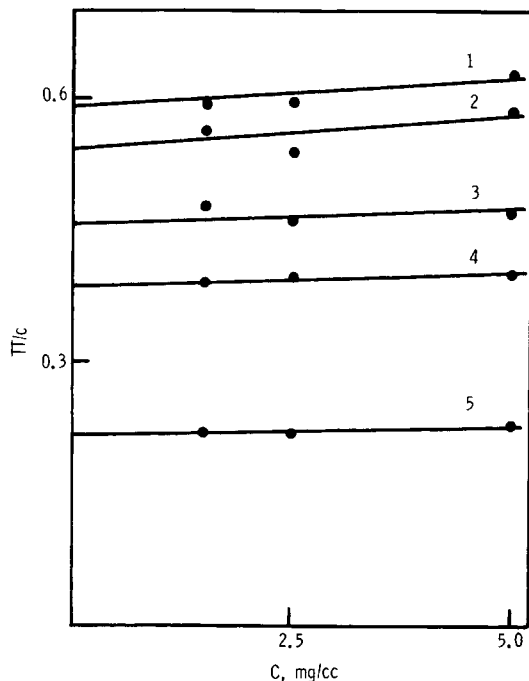


Fig. 2. Osmotic pressures per unit concentration vs. c in mg/cc for PMCA in acetonitrile at 310°K with γ -irradiation doses of (1) 1.76 Mrad, (2) 1.3 Mrad, (3) 0.88 Mrad, (4) 0.44 Mrad, and (5) 0 Mrad.

from the spectral area was 0.9, a lower radical G value than for the standard radical in irradiated PMMA reference. The EPR spectrum of 26% ferrocenyl methacrylate (FEMMA)/MMA at 77°K after irradiation at 77°K consists of a broad singlet with fairly intense shoulders; upon warming to 298°K, the spectrum changes to the nine-line PMMA spectrum. The average G (rads) obtained was 0.2, which is nearly a factor of 10 lower than for PMMA standard radical. The EPR spectrum of irradiated 30% DIF/MMA copolymer at 77°K following irradiation at 77°K consists of a broad singlet which decays to zero when the sample is heated to 298°K. The average G (rads) for the copolymer radicals is 0.7, a value nearly 60% less than for PMMA standard. The EPR spectrum of γ -irradiated 20% DEM/MMA at 77°K is a very anisotropic doublet [G (rads) = 0.7] which changes to the PMMA nine-line spectrum when the sample is heated to 298°K. The average G values obtained by EPR at 77° and 298°K are listed in Table I.

Molecular Weight Change Determinations

The extrapolated osmotic pressures per unit concentration (π/c) at $c = 0$ generally increase with increasing radiation dose for the polar α -substituted vinyl polymers, for copolymers which were free of comonomers with high atomic number (Z), and for comonomers with structures different from $[\text{CH}_2=\text{C}(\text{X})\text{Y}]$. This behavior indicates that number-average molecular weight \bar{M}_n decreases for these polymers upon radiation exposure. Typical π/c -versus- c plots for ir-

radiated PMCA are found in Figure 2. Extrapolated π/c values for 8% $\text{UO}_2\text{MMA/MMA}$, a high- Z substituted copolymer, and 20% DEMAL/MMA [20% $\text{CH}_3\text{CH}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$] generally decrease, thus indicating increases in \bar{M}_n for these copolymers upon exposure to ionizing radiation.

A plot of \bar{M}_n^{-1} versus dose in Mrad yields the difference between scission and crosslinking, $G(s) - G(x)$, in accord with the following equation:¹⁰

$$G(s) - G(x) = 0.48 \times 10^6 \frac{2q_0 - p_0}{w}$$

The proportion of monomer units crosslinked per unit radiation dose is q_0 ; the proportion of main chains fractured is p_0 ; the G difference term is in units of events per 100 eV absorbed; monomer unit molecular weight is w .

A complete analysis of radiation effects in polymers requires separate determination of the competing scission and crosslinking (or endlinking) processes. In addition to the number-average molecular weight, some evidence of change in molecular weight distribution is required. This might be obtained by optical scattering or gel phase chromatography (GPC). In a first evaluation, however, of polymers potentially useful as electron-beam lithographic resists, the feature of immediate interest is the net damage, $G(s) - G(x)$. Thus, the more comprehensive measurements are not included here. A more detailed study of damage mechanisms is in progress.

DISCUSSION

Interpretation of Scission Radical Yields

As observed by EPR, large yields of free radical $-\text{CH}_2-\dot{\text{C}}(\text{CH}_3)(\text{CO}_2\text{CH}_3)$ (I)¹¹ are formed in the main-chain scission¹² of PMMA during ^{60}Co γ radiolysis at 298°K. In a similar fashion, poly(α -methylstyrene), when γ irradiated at 298°K, contains moderately large amounts of radical $-\text{CH}_2\dot{\text{C}}(\text{CH}_3)(\text{C}_6\text{H}_5)$ (II).¹³ In contrast, radiolysis of PMMA at 77°K produces radical III, assigned to be a trapped electron,⁸ which has a different EPR line shape than radical I; radical III shows hyperfine structure which might simply reflect a modification of radical I at the different irradiation temperature.

The G values obtained by EPR [$G(\text{III})$ at 77°K = 1.6 ± 0.3 ; $G(\text{I})$ at 298°K = 2.4]^{8,14} agree well with $G(s) = 1.9$ obtained¹⁵ by molecular weight methods. The G values obtained by EPR, $G(\text{II}) = 0.05$ at 77°K¹³ and $G(\text{II}) = 0.015$ at 300°K⁹ also agree fairly well¹⁶ with $G(s) = 0.25$ within the uncertainties of the techniques. Table I lists the known $G(s)$ and $G(\text{rads})$ values from the literature, and Table II lists G difference values from this work. It is clear from Table I that $G(\text{rads})$ correlates well with $G(s)$. Therefore, $G(\text{rads})$ appears to be a useful measurement (or possibly a lower limit in some cases, e.g., PMCyA) to the radiation degradation susceptibility.

Polar-Substituted Polymers

$G(\text{rads})$ for irradiated PMCA is 5.7 ± 1.5 , a much larger average G value than for PMMA $G(\text{I})$. $G(s) - G(x)$ from membrane osmometry is 9.6 ± 0.8 (see Fig. 3) compared to $G(s) - G(x) = 2.3$ or 1.9 for the irradiated PMMA standard,¹⁵

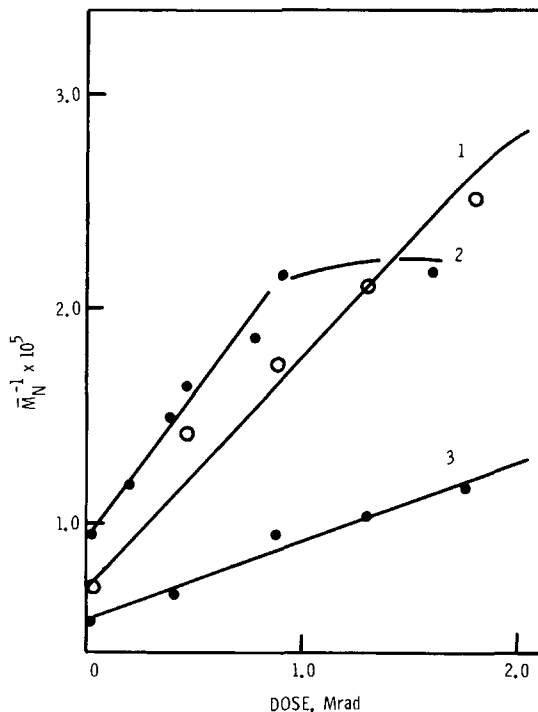


Fig. 3. Plot of \bar{M}_n^{-1} vs. dose for (1) PMCA in acetonitrile, (2) PMCyA in nitromethane, and (3) P α CAN in acetonitrile.

a polymer where $G(x) \cong 0$. These values indicate substantially higher net radiation degradation susceptibility for PMCA with respect to PMMA. We attribute the higher polymer radiation degradation susceptibility versus PMMA to the electron-withdrawing nature of the electronegative Cl substituent in PMCA as compared to $-\text{CH}_3$ in PMMA. $G(\text{rads})$ for PMCyA is 1.9 to 1.6, while $G(s) - G(x)$ is 11 ± 2 . PMCyA, like PMCA, is also more susceptible to radiation degradation than PMMA; again, this is due to the greater electron-withdrawing power of the CN group at the quaternary carbon versus the $-\text{CH}_3$ group in PMMA. Since both of these polymers differ from PMMA only by the electron-withdrawing substituents, this interpretation seems obvious; the high electronegativity value for Cl and the high electron-withdrawing nature of the $-\text{CN}$ group are well known. These electron-withdrawing groups most likely lead to C—C main-chain bond dissociation energies smaller than the average C—C bond energy for PMMA, as has been documented by Steacie¹⁷ for molecular systems; the C—C bond dissociation energy in $\text{CH}_3\text{CO}-\text{COCH}_3$, for example, is 60 kcal/mole, compared to 83 kcal/mole for CH_3-CH_3 .¹⁷

A portion of the higher radiation degradation susceptibilities observed for PMCA and PMCyA versus PMMA can be accounted for on the basis of polymer density. The polymer densities for PMCA and PMCyA are 23% and 11% higher, respectively, than the corresponding PMMA density. Since the amount of energy transferred per unit path length in polymers is proportional to polymer density,¹⁸ one would expect about 11–23% more energy absorption for polymer degradation in PMCA and PMCyA per unit exposure dose.

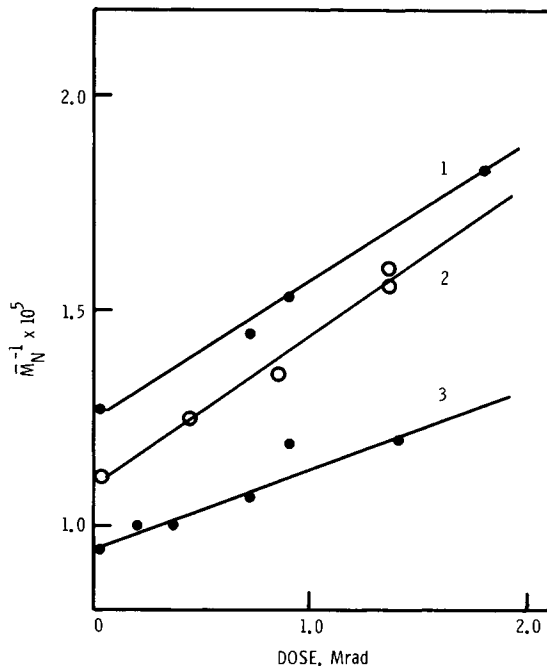


Fig. 4. Plot of \bar{M}_n^{-1} vs. dose for (1) 20% MCA/MMA, (2) 20% MCyA/MMA, and (3) 20% α CAN/MMA copolymers obtained from methyl ethyl ketone polymer solutions.

$G(\text{rads})$ for P α CAN, a polymer with X = Cl and Y = CN (instead of $-\text{CO}_2\text{CH}_3$), is 1.4 ± 0.4 , while $G(s) - G(x)$ is 2.4 (see Fig. 3). These values indicate that P α CAN is equally or very slightly more susceptible to radiation degradation than PMMA. The lower observed G values seem reasonable when compared to the G values for PMCyA and PMCA from Table I and $G(\text{rads}) = 0.6$ for poly(vinylidene chloride), $[\text{CH}_2-\text{C}(\text{Cl})_2]$. The G values of these three polymers suggest that the $-\text{CO}_2\text{CH}_3$ group is more important than CN and Cl and that the apparent general order of group importance on the quaternary carbon is $\text{CO}_2\text{CH}_3 > \text{CN} > \text{Cl} > \text{CH}_3$. More specifically, when Y = CO_2CH_3 , the X group importance order is $\text{CN} > \text{Cl} > \text{CH}_3$. The Y group order when X = Cl is $\text{CO}_2\text{CH}_3 > \text{CN} > \text{Cl}$.

Higher $G(\text{rads})$ and $G(s) - G(x)$ values (see Table I) are also characteristic of the three respective MMA copolymers.⁴ Figure 4 contains plots of \bar{M}_n^{-1} versus dose for the three copolymers. The $G(s) - G(x)$ values for the copolymers are 3.1, 3.2, and 2.2, respectively (see Table I). These results are consistent with the respective homopolymer G values in the sense that they are somewhere between the homopolymer G values and the G value for PMMA standard. The EPR $G(\text{rads})$ value for the 20% MCyA/MMA copolymer, however, is larger than the homopolymer $G(\text{rads})$, which may reflect a lower stabilization population for the $-\text{CH}_2-\dot{\text{C}}(\text{CN})(\text{CO}_2\text{CH}_3)$ radical per unit dose in the homopolymer. Quite revealingly, the EPR spectrum at 298°K of the radical in the copolymer is identical to that of radical I in PMMA.¹¹ This may be the result of the radical migration from the polar cleavage site to the neighboring MMA site of higher radical stability.

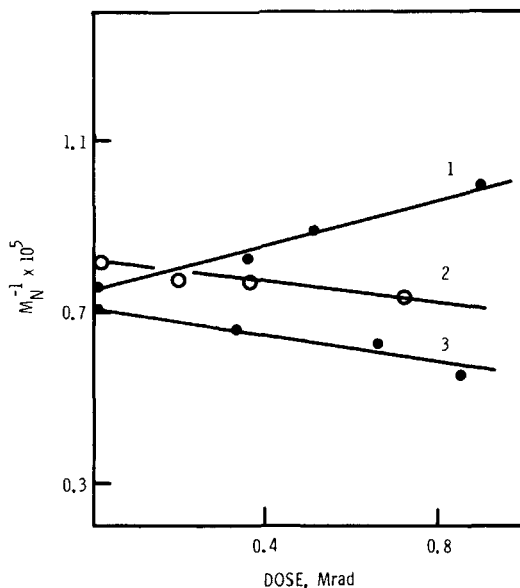


Fig. 5. Plot of M_n^{-1} vs. dose for (1) PMMA, (2) 20% DEMAL/MMA, and (3) 8% UO₂MMA/MMA. Osmotic pressure measurements were made on dilute MEK solutions.

Diester-substituted comonomer units, $-\text{CH}_2-\text{C}(\text{CO}_2\text{R})_2-$, were placed into the methyl methacrylate main chain to weaken it and increase the rate of radiation degradation. Copolymers with 20% compositions of DEM [$\text{C}_2\text{H}_5\text{O}-\text{CH}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$] and DEMAL were tested. As is seen from the respective G values in Table I, G (rads) for 20% DEM/MMA is smaller than G (rads) for PMMA. G (rads) for 20% DEMAL/MMA is slightly larger, but increases in the average molecular weight of that copolymer upon exposure to radiation, as compared to decreases for PMMA, Figures 5(1) and 5(2), indicate a higher crosslinking rate [i.e., $G(x) > G(s)$] in that copolymer. These results, however, cannot be taken as completely conclusive against the original diester-enhancing hypothesis, because the comonomers were not strictly of the degrading structural type (see introduction). This statement is supported by the G values of Table I for 30% DIF, 30% $(\text{CO}_2\text{C}_2\text{H}_5)\text{HC}=\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)$, MMA copolymer. This comonomer is of the nondegrading type by design, $\text{C}(\text{W})\text{H}=\text{C}(\text{X})$ (where $\text{W} \neq \text{H}$ and $\text{X} = \text{H}$), and its radiation behavior closely approximates that of the diester-substituted MMA copolymers above. These results show that incorporation of crosslinking monomers (20–30%) into the MMA chain by copolymerization changes the overall radiation behavior from predominant degradation for PMMA to low degradation or predominant crosslinking in the diester-substituted MMA copolymers.

High-Z Polymers

The high Z - (atomic number)-substituted polymers were in general less susceptible to radiation degradation than the previous series of polymers and PMMA standard. The G (rads) values found in Table I were all below G (rads) for PMMA. A plot of M_n^{-1} versus dose for 8% UO₂MMA/MMA copolymer is located in Figure 5(3). The negative slope of the M_n^{-1} -versus-dose curve, Figure

5(3), indicates the predominance of the crosslinking process over that of scission in the $\text{UO}_2\text{MMA/MMA}$ copolymer.

The $G(\text{rads})$ values for the 2-BrEMA homopolymer and the 26% FEMMA/MMA copolymer are also much lower than $G(\text{rads})$ for PMMA standard. Thus, these polymers with high- Z substituents are also less susceptible to radiation degradation than PMMA and the other test polymers. It is interesting to note that the $G(\text{rads})$ value of 0.2 for 26% FEMMA/MMA is more in line with the

TABLE II
 $G(\text{radicals})$ at 77° and 298°K and $G(\text{scission}) - G(\text{crosslink})$ for γ -Irradiated Polymers and Methyl Methacrylate Copolymers Observed in the Present Study

Polymer	$G(\text{rads})^{\text{a,b}}$ 298°K	$G(\text{rads})^{\text{a}}$ 77°K	$G(s) - G(x)$
PMMA	$1.6 \pm 0.3^{\text{a}}$	$1.6 \pm 0.3^{\text{a}}$	$1.9,^{15} 2.3 \pm 0.2$
Polyisobutylene	—	2.5 ± 0.3	3.0^{12}
Poly(methyl α -cyanoacrylate)	1.9 ± 0.4	1.6 ± 0.4	11 ± 2
Poly(methyl α -chloroacrylate)	1.3 (decay)	5.7 ± 1.5	9.6 ± 0.8
Poly(α -chloroacrylonitrile)	≈ 1 (decay)	1.4 ± 0.4	2.4 ± 0.2
20% MCyA/MMA copolymer	$3.6 \pm 1.5^{\text{c}}$	$3.6 \pm 1.5^{\text{c}}$	3.2 ± 0.2
20% MCA/MMA copolymer	1.8 (decay)	3.1 ± 0.4	3.1 ± 0.2
20% α -CAN/MMA copolymer	$2.3 \pm 1.2^{\text{c}}$	$2.3 \pm 1.2^{\text{c}}$	2.2 ± 0.2
30% DIF/MMA copolymer	(decay)	0.7 ± 0.4	—
20% DEMAL/MMA copolymer	≈ 0.6 (decay)	$3.1 \pm 1.0^{\text{d}}$	$G(x) > G(s)^{\text{e}}$
20% DEM/MMA copolymer	—	0.7 ± 0.4	—
Poly(2-bromoethyl methacrylate)	≈ 0.1 (decay)	0.9 ± 0.4	—
26% Ferrocenyl methacrylate/MMA copolymer	0.2 ± 0.1	0.2 ± 0.1	—
8% Uranyl methacrylate	0.5 ± 0.4	0.8 ± 0.4	$G(x) > G(s)^{\text{e}}$

^a Values listed are averages of three or more determinations. The $G(\text{rads})$ values obtained were taken for exposures on the linear portion of the radical dose—yield curves (0.3–1.3 Mrad).

^b G values determined from EPR measured at 298°K after warming of samples from initial irradiation and EPR measurement at 77°K.

^c These values are lower than previously reported because some earlier samples contained unreacted amounts of comonomer which act as electron scavengers to give higher $G(\text{rads})$. This phenomenon was also observed when saturated solutions of uranyl methacrylate in MMA were polymerized in bulk and irradiated without reprecipitation. The criterion for rejecting the higher $G(\text{rads})$ for bulk-polymerized $\text{UO}_2\text{MMA/MMA}$ as a measure of the radiation degradation susceptibility lies in the observed EPR spectral line shapes. If scavenging by UO_2MMA monomer occurs, the propagating radical⁹ $[-\text{CH}_2-\dot{\text{C}}(\text{CH}_3)\text{CO}_2\text{CH}_3]$ should be observed. This radical is, in fact, observed even at 77°K for bulk-polymerized $\text{UO}_2\text{MMA/MMA}$ copolymer, see Fig. 1(3). If no unreacted monomer scavenging occurs, the line shape is more of the radical III spectral shape,¹⁴ see Fig. 1(2). Electron scavenging by α -CAN monomer in α -CAN/MMA copolymer is not unreasonable because α -CAN does not polymerize via free-radical mechanism. In the α -CAN/MMA copolymer polymerized by ionic polymerization (see ref. 6), this problem is alleviated and smaller $G(\text{rads})$ are observed than previously reported for free radical-polymerized α -CAN/MMA in ref. 4. Comonomer inhibitors, if not removed, can also cause higher $G(\text{rads})$.

^d Considering molecular weight changes, 20% DEMAL/MMA also probably contains unreacted DEMAL or inhibitors which are scavenging secondary radicals to give the observed higher $G(\text{rads})$.

^e Copolymer predominately crosslinks (see discussion).

G (rads) value of 0.05 for poly(α -methylstyrene) than G (rads) for PMMA, even though the copolymer is 70% MMA. We interpret this effect to result from the well-known sponge effect¹⁰ of radiation protection of polymers by aromatic ring systems. This effect tends to counteract the radiation degradation process and, in these examples, dominates.

CONCLUSIONS

Compared to PMMA, increased radiation degradation susceptibilities ranging from slight to large are observed for P α CAN, PMCA, and PMCyA and their respective MMA copolymers. The higher degradation susceptibilities versus PMMA result from carbon-carbon main-chain bond weakening caused by the electron-withdrawing and/or electronegative substituents.

Thompson and Bowden¹⁹ have established a correlation between $G(s)$ and e -beam sensitivity Q . Table I shows an extended correlation between $G(s)$, G (rads), and Q . In Table II, G (rads) is seen to be usefully correlated with $G(s) - G(x)$; this presumably reflects the modest crosslinking expected in polymers with relatively short side chains. These correlations form the basis for a concluding prediction, namely, that the polymers and copolymers of this work with $G(s) - G(x)$ and G (rads) ≥ 1.6 , especially PMCA and PMCyA, are more favorable candidates for positive electron-beam resists¹ than pure PMMA. On the other hand, the copolymers where crosslinking predominates as reflected by smaller G (rads) and where $G(x) > G(s)$ should function as negative electron-beam resists.¹

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