NOTES

Increased Radiation Degradation in Methyl Methacrylate Copolymers

The use of poly(methyl methacrylate) (PMMA) as electron-beam resist material in the production stages of microelectronic circuits has led to renewed interest in radiation degradation studies of polymers. Of special interest are chemical and steric configurations that enhance degradation processes and make the polymer more susceptible to e-beam damage. In the present work, we explore the effect of polar substituents at the quaternary carbon on degradation processes in several polymers and 10–20% copolymers of MMA.

Electron paramagnetic resonance (EPR) is employed to monitor radiation degradation products and to determine radiation G values (degradation radicals produced/100 eV absorbed energy). As observed by EPR, large yields of free radical (I)[1,2,3] —CH_2—$\dot{C}(CH_3)(CO_2CH_3)$, are formed in the main-chain scission[4] of PMMA during [60]Co γ-radiolysis at 298°K. In contrast, radiolysis of PMMA at 77°K produces trapped electrons[5] (radicals) (II) which are the precursors of radical (I). Heating to 298°K following irradiation of PMMA at 77°K activates the conversion from radical (II) to radical (I). The G values obtained by EPR [G(II) at 77°K $-$ 1.6 $\pm$ 0.3[5]; G(I) at 298°K = 2.4[6]] agree well with G(scission) = 1.9 $\pm$ 0.3[7] obtained from $\bar{M}_v$ viscosity data. Polymers with the repeating structure —CH_2—$C(X)(CO_2CH_3)$—, with X not H, primarily degrade to —CH_2—$\dot{C}(X)(CO_2CH_3)$ upon γ-radiolysis,[8] so that G(radicals) can be taken as a good measure of the degree of polymer degradation and of G(scission).

Polymerizations for all polymers, except poly(α-chloroacrylonitrile) (see Table I) were carried out by heating at 85–90°C in vacuo for 12–24 hr, using trace amounts of azodiisobutyronitrile as free-radical initiator. Where necessary, inhibitors were removed by conventional chemical treatment and distillation. Poly(α-chloroacrylonitrile) was polymerized by standard ionic polymerization. The final products were free of initiators or inhibitors.

Example ANAL. Calcd for PMMA: C, 60.05; H, 8.00; N, 0.00. Found: C, 60.22; H, 8.19; N, <0.1.)

Solid cylindrical samples (8 $\times$ 3–4 mm) were sealed at $P < 10^{-4}$ mm Hg into quartz tubes for irradiation; tubes were annealed after irradiation without sample heating. Irradiations were carried out at 77°K in a [60]Co γ-irradiator at a dose rate of 0.3 Mrad/hr. EPR measurements were taken at 77°K following irradiation and at 298°K immediately after warming. All EPR measurements were made on a Varian 4500 spectrometer equipped with a dual cavity.

The EPR spectra at 77°K ascribed to trapped electrons, radicals (II), in the polymers and copolymers investigated differ only in the degree of anisotropic broadening from the EPR spectra obtained by Omerod and Charlesby[5] for pure PMMA and otherwise are of the same basic signal shape or form. EPR spectra of the copolymers at 298°K are identical to the well-known nine-line spectrum found for radical (I) in pure PMMA.[1,2,3] EPR spectra at 298°K of radicals —CH_2—$\dot{C}(X)(CO_2CH_3)$, with X = Cl, CN, are anisotropic triplets of total spectral width 75 gauss, about half the width of the radical (I) spectrum. Radicals trapped at 77°K were stable indefinitely at that temperature, but in some cases suffered some radical decay upon warming as reflected by lower G values at 298°K. All G values were determined by double-integration computer analysis of the respective derivative EPR spectra, using irradiated PMMA as reference.

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TABLE I

G(radicals) and e-Beam Sensitivities of Several Polymers and Methyl
Methacrylate Copolymers

System	G(radicals)[a,b] (298°K)	G(II)[a] (77°K)	Q, coul/cm²
PMMA	1.6 ± 0.3[c]	1.6 ± 0.3[c]	
Poly(methyl methacrylic acid)	—	4.8 ± 1.2	
Poly(methyl α-cyanoacrylate)	1.9 ± 0.4	1.6 ± 0.4	
Poly(methyl α-chloroacrylate)	1.3 (decay)	5.1 ± 1.5	
Poly(α-chloroacrylonitrile)	≈1 (decay)	1.4 ± 0.4	
20% DEMAL/MMA copolymer	≈0.7 (decay)	2.9 ± 0.4	
20% MCyA/MMA copolymer	5.4 ± 1.2	5.9 ± 2.0	
14% MCA/MMA copolymer	1.8 (decay)	3.1 ± 0.4	
14% α-CAN/MMA copolymer	6.7 ± 2.7	6.6 ± 2.7	
Poly(α-methylstyrene)		0.05[d]	1×10^{-4} [e]
Poly(methyl methacrylate)		1.6 ± 0.3[c]	5×10^{-5} [e]
Polyisobutylene		2.5 ± 0.4	$2–3 \times 10^{-5}$ [e]
Poly(butene-1 sulfone)		3 ± 1[f]	2×10^{-6} [e]

[a] Values listed are averages for four or more determinations.

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

[c] Reference 5.

[d] R. E. Florin, L. A. Wall, and D. W. Brown, *Trans. Faraday Soc.*, **56**, 1304 (1960).

[e] Reference 11.

[f] J. R. Brown and J. H. O'Donnell, *Macromolecules*, **5**, 109 (1972).

The dose–yield curves were quite linear for every system over the employed 0.3–1.3
Mrad dose range.

Compared to PMMA, increased radiation degradation susceptibility is observed
for the Cl derivative poly(methyl α-chloroacrylate) PMCA, while only equivalent
amount of apparent radical formation is observed for the CN derivative poly(methyl α-
cyanoacrylate) PMCyA (see Table I).   However, the dose dependence of $\bar{M}_v{}^{-1}$ in the
viscosity measurements of Graham et al.[9] for irradiated PMCyA and pure PMMA indi-
cates that scission for the former polymer is 3.4 times the value for PMMA.   The elec-
tron-withdrawing effect of the CN group makes the quaternary carbon more susceptible
to radiolysis, but should also make the resultant —CH₂—Ċ(CN)(CO₂CH₃) radical more
susceptible to attack by neighboring groups.   The higher sensitivities of PMCA and
PMCyA toward radiation degradation must result from bond weakening along the
main chain induced by the electron-withdrawing substituents on the quaternary carbon.

Increased radiation susceptibility is also observed for the α-chloroacrylonitrile (α-
CAN), methyl α-chloroacrylate (MCA), methyl α-cyanoacrylate (MCyA), and di-
ethylethylidene malonate (DEMAL)–methyl methacrylate copolymers.   For similar
MMA copolymer systems, increased thermal degradation compared to pure PMMA
has been observed.[10]   Introduction of 10–20% comonomers containing polar electron-
withdrawing substituents thus significantly decreases main chain stability.   The in-
creased extent of main-chain scission again appears to be a result of bond weakening due
to the influence of the electron-withdrawing substituents replacing the methyl group on
the copolymer quaternary carbon.

Quite revealingly, the EPR spectra of the copolymer systems at 298°K are identical
to those of the PMMA radical (I) and do not exhibit features of the —CH₂—Ċ(X)-
(CO₂CH₃) radical.   But higher susceptibility to chain degradation than in pure PMMA
must be due to the effect of the —CH₂—C(X)(CO₂CH₃)— comonomer fragments.   The
predominating methyl methacrylate groups in the copolymer can be expected to yield the
methyl-substituted radical (I) in commensurate amounts as in PMMA itself.   The sub-
stantial additional amount of radical (I) found in the irradiated copolymer system must
be due to radiolysis at the more susceptible C—X site, followed by spin migration to the

neighboring C—CH$_3$ MMA site to give the chemically more stable MMA radical (I). It is interesting to note that the observed G(radical) values for PMCyA/MMA and PαCAN/MMA copolymer systems are substantially higher than the G values found for the pure polymers PαCAN and PMCyA, respectively. The MCyA copolymer G value agrees much better with G(scission) found from viscosity data. The absence of stabilized radical sites in pure PMCyA results, as noted, in lower amounts of observable radicals, although G(scission) is substantial.[9] Analogously, the absence of stabilized radical sites in pure PαCAN results in reduced G by EPR.

Thompson and Bowden[11] have established a correlation between the scission susceptibility G(scission) and e-beam sensitivity Q. In Table I we list recently determined Q values as well as G(radical) from EPR data. The correlation between G and Q is clear-cut and forms the basis for the concluding prediction that the polymers of this work with $G > 2$, and similar chemical systems, should be more sensitive e-beam resists than pure PMMA.

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