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High-Energy Radiation-Induced Main-Chain Scission and Crosslinking of Poly-2.2.2-Trichloroethylmethacrylate

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Summary

Poly-2,2,2-trichloroethylmethacrylate was irradiated with ^{60}Co-γ-rays and 16 MeV electrons. The 100 eV yields for main-chain scission and crosslinking were determined as $G(S) = 3.7$ and $G(X) = 0.03$, respectively. Neither dose rate (1.6×10^{1} to 5×10^{10} rad/s) nor temperature changes (25 to 165°C) influenced the radiation chemical yields. At 165°C, thermal crosslinking commenced to compete with radiation-induced main-chain rupture.

Introduction

Recently, poly-2,2,2-trichloroethylmethacrylate (PTCEMA) has attracted the interest of researchers working in the field of electron beam and X-ray lithography. TADA (1979) reported that PTCEMA that had been thermally crosslinked at 200°C prior to irradiation, exhibited - in terms of lithographic properties - a sensitivity towards fast electron beam irradiation about 40 times higher than that of polymethylmethacrylate which is considered a standard among positive-working resists. More recently, 2,2,2-trichloroethylmethacrylate was reported to be an appropriate comonomer in copolymers that crosslink prior to irradiation and possess a high radiation sensitivity in X-ray lithographic processes (ASMUSSEN et al. 1983). According to TADA (1979), electron beam irradiation causes predominant main-chain scission and, therefore, solubilization of thermally crosslinked PTCEMA at exposure doses lower than 25 $\mu C/cm^2$ (ca. 60 Mrad at a resist thickness of 0.5 µm), but additional crosslinking at higher absorbed doses.

The aim of the present work was to gain some fundamental knowledge about the radiation chemistry of PTCEMA. For this purpose it appeared appropriate to investigate the behavior of the linear (non-crosslinked) polymer under the influence of ^{60}Co-γ-ray and of electron beam irradiation.

In the following, results concerning the radiation-chemical yields of main-chain scission, G(S), and of crosslinking, G(X), will be reported. Moreover, the influence of absorbed dose rate and temperature on the radiation chemical behavior of PTCEMA will be dealt with.

Experimental Part

Poly-2,2,2-trichloroethylmethacrylate (PTCEMA) was synthesized by free radical polymerization at 60°C using AIBN as initiator. The polymer was reprecipitated twice from tetrahydrofuran solution with n-hexane. Weight average molecular weights were determined in 1,4-dioxane solution by light scattering measurements using an instrument from Chromatix (KMX-6). For the determination of the number average molecular weight in 1,4-dioxane, a membrane osmometer (Mechrolab) was used. The initial molecular weights were $\overline{M}_{w,o} = 1.7 \times 10^6$ and $\overline{M}_{n,o} = 7.4 \times 10^5$. The molecular weight distribution was unimodal as indicated by GPC using an instrument from Knauer, Berlin.

The irradiations were carried out with a ^{60}Co-γ-source or a linear accelerator (Vickers) for electrons (16 MeV). For dosimetry the Fricke dosimeter was used ($G(Fe^{3+}) = 15.4$ and 13.0 for γ- and electron irradiations, respectively). In the case of electron irradiations, a slow pulse rate of 2 pulses/s was used in order to prevent the sample heating up.

Results

(a) Determination of G(S) and G(X) at room temperature

Fig.1 shows plots of the reciprocal weight and number-average molecular weights vs. the absorbed dose. With the aid of equations (1) and (2)

$$\overline{M}_w^{-1} = \overline{M}_{w,o}^{-1} + [G(S)/2 - 2\,G(X)]\,D_a/100\,N_A \qquad (1)$$

$$\overline{M}_n^{-1} = \overline{M}_{n,o}^{-1} + [G(S) - G(X)]\,D_a/100\,N_A \qquad (2)$$

(N_A: Avogadro's number; D_a absorbed dose in eV/g)

the radiation chemical yields were calculated: G(S) = 3.7 scissions/100 eV and G(X) = 0.03 crosslinks/100 eV. Thus, crosslinking is rather unimportant and chain scission occurs quite effectively: G(S) is about 2.5 times higher than in the case of PMMA (G(S) = 1.5 ± 0.2, EGUSA et al. 1979; LAI et al., 1978; SCHNABEL et al., 1976).

Our values are somewhat at variance with those reported by PITTMAN et al. (1982): G(S) = 2.7 and G(X) = 0. These authors did not specify their method of determining the radiation chemical yields.

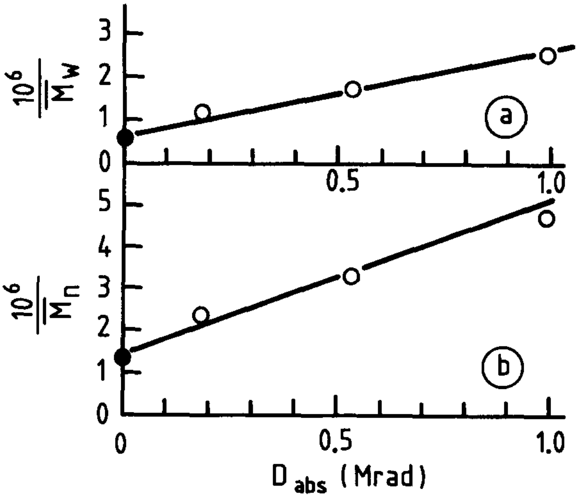


Fig.1
Irradiation of PTCEMA in vacuo at room temperature with ^{60}Co-γ-rays. Absorbed dose rate: 16 rad/s. Reciprocal weight (a) and reciprocal number average molecular weights (b) vs. the absorbed dose

(b) Irradiation at higher temperatures

The glass transition temperature of PTCEMA lies at about 138°C. Irradiations of PTCEMA at 143°C in vacuo revealed that the decrease of the weight average molecular weight and of the intrinsic viscosity as a function of dose is independent of temperature within the experimental error. When the polymer was heated for 20 hours at 165°C, it became partially insoluble due to intermolecular crosslinking. Subsequent irradiation at 165°C caused resolubilization as a consequence of main-chain scission. The reciprocal weight average molecular weight of γ-irradiated polymer samples did not increase linearly with the absorbed dose as at 25 and 143°C, as is shown in Fig.2. The curve measured at 165°C bends off at relatively low doses indicating that thermally induced crosslinking is competing with radiation-induced main-chain scission. From these experiments it can be inferred that, in the temperature range from 25 to 165°C, main-chain scission is the predominant radiation-induced process.

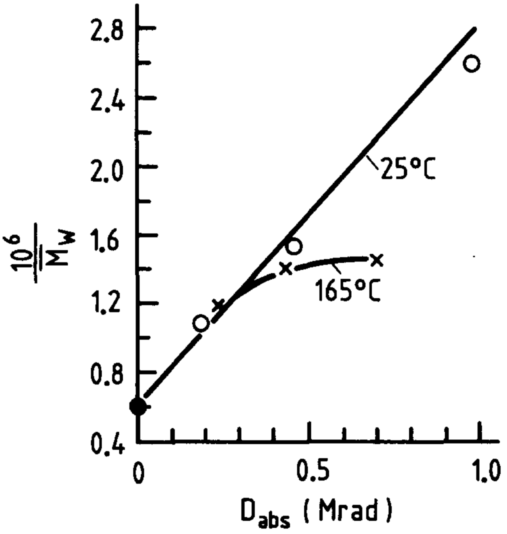


Fig.2 - The reciprocal weight average molecular weight of PTCEMA samples irradiated in vacuo at 25°C and at 165°C vs. the absorbed dose

(c) Irradiation at different absorbed dose rates

PTCEMA was irradiated at room temperature in vacuo also with 16 MeV electron pulses. In this case, the absorbed dose rate was ca. 5×10^{10} rad/s. After irradiation, the intrinsic viscosity $[\eta]$ of the polymer in dioxane solution was measured. The results are shown in Fig.3, where one can see that the same dependence of $[\eta]$ on the absorbed dose was found as for γ-irradiation at an absorbed dose rate of 16 rad/s. From these results it is concluded that the radiation-chemical yields G(S) and G(X) do not depend on the absorbed dose rate.

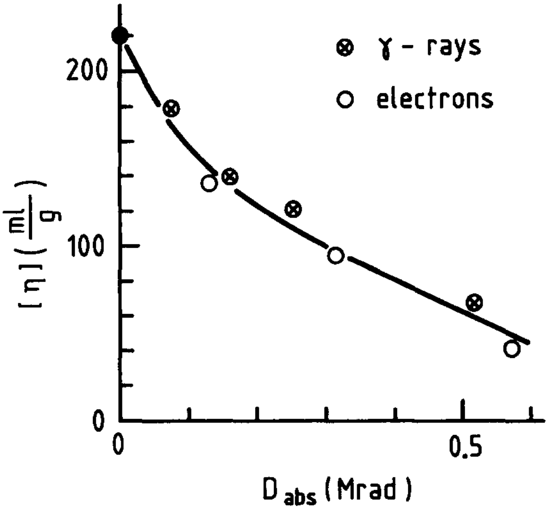
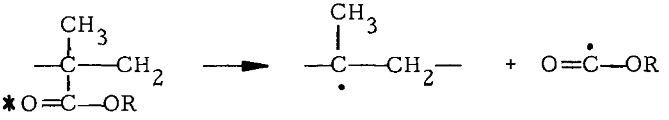


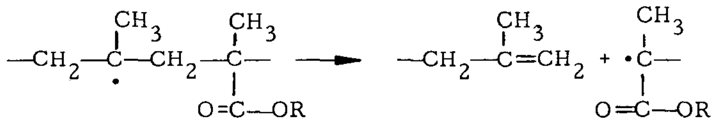
Fig.3 - The intrinsic viscosity in dioxane at 25°C of PTCEMA samples subjected to electron beam (EB) or ^{60}Co-γ-irradiation at room temperature in vacuo. DR(EB) = 5 x 10^{10} rad/s (O); DR(γ-rays)=16rad/s (⊗)

Discussion

The results show that the high radiation sensitivity of PTCEMA observed in lithographic processes is to some extent, at least, explainable in terms of a high G(S)-value. A mechanism explaining the high radiation susceptibility of PTCEMA relative to polymethylmethacrylate or polyethylmethacrylate cannot be derived from the results of this work. However, it appears very probable that main-chain scission involves lateral macroradicals produced by decomposition of electronically excited carbonyl groups according to reactions (3) and (4)



$$-\overset{\mathrm{CH_3}}{\underset{{}^{*}\mathrm{O=C-OR}}{\mathrm{C}}}-\mathrm{CH_2} \longrightarrow -\overset{\mathrm{CH_3}}{\underset{\bullet}{\mathrm{C}}}-\mathrm{CH_2}- + \mathrm{O}=\overset{\bullet}{\mathrm{C}}-\mathrm{OR} \qquad (3)$$



$$-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\bullet}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{O=C-OR}}{\mathrm{C}}}- \longrightarrow -\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\mathrm{C}}=\mathrm{CH_2} + \bullet\overset{\mathrm{CH_3}}{\underset{\mathrm{O=C-OR}}{\mathrm{C}}}- \qquad (4)$$

Trichloroethyl groups enhance presumably the probability of α-scission according to reaction (3).

Acknowledgement

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