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Degradation of Polymethylmethacrylate by Synchrotron Radiation

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Summary

Polymethylmethacrylate was irradiated with X-rays at absorbed dose rates between 3.8×10^3 and 7.1×10^5 $J.g^{-1}.h^{-1}$. The 100 eV-yield for main-chain scission was determined as $G(S)_{X\text{-}ray} = 0.33$. It is independent of the absorbed dose rate. The difference between $G(S)_{X\text{-}ray}$ and $G(S)_{\gamma\text{-}ray}$ ($G(S)_{\gamma\text{-}ray} = 1.5 \pm 0.2$) is attributed to a true linear energy transfer (LET) effect.

1. Introduction

Synchrotron orbit radiation (SOR) has been used recently as a X-ray source for X-ray lithography[1,2]. Characteristic for SOR is its high intensity, the continuous spectrum and the small divergence of the beam. At present, polymethylmethacrylate (PMMA) acts as a positiv resist at absorbed doses below 10^5 J/cm^3, i.e., main-chain scission occurs causing a diminution of the average molecular weight[1]. The degree of degradation can be evaluated on the basis of changes in number average molecular weight.

The purpose of this work was to study the decrease of the average molecular weight of PMMA at various absorbed dosis rates. Two types of radiation, i.e., synchrotron radiation and Al-K_α-X rays were applied. For comparison, also irradiations with ^{60}Co-γ-rays were performed.

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2. Experimental Part

2.1 Sample preparation

A PMMA fraction ($\frac{M_w}{M_n}$ = 1.35, M_w = 190 000) was used. For X-rays irradiations the polymer was dissolved in chlorbenzene. The solutions were cast on silicon wafers to a thickness of 0.6 - 0.8 µm. The polymer coated wafers were baked at 150°C for 15 minutes prior to irradiation. The absorbed dose was estimated on the basis of linear absorption coefficients (see spectrum in Fig. 1). Except for the carbon absorption edge at 4.48 nm, the absorption coefficient increases steadily with increasing wavelength.
For the γ-ray experiments PMMA was degassed in glass ampolues at a vacuum line.

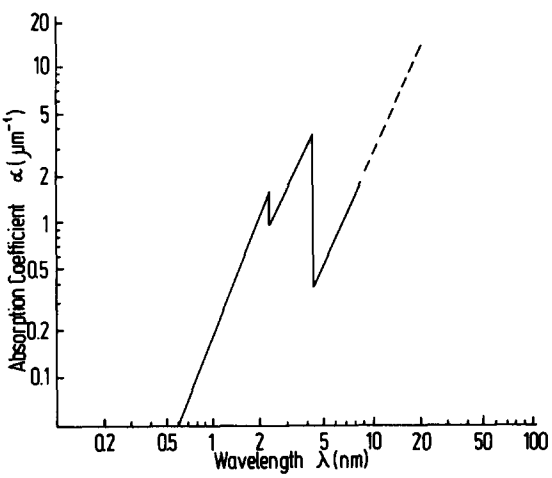


Figure 1. Linear absorption coefficient α of Polymethylmethacrylate as a function of the wavelength λ

2.2. Radiation Sources

2.2.1. Synchrotron Radiation

The synchrotron of Physikalisches Institut der Universität Bonn was used. Because of the small angular spread of the beam in the vertical direction, uniform exposures were achieved only by scanning the samples perpendicular to the beam. The exposures were performed at a distance of 10 m from the orbit at an aperture of 1 cm height, corresponding to 1 msterad and of 5 cm width, corresponding to 5 msterad. Fig.2 shows the spectral distribution for maximum electron energies of 1.7, 1.3 and 0.8 GeV at an aperture of 1 msterad(width) and 1 msterad (height) as obtained according to Schwinger's equation[6]. The incident intensity was obtained by numerical integration of the curves.

2.2.2. Al-K_α- X-rays

Exposures were carried out at Institut für Festkörpertechnologie der Fraunhofer-Gesellschaft, München. The absorbed dose rate was estimated according to Green's equation[7] as 3.8×10^3 $J.g^{-1}.h^{-1}$.

2.2.3. ^{60}Co-γ-rays

Irradiations were performed at the Hahn-Meitner-Institut, Berlin. The absorbed dose rate, as determined by the Fricke dosimeter ($G(Fe^{3+})=15.5$), was 3.7 $J.g^{-1}.h^{-1}$.

2.3. Determination of Molecular Weight Distributions (MDW)

Gel permeation chromatography (GPC-Waters) with a set of 5 μ-Styragel columns ($5oo, 1o^3, 2x1o^4, 1o^5$ Å) and tetrahydrofuran as solvent was applied. A technique using only a few micrograms per run was employed. Calibration was done with a series of PMMA fractions of narrow MWD. For the evaluation of MWDs a Gaussian quadrature approximation method, using linear programming as proposed by Tung[8], was applied.

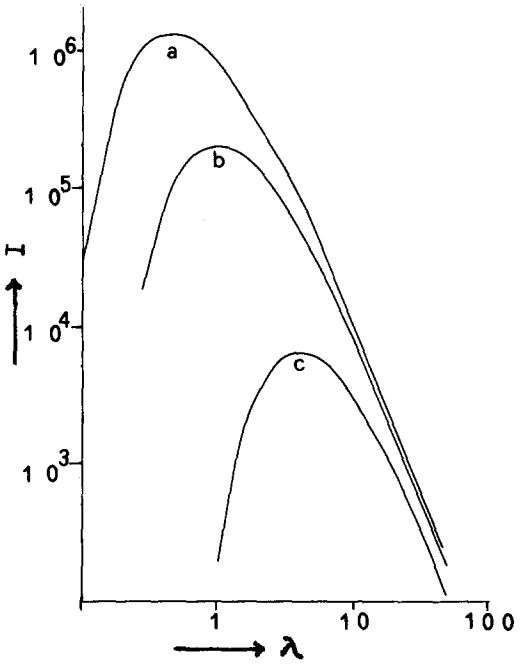


Figure 2 . The spectral distribution of synchrotron radiation for maximum electron energies E_{max}= 1.7 GeV(a), 1.3 GeV(b) and o.8 GeV(c) at an aperature of 1 msterad (width) and 1 msterad (height), (-o.5 to +o.5), according to Schwinger's equation[6]. I:(w.m^{-1}.mA^{-1}.mrad^{-1}.mrad^{-1})and λ:(nm)

3. Results and Discussion

For polymers undergoing random scission without crosslinking, the 1oo eV-yield of main-chain scissions G(S) depends on the number average molecular weight M_n according to eq.(1)[9]:

$$\frac{1}{\overline{M}_{n,D}} = \frac{1}{\overline{M}_{n,0}} + \frac{G(S)\ D}{1oo\ N_A} \qquad (1)$$

$\overline{M}_{n,0}$ and $\overline{M}_{n,D}$: number average molecular weights befor and after irradiation with absorbed dose D (eV/g)

N_A : Avogadro number

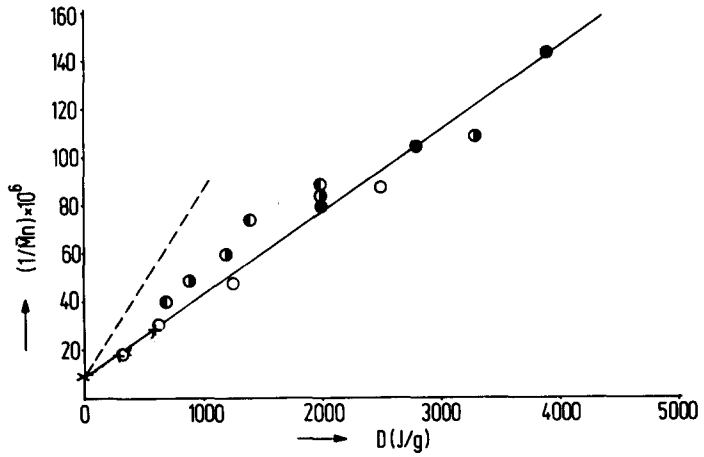
From plots of the invers number average molecular weight vs. the absorbed dose (see Fig. 3) G(S)=o.33 was found for the four absorbed dose rates (X-ray irradiation). Upon irradiation of PMMA with γ- rays or fast electrons G(S) values between 1.1 and 1.9 were found[1o]. Two of the authors[11] reported G(S)= 1.75 some time ago. Recently, Lai and Helbert[12] reported G(S) = 1.3, a value which was also found during this work.

The relatively low G(S) value found for X-ray irradiations could, in principle, be due to a linear energy transfer (LET) effect and/or an absorbed dose rate effect.

The mean LET values (for water) are o.o2 eV/Å (γ-radiation) and o.23 eV/Å (hard X-rays)[1o]. There is no dose rate effect in the range from $3.8 \times 1o^3$ to $7.1 \times 1o^5$ $J.g^{-1}.h^{-1}$ as revealed from this work.

On the other hand, no dose rate effect has been observed for G(S) upon irradiating PMMA with low LET radiation (γ-rays, fast electrons)[13]. A dose rate range from 5 to about $3 \times 1o^3$ $J.g^{-1}.h^{-1}$ was covered in that case[13], the upper value corresponding about to the lowest value of X-ray irradiation in this work.

Although real overlapping of the dose rate ranges has not yet been accomplished it appears that the difference in G(S) values is to be attributed to a real LET effect.



Symbol	Radiation	Absorbed Dose Rate ($J.g^{-1}.h^{-1}$)x)
	Synchrotron:	
●	o.8 GeV, 4o mA	85ooo
◑	1.3 GeV, 6o mA	71oooo
◐	1.7 GeV, 2o mA	45oooo
O	Al-Kα-X-rays (λ=o.83 nm)	
	(19.5 KV, 465 mA, 21.5 cm	38ooo
- - -	^{6o}Co-γ-rays	3.7
(G(S) = 1.3)		

x) 1 $J.g^{-1}.h^{-1}$ = o.1 $Mrad.h^{-1}$

Figure 3 .
The dependence of the inverse number-average molecular weight on the absorbed dose

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