Postirradiation Reactions of Monomer in Poly(methyl methacrylate): Analysis by CP/MAS ^{13}C NMR

S. Kalachandra* and D. T. Turner†

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

J. P. Burgess and E. O. Stejskal

Department of Chemistry, Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204

Received March 29, 1994; Revised Manuscript Received July 18, 1994®

ABSTRACT: Small amounts of residual monomer in poly(methyl methacrylate) (PMMA) have been estimated accurately by cross-polarization/magic-angle-spinning ^{13}C NMR spectroscopy. It has been verified that residual monomer decreases when PMMA is γ-irradiated. In contrast to previous suggestions, a case is made that removal of monomer is due to slow postirradiation reaction with polymer free radicals. An additional unexpected finding is that radiolysis can result in the formation of additional monomer which can be detected in samples frozen immediately after irradiation.

Introduction

Poly(methyl methacrylate) (PMMA) as usually prepared contains small amounts of unsaturated groups mainly in the form of unreacted monomer (MMA) along with much smaller amounts in the chain ends. Residual monomer has a pronounced and often adverse influence on properties. For this reason, Fydelor's report that γ-irradiation of PMMA at room temperature reduces unsaturation due to chemical reaction of monomer is of practical interest. More basically, as he pointed out, it is surprising that as many as 36 MMA molecules react per 100 eV of energy deposition—i.e., G(MMA) = 36—well below the glass transition temperature (T_g) of PMMA, i.e., well below 105 °C. Tentative suggestions were made to account for rapid reactions in the glassy state invoking special mechanisms of rapid diffusion or of favorable reactivity due to clustering of reactants.[1] Subsequently, Pratt reported that γ-irradiation of PMMA resulted in an initial increase in T_g. He pointed out that an increase in T_g could be explained by Fydelor's observations, i.e., by removal of MMA, which acts as a plasticizer.[2]

The purpose of the present investigation is to check Fydelor's finding and to consider whether it might be explained by more conventional processes. The working hypothesis to be tested is that residual monomer can react with relatively immobile polymer free radicals after irradiation. To test this hypothesis it is necessary to make precise measurements of low levels of residual unsaturation in PMMA. Measurements which require extraction of residual monomer[3] were discounted in favor of a nondestructive technique. Previous investigators have used different spectroscopic techniques such as near infrared[4] and solid-state ^{13}C NMR.[5] Earnshaw et al. used the latter technique to make quantitative distinctions among cross-linked polymethacrylates containing large concentrations of unreacted methacrylate groups. However, more discriminating analyses are needed for the present purpose.

Experimental Section

Cylinders of PMMA (commercial Plexiglas, Rohm and Haas, Philadelphia) and PMMA polymerized from monomer with 3.2 Mrad of γ-rays from a ^{137}Cs source (dose rate = 0.8 Mrad/h; ambient temperature 40 °C) were used.[6,7] Immediately after irradiation, one set of samples was transferred to dry ice for transportation and then stored below 0 °C until just before analysis. These samples were machined to fit the magic-angle smoke spinner (diameter 0.6 cm, length 1.0 cm) as they warmed to room temperature. The other set of samples was stored at room temperature prior to the final machining. After the first postirradiation measurements, all samples were stored at room temperature. At the same time that the two different kinds of PMMA were being irradiated, an equivalent pair of samples was analyzed to establish a starting monomer concentration.

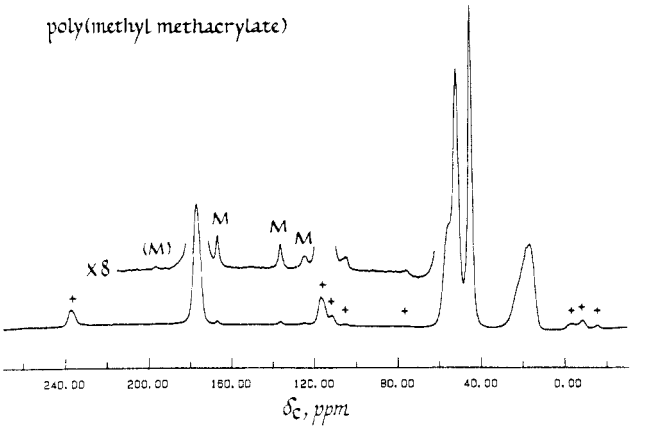

Figure 1. 50.1 MHz CP/MAS ^{13}C NMR spectrum of poly(methyl methacrylate) with 1.1% monomer. The complete spectrum is marked with a + wherever spinning sidebands arising from the polymer resonances occur. The portion of the spectrum expanded eightfold vertically has the three monomer lines marked with an M and the one spinning sideband, arising from the monomer line at 136 ppm, marked with (M).

Results

High-resolution, 50.1 MHz, cross-polarization/magic-angle-spinning (CP/MAS) ^{13}C NMR spectra of solid PMMA plugs were obtained with a Chemagnetics CMC-200S NMR spectrometer. A typical spectrum is shown in Figure 1. For this spectrum 30 000 transients were collected. A recycle delay time of 3 s and a cross-polarization contact time appropriate to the thermal treatment of the samples were used. Matched Hartmann–Hahn conditions were achieved with a radio frequency field of 65 kHz in the ^1H channel and a radio frequency field in the ^{13}C channel equal to 65 kHz less the rotor frequency to allow for the modulation of the ^1H–^{13}C

* To whom correspondence should be addressed.
† Deceased.
® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0024-9297/94/2227-5948$04.50/0

Table 1. Effect of Irradiation and Storage Conditions on Monomer Concentration in PMMA

	commercial PMMA		radiation-polymerized PMMA	
residual monomer (%)	1.43		0.22	
irradiation (Mrad)	1.13		1.13	
wait/store	35 days/cold	34 days	29 days/cold	30 days room temp
residual monomer (%)	1.69	0.70	0.62	0.10
wait/store	53 days/room temp	57 days/room temp	56 days/room temp.	63 days/room temp
residual monomer (%)	1.13	0.66	0.18	0.05

coupling. The magic-angle spinning frequency had to be chosen carefully to avoid overlap between the spinning sidebands associated with the polymer resonance lines and the monomer lines. This normally would not be a problem since spinning greater than 6 kHz reduces the spinning sidebands to near the 1% level at this resonant frequency. In this case this effect is comparable to the monomer lines to be detected. Accordingly, a spinning speed of 3.0 kHz was chosen because that put all the monomer lines clear of any suspected sidebands.

Three monomer lines were detected. The line at 177 ppm corresponds to the carbonyl carbon, while the lines at 136 and 125 ppm correspond to the vinyl carbons. The methyl and methoxy lines were obscured by the methyl and methoxy lines of the polymer. To determine the monomer concentration, a comparison was made between the integrated area of the polymer carbonyl line at 177 ppm and that of the monomer line at 136 ppm. Since each represents one carbon in the monomer and since cross-polarization conditions were such as to expect that they would be proportionately represented based on the knowledge of motional properties of monomer and polymer, a simple ratio of the areas indicated the fraction of the monomer present. Because of the presence of spinning sidebands in the spectrum, a correction had to be made to account for the intensity lost to the spinning sidebands. Fortunately, in some of the spectra (cf. Figure 1) it is possible to see spinning sidebands associated with the monomer lines and to estimate how much intensity is lost in monomer spinning sidebands in relation to polymer spinning sidebands. The adjustment factor, 0.92 for 3.0 kHz spinning, is minor in view of the estimated accuracy of the monomer percentage, i.e., ±0.04%. The size of the monomer sidebands does not allow for much mobility of the monomer molecules, indicating that they do not occur in highly plasticized aggregations.

Discussion

Storage of irradiated PMMA at room temperature results in a decrease of unsaturation. For example, a sample which had 1.43% unsaturation before irradiation showed to 0.70% unsaturation when analyzed after storage for 34 days (Table 1). Qualitatively, this finding is comparable to Fydelor's report, the above results giving G(MMA) = 62. The main theme is to discuss the reaction for this decrease. However, before going into details, attention will be given in the following paragraph to an additional unexpected finding.

Cold storage of irradiated samples limits the postirradiation decrease of unsaturation so effectively that it is made apparent that irradiation can result in an increase in unsaturation. This increase is most marked in the radiation polymerization sample of PMMA, in which the monomer content increased from 0.22 to 0.62% after a dose of 1.13 Mrad (Table 1). This increase corresponds to G(MMA) = 34. A possible explanation for this high yield of 34 molecules per 100 eV of energy deposition is monomer production by depolymerization, i.e., by unzipping of polymer free radicals before dissipation of the thermal energy accompanying ionization. This general idea of enhanced radiation damage to an organic target in a "hot spot" is very old and not generally accepted. Nevertheless, it would seem to be the most plausible explanation of the present results.

Returning to the main theme, the postirradiation disappearance of monomer (M) may be attributed to reaction with polymer free radicals (P_n°), as demonstrated in ESR spectra.[8,9] The polymer radicals persist in the glass ($T_g \sim 105$ °C) for a long time after irradiation but slowly disappear by a bimolecular reaction (reaction II) with a specific rate of $k = 3.3$ (mol/cm^3)$^{-1}$ s^{-1} at 28 °C in vacuum according to Ohnishi and Nitta.[10]

$$M + P_n^\circ \rightarrow P_{n+1}^\circ \quad \text{(I)}$$

$$P_n^\circ + P_n^\circ \rightarrow \text{nonradical products} \quad \text{(II)}$$

The results seem to indicate that this method of measuring is capable of identifying the presence of unreacted vinyl double bonds independent of the size or composition of the esterified structures.

In the present study, we have evaluated the monofunctional monomers. The studies of Earnshaw et al.[5] supplement our finding by extending them to include polyfunctional monomers.

Thus it appears that the radiation-induced disappearance of monomer can be explained by conventional, though very slow, reaction and that it is not necessary to invoke special reactions peculiar to high-energy irradiation or involving clustering of monomer molecules. Of more general interest in polymer science is that the present approach could lead to greater knowledge of the last stage of polymerization in the glassy state, about which relatively little is known.[11] However, this would entail a laborious program involving simultaneous characterization by both NMR and ESR.

Acknowledgment. S.K. and D.T.T. were supported by USPHS Research Grant Nos. DE06201 and DE09425 and General Research Support Grant No. RR053333. The NMR spectrometer was purchased by means of North Carolina Biotechnology Center Grant No. 86-11-00787, and spectrometer operating expenses for this project were provided by North Carolina Biotechnology Center Grant No. 87-11-00745. The authors wish to thank Professor Duane F. Taylor of the Dental School, University of North Carolina, Chapel Hill, North Carolina, for his valuable comments.

References and Notes

(1) Fydelor, P. J. *Eur. Polym. J.* **1971**, *7*, 401.
(2) Pratt, G. J. *J. Mater. Sci.* **1975**, *10*, 809.
(3) Austin, A. T.; Basker, R. M. *Br. Dent. J.* **1980**, *149*, 281.
(4) Willis, H. A.; Miller, R. G. *J. Spectrochim. Acta* **1959**, *14*, 119.
(5) Earnshaw, R. G.; Price, C. A.; O'Donnell, J. H.; Whittaker, A. K. *J. Appl. Polym. Sci.* **1986**, *32*, 5337.
(6) Turner, D. T. *J. Polym. Sci., Part A* **1964**, *2*, 1699.
(7) Kalachandra, S.; Turner, D. T. *Polymer* **1987**, *28*, 1749.
(8) Kircher, J. F.; Sliemers, F. A.; Markle, R. A.; Gager, W. B.; Leininger, R. I. *J. Phys. Chem.* **1965**, *69*, 189.
(9) Dole, M. *The Radiation Chemistry of Macromolecules*; Academic Press: New York, 1973; Vol. II, p 109.
(10) Ohnishi, S.-I.; Nitta, I. *J. Polym. Sci.* **1959**, *38*, 451.
(11) Gladyshev, G. P.; Gibov, K. M. *Polymerization at Advanced Degrees of Conversion*, Translated from Russian, Israel Program for Scientific Translations, Jerusalem, 1970.