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One- and Two-Dimensional Nuclear Magnetic Resonance Spectra of X-ray-Degraded Poly(methyl methacrylate)[†]

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ABSTRACT: The one- and two-dimensional nuclear magnetic resonance spectra of X-ray-irradiated poly(methyl methacrylate) (400-MHz ^{1}H and 100-MHz ^{13}C) have been obtained. The one-dimensional hydrogen spectrum and the two-dimensional H, H-COSY, HMQC, and HMBC spectra allow the assignment of 28 hydrogen and carbon NMR signals for the four polymeric degradation products plus six signals for minor stereoisomers. Methyl formate and acetaldehyde were also observed.

Introduction

Poly(methyl methacrylate) (PMMA) is an exceptionally important polymer with many applications including major uses as a resist in advanced microlithography and micromachining.[1] Its wide-ranging importance has led to its extensive study by nuclear magnetic resonance spectroscopy (NMR).[2] This NMR work has provided a great understanding of the microstructure or tacticity of PMMA prepared by various methods.

In 1991, Moore and Choi reported the 200-MHz ^{1}H NMR spectra for PMMA which had been irradiated with X-ray, ultraviolet (UV), electron beam, and ion beam sources.[3] Two ^{13}C signals from UV-irradiated PMMA were also reported. They postulated the formation of the alkene degradation products **1**−**4** from a knowledge of photochemical reaction mechanisms and by comparison with the NMR spectra of known alkene model compounds. Chain-scission products (**1** and **2**) and chain-intact products (**3** and **4**) resulted from the elimination of methyl formate.

One-dimensional (1-D) ^{1}H NMR results for the γ-induced decomposition of some poly(alkyl methacrylates) have also been reported.[4] Alkyl formates were formed except in the case of poly(benzyl methacrylate), indicating that the benzyl group might offer protection of the polymer chain against γ radiolysis.

We now report the 400-MHz ^{1}H NMR spectra and, more importantly, two-dimensional (2-D) H,H-COSY, HMQC, and HMBC spectra[5] of X-ray-degraded PMMA. These spectra allow us to assign a total of 34 hydrogen and carbon signals including minor stereoisomers and to modify some of the previous assignments. Knowledge of the major alkene products of degradation will lead to systematic studies of the effects of dosage and wavelength on the decomposition of PMMA.

Experimental Section

Starting Material. Commercial PMMA in 1.5 mm sheets was used. The tacticity could be determined from the methyl signals in the ^{1}H spectrum. It was “syndiotactic rich” (4.8% mm, 39.5% mr, and 55.7% rr, as triads).[6] The spectrum also showed the presence of about 0.5% of the monomer, methyl methacrylate, in the bulk material (6.09, 5.55, 3.74, and 1.94 ppm).

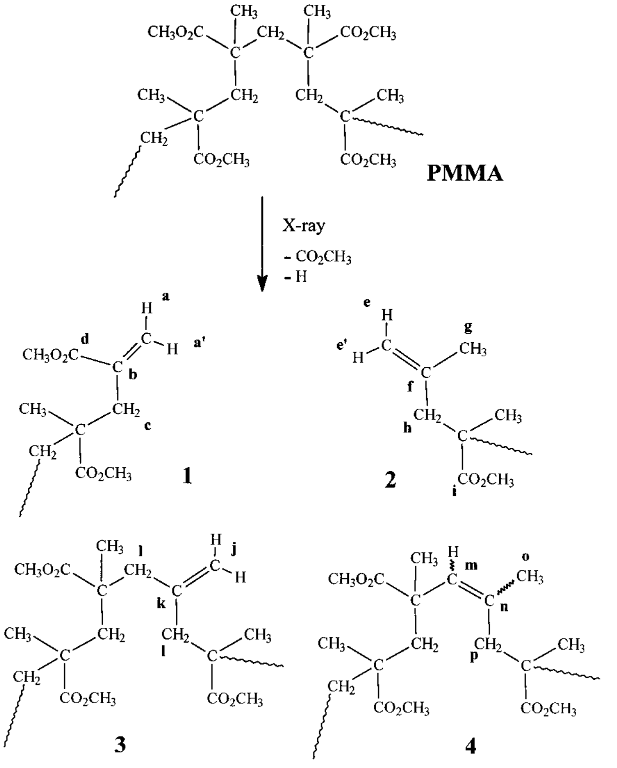

Figure 1. Structures of PMMA and its X-ray degradation products. The arrangement of the chain in the PMMA does not indicate tacticity.

X-ray Irradiations. The irradiations were performed on the ~3 keV X-ray lithography beamline installed on the 1.2−1.5 GeV electron storage ring at CAMD-LSU. A beryllium filter was employed. The top surface dose was 6.5−13 kJ/cm^{3}. Exposure times were approximately 7−14 min.

The degraded material could be isolated by washing with a 2:1 solution of isopropyl alcohol (IPA)/isobutyl methyl ketone (MIBK) followed by evaporation of the solvent. For improved signal-to-noise ratio (especially necessary in the two-dimensional NMR spectra described below), more heavily irradiated material was used. In this case, the irradiated material was physically removed by scraping with a stainless steel scalpel and dissolved in deuteriochloroform for NMR analysis. The same alkene signals were observed whether the degraded material was removed physically or with IPA/MIBK solvent.

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NMR. The samples were dissolved in $CDCl_3$ using 5 mm tubes. The tubes were sealed under vacuum after two freeze−pump−thaw cycles. A Varian Unity Plus spectrometer at 399.95 and 100.58 MHz for ^1H and ^{13}C, respectively, was used. All hydrogen-detected NMR experiments used a 5-mm “inverse” probe which has the hydrogen coil in closer proximity to the sample than the carbon coil, giving large signal-to-noise gains for hydrogen. Hydrogen chemical shifts are reported in ppm (δ) where $CHCl_3$ was set to 7.26 ppm. Carbon chemical shifts (δ units) are referenced to $CDCl_3$, which was set to 77.0 ppm. The temperature was controlled to 30.0 °C. The 2-D spectra (Figures 5−10) show separately obtained hydrogen 1-D spectra along the top axes and not projected 2-D information.

COSY. Generally, the H,H-COSY spectra[5] were obtained using 144 increments of 2K real data points with 256 transients for each free induction decay (FID). The t_2 acquisition time was 0.394 swith a recycle delay of 1 s. Total time was 14 h. Before Fourier transformation the data set was zero-filled to 4K × 4K. Sinebell weighting functions were used in both dimensions. Symmetrization completed the processing.

Many of the ^1H-^1H couplings in **1-4** are between hydrogens with geminal alkene or allylic relationships. Since these coupling constants are at best small (a few hertz), delayed COSY spectra with preacquisition delays of 0.100 s produced better results.

HMQC. Hydrogen−carbon heteronuclear multiquantum coherence spectroscopy (HMQC)[5] gives the same one-bond H−C correlations as HETCOR. A large advantage with HMQC is that a hydrogen FID, with the inherent higher sensitivity of ^1H, is detected using the inverse coil arrangement described above. HETCOR, on the other hand, uses a pulse sequence which ends with the detection of a ^{13}C FID. The carbon-decoupled HMQC spectrum in this work was acquired with 128 increments of 1K real data points and 128 transients for each FID for a total time of 16 h. Zero-filling to 4K × 4K and multiplication of both dimensions by Gaussian functions were used.

HMBC. A heteronuclear multibond correlation pulse sequence (HMBC)[5] is basically the same as with HMQC except that a short delay (0.055 s in this case) occurs after the first 90° ^1H pulse. In general, during delays such as this, stronger correlations between nuclei which have larger coupling constants (one-bond H-C correlations in this case) can disappear, leaving the multibond correlations which have smaller couplings. The HMBC spectrum in this work used 192 increments of 2K real data points with 256 transients for each FID and took 39 h. Zero-filling to 4K × 4K was also done. A combination of sinusoidal and exponential multiplication was used in the t_2 dimension and Gaussian multiplication in the t_1 dimension was used before the FT was done.

The HMQC and HMBC spectra have been plotted with the F_2 axis (hydrogen) horizontal for ease in comparison with the one-dimensional hydrogen spectra. The carbon decoupling used in the HMQC spectra can cause temperature gradients in the sample. This is illustrated with the fact that a temperature rise of 2° occurs after 128 HMQC transients if temperature control is turned off. Thus, with the very large expansion of the hydrogen axis in Figures 8−10, slight variations of chemical shift might be seen.

Results and Discussion

General Strategy. A scheme for hydrogen and carbon chemical shift assignments is shown in Figure 2. The alkene hydrogens observed in the one-dimensional spectrum provided the starting point. A delayed COSY spectrum showed which of those were correlated and also revealed the allylic hydrogens. The HMQC spectrum gave the chemical shift of the alkene carbon. The HMBC spectrum could confirm the chemical shifts of the allylic hydrogens, the second alkene carbon, and the allylic carbon. The two diastereotopic methylene hydrogen signals could in some cases be identified with their own COSY correlation. The chemical shifts of some carbonyl carbons not shown in Figure 2 could also be determined from the HMBC spectrum. The results are summarized in Table 1.

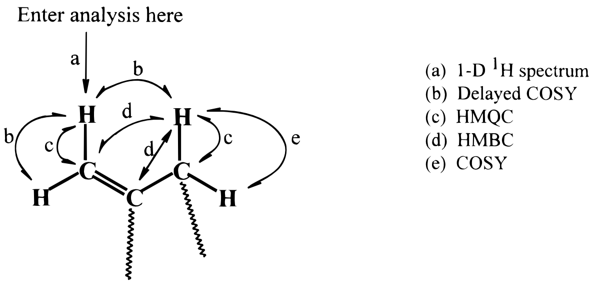

Figure 2. Possible strategies for assigning hydrogen and carbon chemical shifts in **1**−**4**.

Table 1. Hydrogen and Carbon NMR Chemical Shifts for 1−4

product	nucleus	obsd chem shift, ppm	pred chem shift, ppm
1	H_a	6.19	6.15^a (6.09^b)
	$H_{a'}$	5.46 (and 5.48^c)	5.58^a (5.55^b)
	H_c	2.43	
	$H_{c'}$	2.60	
	C_a	128.2 (and 128.1^c)	130.3^d (125.3^b)
	C_b	143.6	144.2^d (136.1^b)
	C_c	43.6	38.7^e
	C_d	167.3	165.0^e (167.7^b)
2	H_e	4.60	4.75^a
	$H_{e'}$	4.81 (and 4.86^c)	4.75^a
	H_g	1.59	
	H_h	2.35 (and 2.62^c)	
	$H_{h'}$	1.95 (and 1.94^c)	
	C_e	115.6 (and 112.7^c)	114.4^f
	C_f	141.1	143.7^f
	C_g	23.6	23.6^e
	C_h	51.2	46.4^e
	C_i	176.2	176.0^e
3	H_j, $H_{j'}$	4.73	4.75^a
	H_l	1.77	
	$H_{l'}$	2.23	
	C_j	118.6	114.4^f
	C_k	*g*	
	C_l	49.5	44.5^e
4	H_m	5.0	5.20^a
	H_o	1.35	
	H_p	*g*	
	C_m	135.8	132.5
	C_n	*g*	
	C_o	17.7	17.7^e
	C_p	54.4	46.5^e

[a] Reference 7a, pp H215−220. [b] Methyl methacrylate’s analogous chemical shifts. [c] Major and minor isomers, respectively, differing in stereochemistry down the chain. [d] Reference 7a, p C90. [e] Reference 7c. [f] Reference 7b, p 237. [g] Not detected.

One-Dimensional Spectra. The 400-MHz ^1H spectra of PMMA before and after X-ray irradiation are shown in Figure 3. The spectrum in Figure 3b shows the formation of considerable degradation product with upfield signals at *ca.* 0.96, 1.1, 1.6, and 2.1−2.5 ppm. Analysis of this region alone, though, was impossible. Progress was instead made by using the alkene region (Figure 4) as the starting point. The seven alkene hydrogen assignments (including minor stereoisomers) are indicated in Figure 4. The proposed chemical shifts are all supported by known compounds and/or chemical shift calculations[7] and are shown in Table 1.

The areas of the new upfield signals are much greater than the areas of the alkene hydrogens might suggest. This is probably due to cross-linking of the polymer

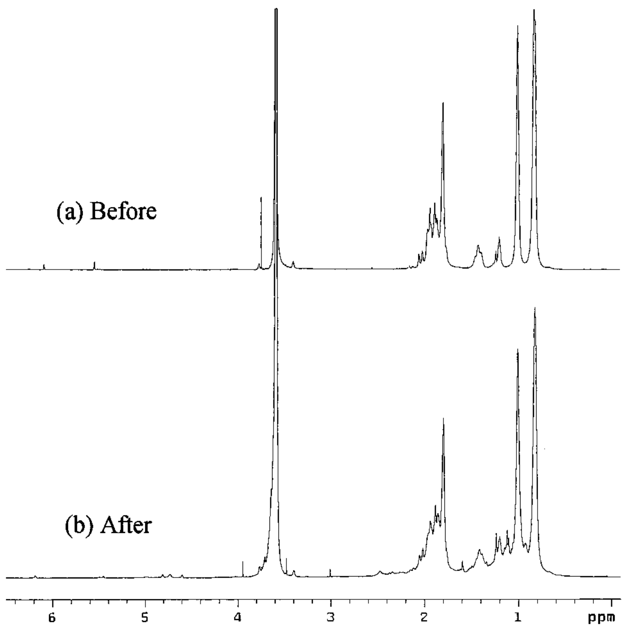

Figure 3. ^{1}H NMR spectra of PMMA: (a) before X-ray exposure; (b) after X-ray exposure.

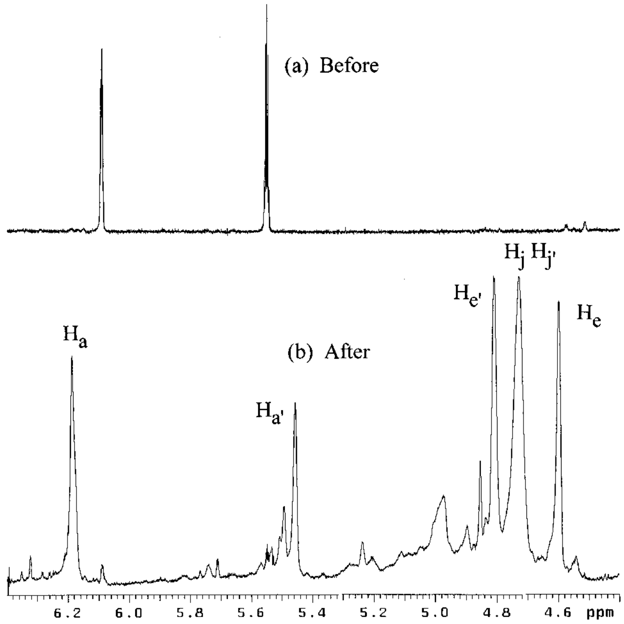

Figure 4. ^{1}H NMR spectra of PMMA in the alkene region: (a) before X-ray exposure showing the 0.5% methyl methacrylate impurity in the bulk material; (b) after X-ray exposure. The relative intensities of signals in (a) have no relationships to those in (b).

chains, which would consume alkene linkages or, at least, not incorporate them. Indeed, the relative amount of fragment **1** decreases with high X-ray doses. Cross-linking of the rather polarized and reactive α,β-double bond in **1** might be expected and is illustrated by the ease with which methyl methacrylate itself undergoes addition polymerization to form PMMA. Assignment of NMR signals for cross-linked residues is extremely difficult and will be addressed in a later paper. Integration of the alkene area and the large methoxy signal indicates the products **1-4** are present in the following yields based on monomer units present in the polymer: **1** (0.50%), **2** (0.47%), **3** (0.52%), **4** (0.18%).

Methyl formate was also found: ^{1}H NMR, 8.06 (q, 0.80 Hz), 3.74 ppm (d, 0.80 Hz); the 8.06 ppm ^{1}H formyl hydrogen correlated to a 161.1 ppm ^{13}C carbonyl signal in the HMQC spectrum and a 50.7 ppm methoxy carbon signal. Acetaldehyde was also seen: ^{1}H NMR, 9.78 ppm (q, 2.85 Hz).

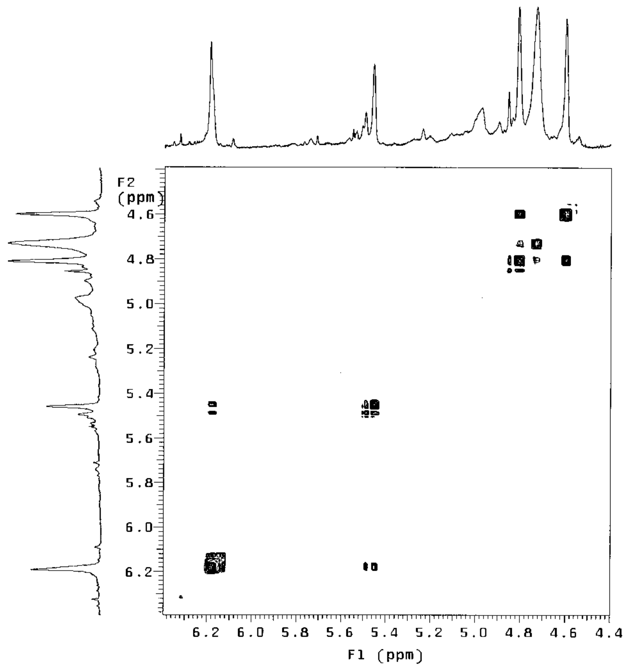

Figure 5. Delayed COSY spectrum of irradiated PMMA in the alkene region.

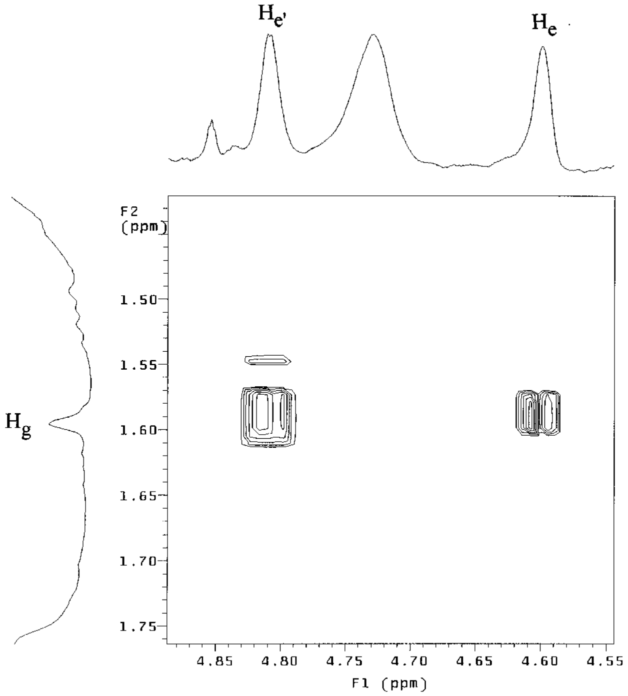

Figure 6. Delayed COSY spectrum of irradiated PMMA showing the correlation of alkene hydrogens in **2** with the allylic methyl hydrogens.

Two-Dimensional Spectra. The spectra shown in Figures 5–10 are typical. Many more expansions at a variety of vertical scalings were required to produce the chemical shifts reported in Table 1.

The intensity of the three-bond correlation between an alkene hydrogen and an allylic methyl group was always greater than a correlation to an allylic methylene group, probably due to the fact that there are more hydrogens in the methyl group and that the methylene

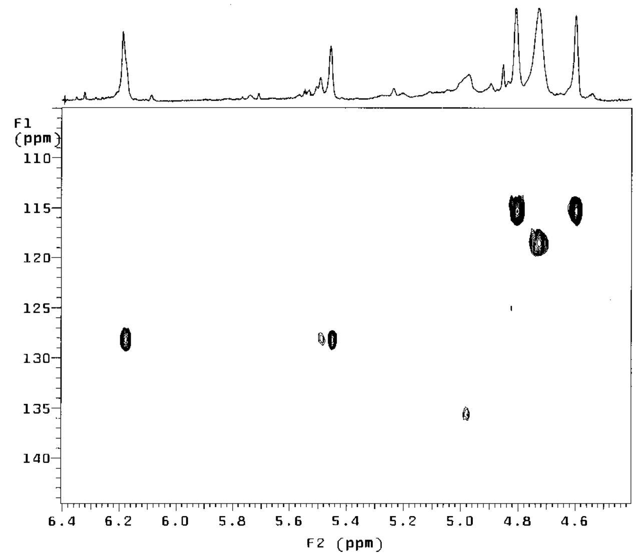

Figure 7. HMQC spectrum of irradiated PMMA in the alkene region.

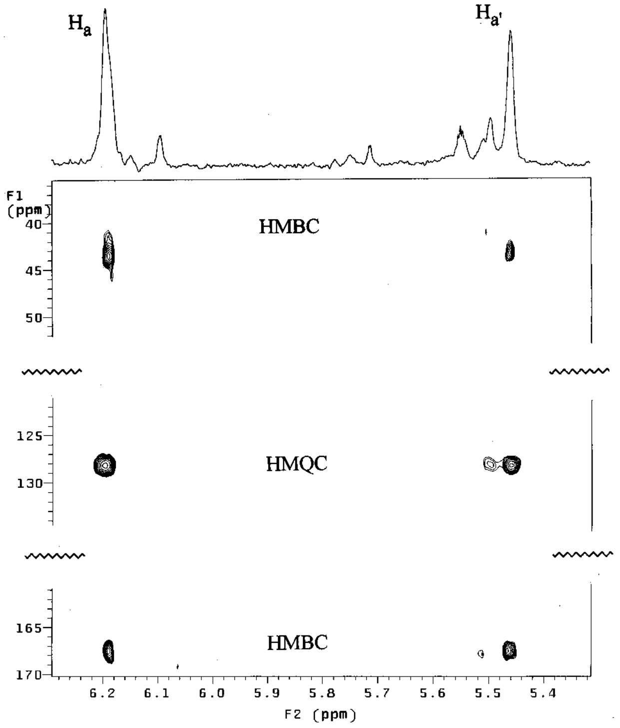

Figure 8. Composite of HMQC and HMBC spectra of **1** in the alkene hydrogen (H_a and $H_{a'}$) region. Positive contours shown.

hydrogens are diastereotopic and usually appear as single hydrogen correlations in different regions of the spectrum.

The HMQC spectrum (Figure 7) gives one-bond C−H correlations for the four alkene carbons in **1-4** which have hydrogens directly bonded to them. H_a and $H_{a'}$ are indeed bonded to the same carbon (128.2 ppm) as are H_e and $H_{e'}$ bonded to their carbon (115.6 ppm).

HMBC spectra, correlating weakly coupled carbons and hydrogens at longer range, give a wealth of ^{13}C chemical shift information. We were unable to detect the two-bond correlations between the alkene hydrogens and the alkene carbon at the opposite ends of the double bonds. These carbons could be identified, though, from the allylic hydrogens in the HMBC spectra. Composite HMQC/HMBC spectra are shown in Figures 8−10.

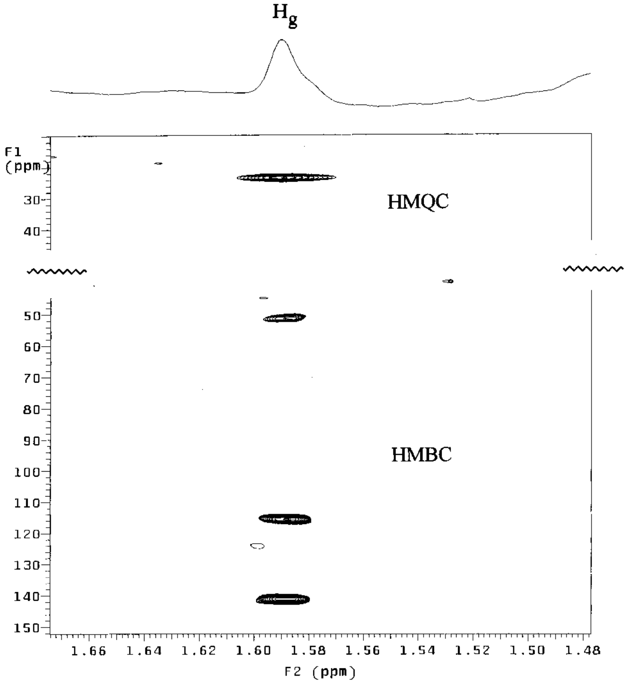

Figure 9. Composite of HMQC and HMBC spectra for **2** in the methyl hydrogen (H_g) region. Positive contours shown.

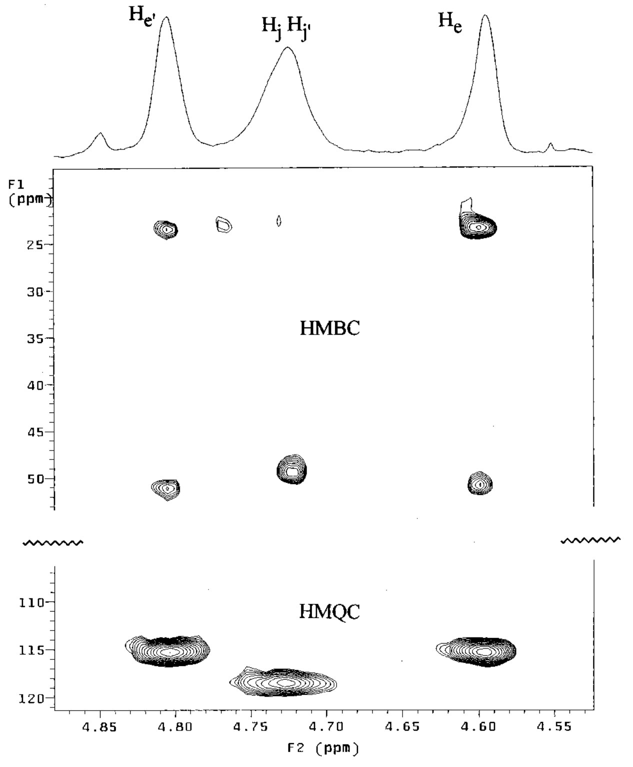

Figure 10. Composite of HMQC and HMBC spectra for **2** and **3** in the alkene hydrogen region (H_e, $H_{e'}$, H_j, and $H_{j'}$). Positive contours shown.

Product 1 (Chain Scission). The downfield alkene hydrogen chemical shifts of **1** (5.46 and 6.19 ppm) are strong support for its α,β-unsaturated carbonyl structure. The delayed COSY spectrum (Figure 5) shows unequivocally that they are coupled. The HMQC/HMBC data in Figure 8 show both alkene hydrogens correlated with the allylic methylene carbon (43.6 ppm) and terminal alkene carbon (128.2 ppm). Figure 8 also shows the conjugated carbonyl carbon at 167.3 ppm at somewhat higher field than the unconjugated ester carbonyl carbons of PMMA itself (176−178.5 ppm). The lower field hydrogen at 6.19 ppm is cis to the methoxycarbonyl group. There is a smaller peak at 5.48 ppm (Figure 4) which is also correlated with the 6.19 ppm region in Figure 5. This is probably a type of hydrogen analogous to the 5.46 ppm hydrogen ($H_{a'}$ in Figure 1) but with a difference in stereochemistry down the polymer chain. $H_{a'}$ is cis to the polymer chain and would be more sensitive to such stereochemical differences than would H_a. Table 1 summarizes these and other chemical shifts.

As stated above, heavier irradiation reduces the relative amount of **1**.

Product 2 (Chain Scission). The alkene hydrogen peaks at 4.60 and 4.81 ppm are correlated with one another (Figure 5) and with the allylic methyl hydrogens (1.59 ppm) in the delayed COSY spectrum (Figure 6). The combined HMQC/HMBC data of Figure 9 show the methyl hydrogens correlated to both alkene carbons (115.6 and 141.1 ppm), the methylene carbon (51.2 ppm), and the methyl carbon itself (23.6 ppm).

Figure 10 shows more combined HMQC/HMBC data. The 4.81 and 4.60 ppm alkene hydrogens are both correlated with their own carbon (115.6 ppm), the methylene carbon (51.2 ppm), and methyl carbon (23.6 ppm).

The HMBC spectrum also showed the methylene hydrogens as a pair of doublets (^{13}C splitting evident) centered at 2.35 and 1.95 ppm and correlated with the 141.1 and 115.6 carbons which had been previously assigned. The methylene hydrogens are diastereotopic (2.35 and 1.95 ppm) and are correlated to one another in the COSY spectrum.

The 176.2 ppm carbonyl carbon of the methoxycarbonyl group was found at a carbon chemical shift similar to that of PMMA itself.

Product 3 (Chain Intact). Correlation of the 4.73 ppm hydrogen signal with any other alkene hydrogens in the COSY or delayed COSY spectra was not detected. The two alkene hydrogens in **3** are approximately chemical shift equivalent, differing only by stereochemistry down the chains. The delayed COSY shows correlations with signals at 1.77 and 2.24 ppm. These are consistent with the diastereotopic methylene hydrogens in **3**. The HMQC portion of Figure 10 shows the 4.73 ppm hydrogen correlated with its carbon at 118.6 ppm. The HMBC spectrum shows only one allylic carbon (49.5 ppm). This is also consistent with the structure of **3**.

The previously reported ^{13}C signals at 128.9 and 161.9 ppm which were assigned to **3**[3] were probably due to C_a and methyl formate, respectively.

Product 4 (Chain Intact). The least distinct alkene signal for the four products is the broad signal at *ca.* 5.0 ppm due to **4**. The broadness could be explained by the fact that **4** has the only double bond which is capable of cis/trans isomerism. This hydrogen is also closer to differences in chain stereochemistry than the alkene hydrogens in **1-3.** The delayed COSY spectrum shows the 5.0 ppm signal correlated to allylic methyl hydrogens at 1.35 ppm. The HMQC shows the carbon at 135.8 ppm, while the HMBC spectrum gives the methyl (17.7 ppm) and methylene (45.6 ppm) carbons. While all of this is consistent with **4**, its structural assignment is less secure than **1**−**3**.

Conclusion

Thirty four ^1H and ^{13}C NMR chemical shifts for X-ray-irradiated PMMA have been assigned using one- and two-dimensional NMR spectroscopy. The major alkene products have been identified. Each product results from the loss of methyl formate which was also detected. The chain-scission products (**1** and **2**), desirable from the standpoint of facile dissolution using appropriate solvent systems, are formed in significant amounts using X-ray irradiation (but are relatively minor products under ultraviolet photolysis[3a,8]). The present work provides the foundation for future experiments at lower irradiation doses using energies from the ultraviolet through hard X-ray regions. Work continues on the identification of cross-linked structures.

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References and Notes

(1) (a) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography: Theory, Materials, and Processing;* ACS Symposium Series 219; American Chemical Society: Washington, DC, 1983; pp 122−125. (b) Ocola, L. E.; Cerrina, F. *J. Vac. Sci. Technol. B*, **1993**, *11*, 2839. (c) Spiller, E; Feder, R. X-ray Lithography. In *X-ray Optics*; Quesser, H. J., Ed.; Springer: Berlin, 1977; p. 35.

(2) See the following for representative PMMA NMR references: (a) Kawamura, T.; Toshima, N.; Matsuzaki, K. *Macromol. Chem. Phys.* **1994**, *195*, 2677. (b) Kotyk, J. J.; Berger, P. A.; Remsen, E. E. *Macromolecules* **1990**, *23*, 5167. (c) Ferguson, R. C.; Ovenall, D. W. *Macromolecules* **1987**, *20* (4), 1245. (d) Moad, G.; Rizzardo, E.; Solomon, D. H.; John, S. R.; Willing, R. I. *Macromolecules* **1986**, *19* (10), 2494. (e) Ferguson, R. C. *Macromolecules* **1969**, *2* (3), 237. (f) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.

(3) (a) Moore, J. A.; Choi, J. O. *Radiation Effect on Polymers*; ACS Symposium Series 475; Clough, R. L., Shalaby, S. W., Eds.; American Chemical Society: Washington, DC, 1991; pp 156−192. (b) The ^1H NMR assignments for the alkene hydrogens of the products of X-ray-, electron-, and proton-irradiated PMMA were as follows: **1** (5.46 and 6.19 ppm), **2** (4.62 and 4.82 ppm), **3** (4.75 and 5.0 ppm), and **4** (broad signal, 5.14−5.22 ppm). (c) The only ^{13}C NMR signals reported were for UV-irradiated PMMA film[3] (128.9 and 161.9 ppm) and were assigned to **3**.

(4) Dong, L.; Hill, D. J. T.; O'Donnell, J. H.; Pomery, P. J.; Hatada, K. *J. Appl. Polym. Sci.* **1995**, *59*, 589.

(5) For a review of COSY, HETCOR, HMQC, and HMBC NMR, see: Bruch, M. D. Multidimensional Spectroscopy of Liquids. In *NMR Spectroscopy Techniques*; Bruch, M. D., Ed.; Marcel Dekker: New York, 1996; pp 145−238.

(6) See ref 2 for discussions of NMR determination of tacticity in PMMA.

(7) (a) Pretsch, E.; Seibel, J.; Simon, W.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds* (English Edition); Springer-Verlag: Berlin, 1983. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley and Sons: New York, 1991. (c) Chem Windows C13 Module by E. Pretsch, Softshell International Ltd., Grand Junction, CO.

(8) Hayataka, K. M., unpublished results, Department of Chemistry, University of Montana, 1996.

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