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Investigation of High-Temperature Radiation Effects on Poly(methyl methacrylate) of Specific Tacticity

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ABSTRACT: The high-temperature radiation properties of isotactic and syndiotactic poly(methyl methacrylate) (PMMA) have been investigated by NMR spectroscopy. The tacticity changes for the isotactic PMMA during γ-irradiation have been simulated by a model which allows for recombination of a scissioned bond and for the recombined bond to be in either the meso or racemic configuration with probability P_t. The calculated values of P_t were found to be consistent with the tacticity parameter P_m values for the free-radical polymerization of a methyl methacrylate monomer. The *G*-value of the temporary chain scission and then recombination, *G*(TCS), for the isotactic PMMA sample which was γ-irradiated at 80 °C was found to be 18.6, which is much higher than the *G*-value of the permanent main-chain scission, *G*(S). A mechanism to explain the observed tacticity changes have been proposed.

Introduction

Poly(methyl methacrylate) (PMMA) is used as a positive resist in advanced microlithography with electron beams, proton beams, X-rays, or ultraviolet light.[1] Irradiation of PMMA causes main-chain scission, which is desired in microlithography because it increases solubility in the exposed areas. Hydrogen abstraction occurs upon irradiation, producing carbon−carbon double bonds in either the main chain or the methyl side chain by cleavage of methyl groups but without causing main-chain scission.[2] It has also been found that there is a possibility of recombination of the scissioned bonds in the polymer.[3,4] This process has been referred to as temporary chain scission (TCS). Formation of double bonds and recombination of scissioned bonds in the polymer are undesirable for microlithographic applications because fragments of PMMA with substantially increased solubility are not produced. There have been numerous studies on main-chain scission and formation of double bonds,[5−10] but, by comparison, little attention has been given to the recombination of scissioned bonds in the polymer.

The first observation of recombination of the scissioned bonds in the polymer was reported by Thomson[3] using electron beam irradiation of isotactic PMMA, by monitoring the change in the α-CH$_3$ triads by proton NMR spectroscopy. It has been suggested that, on irradiation, a temporary chain scission followed by rotation and recombination at the quaternary carbon would lead to racemization. David and co-workers[4] repeated this experiment using γ-irradiation in the presence and absence of ethanethiol, an electron scavenger. They reported that racemization was observed in the absence of ethanethiol, but in the presence of ethanethiol, there was no change in the isotactic triad fraction on irradiation. David *et al.* suggested that the excited state of the PMMA molecule in the presence of ethanethiol does not have enough energy to cause temporary bond cleavage and resultant racemization.

Table 1. Properties of PMMA of Specific Tacticity

sample	M_n	M_w/M_n	tacticity (%) mm	 mr	 rr
ON72-C	20 700	1.25	98	1	1
NF656-ISO	3 100	1.18	97	2	1
DPI-1	22 700	1.26	3	8	89

Tacticity is a fundamental microstructural feature in polymers that directly affects the physical properties and the chemical reactivity of the polymers. Although the importance of tacticity is widely known,[11−15] the role that tacticity may play in the radiation chemistry of PMMA has only been investigated to a limited extent.[3,4,16] No previous reported has been found of changes in the tacticity in the high-temperature γ-irradiation of PMMA.

The purpose of this work is to investigate the radiation chemistry of PMMA with various tacticities by NMR spectroscopy. High-temperature irradiation at different temperatures and radiation doses has been carried out to examine the mechanism of recombination of the scissioned bonds in the polymer. A mathematical model has been proposed in order to simulate the tacticity changes after γ-irradiation and to estimate the *G* value for temporary chain scission, *G*(TCS).

Experimental Section

Materials. The amorphous isotactic and syndiotactic PMMA was prepared in the Department of Chemistry, Osaka University, Osaka, Japan. The properties of these polymers determined in Osaka are shown in Table 1.

γ-Irradiation. The polymers were pumped under vacuum (~1 mPa) for at least 24 h prior to being sealed. These samples were γ-irradiated with different radiation doses in a ^{60}Co AECL Gammacell 220 radiation unit at room temperature and in a pond facility of the Australian Nuclear Science and Technology Organization at Lucas Heights, Sydney, Australia, using ^{60}Co γ-irradiation at 80 and 110 °C. The radiation

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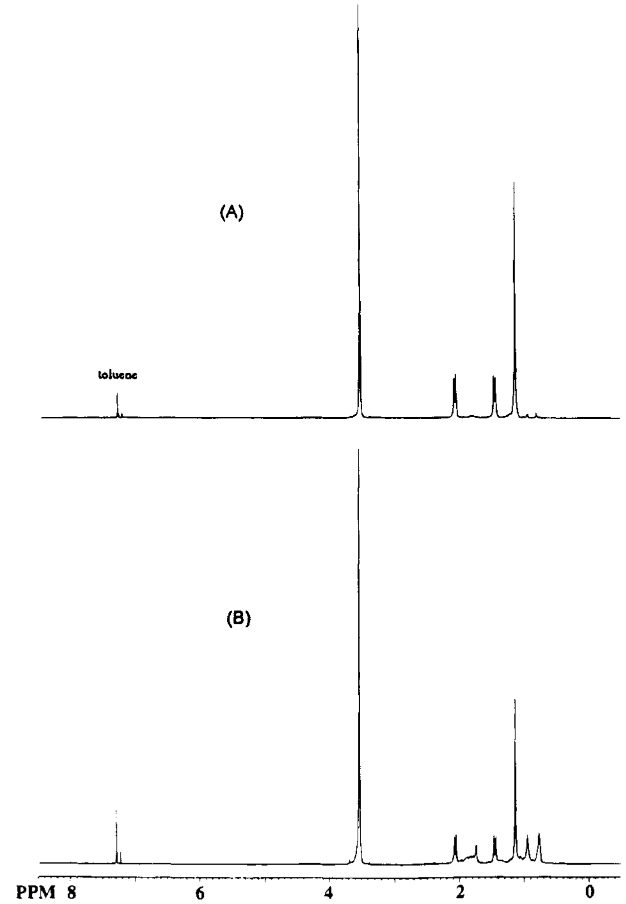


Figure 1. ^1H NMR spectra of isotactic PMMA (ON72-C): (A) unirradiated; (B) 500 kGy of γ-irradiation at 80 °C.

temperature has been limited in order to avoid any radiation-induced depolymerization at higher temperatures.

NMR Measurements. The ^1H and ^{13}C NMR spectra of the samples were recorded on a Bruker AMX-500 spectrometer using ca. a 7% (w/v) solution in $CDCl_3$ at 303 K. Two-dimensional (2D) proton shift correlation using 45° read pulse (COSY) spectroscopy was used to assign the new peaks in the ^1H spectrum after γ-irradiation. The experiments employed a recycle time of 3 s, with 32 transients being collected for each t_1 value. A total of 512 spectra, each containing 2048 data points, was accumulated.

Computer Simulations

It has been shown previously that computer simulation can be an effective way to examine the compositional heterogeneity in copolymers and the tacticity in homopolymers.[15,17] We have extended the simulation to the tacticity changes after γ-irradiation of PMMA.

In this work, the original polymer chains with desired tacticity parameters were generated by the reaction probability model, in which it has been assumed that the tacticity in the polymer chain is controlled by Bernoullian probability statistics.[12] The polymerization degree was set large enough (N = 20 000) so that the effects of chain ends can be neglected.

The tacticity changes on γ-irradiation of a polymer were simulated by choosing two parameters, D and P_t. D represents the yield of temporary chain scission per monomer unit. The G value for temporary chain scission may be calculated from the dependence of D on absorbed dose. P_t represents the probability for a recombined bond to be in the meso configuration. An equal scission probability for each monomer unit and random scission at the quaternary carbon of the main chain was used in the simulation. Cross-linking was not included in the model, since all experimental evidence indicates that it is negligible, $G(x) \sim 0$.[18] Therefore, the scission and recombination would occur randomly in the polymer main chain at a rate given by D. The tacticity for the recombined monomer unit in the main chain is controlled by the value of P_t. The total tacticity change after the simulation of the γ-irradiation may be calculated for various values of the parameters D and P_t, and the values which provide the best fit to the data can be identified. Multiple repetitions (NP = 1000) have been used in order to generate enough data that statistical noise is relatively unimportant.

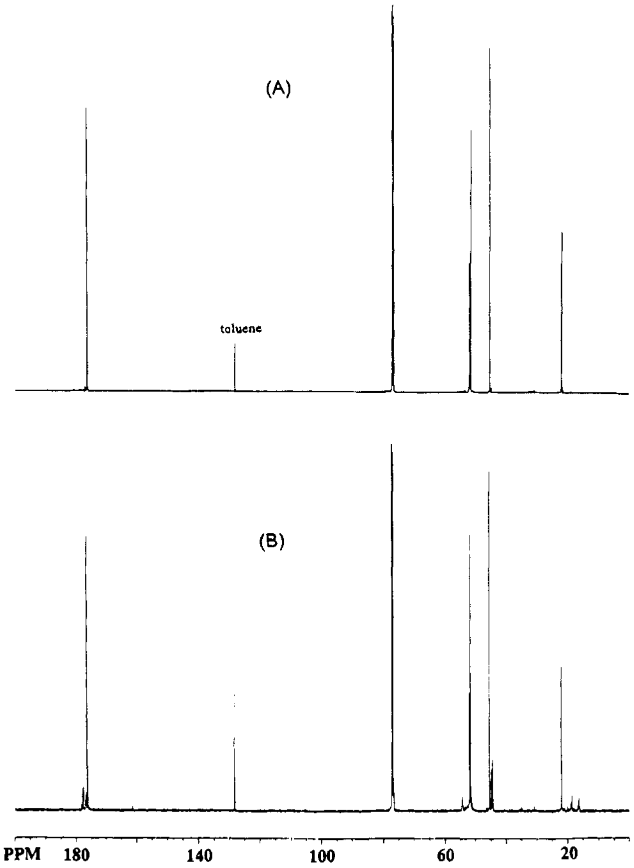


Figure 2. ^{13}C NMR spectra of isotactic PMMA (ON72-C): (A) unirradiated; (B) 500 kGy of γ-irradiation at 80 °C.

Table 2. Major New ^1H Resonance Peaks after γ-Irradiation

peak position (ppm)	assignment[a]	peak position (ppm)	assignment[a]
8.06	H*COOCH$_3$	4.49	CH$_3$OCH$_2$*OCH$_3$
4.92	unsaturation in main chain	3.72	HCOOCH$_3$*
4.75	unsaturated chain end	3.45	CH$_3$*OCH$_2$OCH$_3$*
4.68	unsaturation in main chain	3.32	CH$_3$*OH
4.53	unsaturated chain end	1.55	CH$_2$=C(CH$_3$*)–

[a] The protons marked with an asterisk are those to which the resonance peaks are assigned.

Results and Discussion

New Structures and Small-Molecule Compounds Formed during γ-Irradiation. ^1H and ^{13}C NMR spectroscopies were used to investigate the formation of new molecular structures and small-molecule compounds in PMMA samples during γ-irradiation. Figures

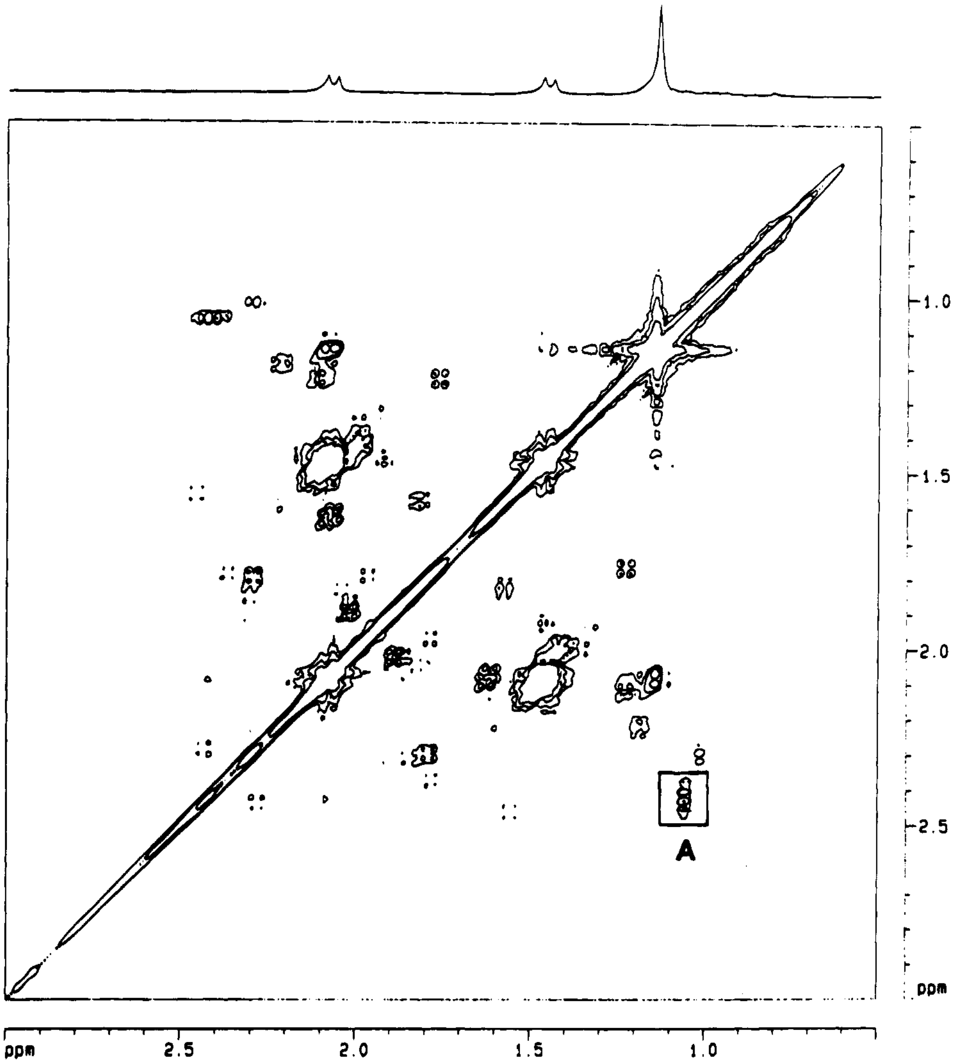


Figure 3. COSY spectrum of isotactic PMMA (ON72-C) which was γ-irradiated at room temperature to a dose of 1600 kGy.

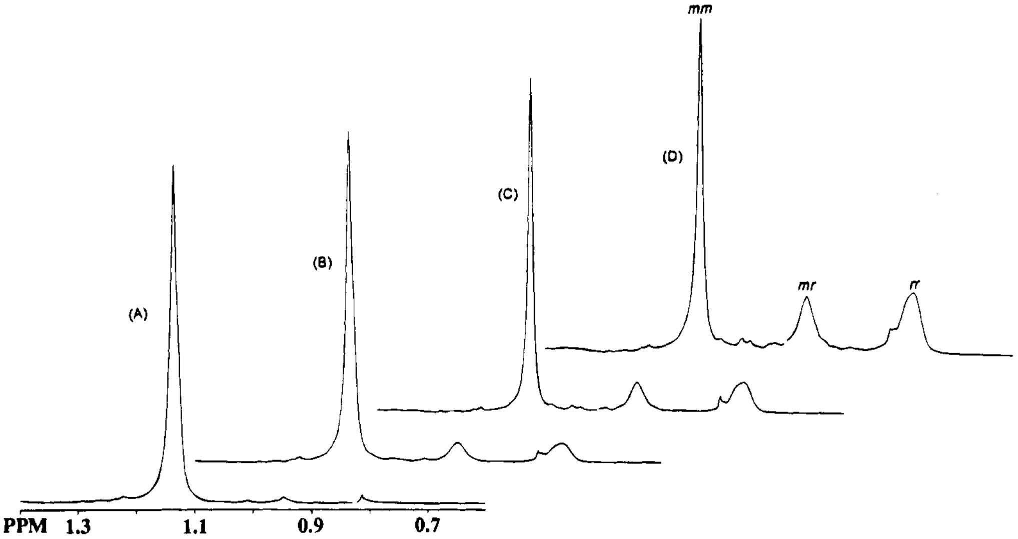


Figure 4. ^{1}H NMR spectra (methyl region) of isotactic PMMA (ON72-C) which was γ-irradiated at 80 °C to doses of (A) 0, (B) 165, (C) 300, and (D) 500 kGy.

1 and 2 show the ^{1}H and ^{13}C NMR spectra for isotactic PMMA (ON72-C) which had been γ-irradiated at 80 °C to a dose of 500 kGy. New resonance signals arising from γ-irradiation of the sample are more clearly observed in the ^{1}H NMR spectrum than that in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum can provide a lot of information concerning the new molecular structures and small-molecule compounds formed during γ-irradiation.

Most of the new peaks which appear in the ^{1}H NMR spectrum for the sample after γ-irradiation can be assigned to new structures and small molecules which

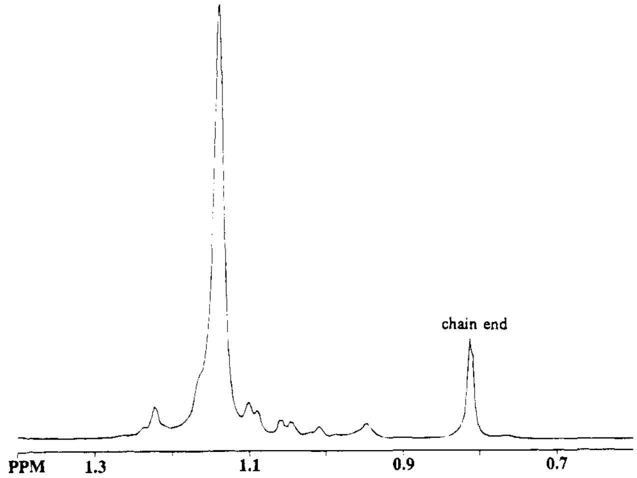


Figure 5. ^{1}H NMR spectrum (methyl region) of isotactic low molecular weight PMMA (NF656-ISO).

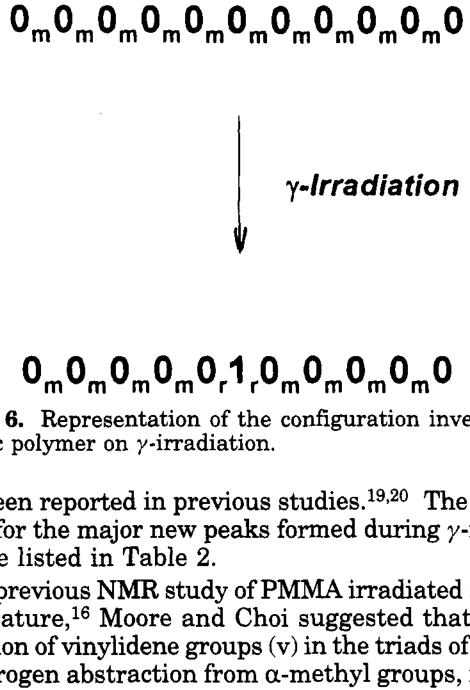


Figure 6. Representation of the configuration inversion in isotactic polymer on γ-irradiation.

have been reported in previous studies.[19,20] The assignments for the major new peaks formed during γ-irradiation are listed in Table 2.

In a previous NMR study of PMMA irradiated at room temperature,[16] Moore and Choi suggested that on the formation of vinylidene groups (v) in the triads of PMMA by hydrogen abstraction from α-methyl groups, rr, mm, and mr triad units give rise to two different types of segments (rv and mv). It has been suggested by Moore and Choi[16] that the new peaks in the ^{1}H spectrum in the region 1.0−1.2 ppm after γ-irradiation may be assigned to α-methyl protons (in the racemic configuration) next to a vinylidene group (rv). In this work, COSY spectroscopy was used to identify some of the new peaks formed during γ-irradiation. Figure 3 shows the COSY spectrum for isotactic PMMA (ON72-C) which had been γ-irradiated at room temperature to a dose of 1600 kGy. Of interest is the cross peak (A), which is due to the correlation between a CH_3 resonance in the region 1.0−1.1 ppm and a CH resonance in the region 2.4−2.5 ppm. This cross peak may be assigned to the new structure $-CH(CH_3)-$ formed during γ-irradiation. This structure has not been reported previously. Therefore, our assignments of the new peaks in the region 1.0−1.2 ppm are different from those by Moore and Choi.[16]

Tacticity Changes in γ-Irradiated Isotactic PMMA. The α-methyl region of the ^{1}H NMR spectra of the isotactic PMMA (ON72-C) which was γ-irradiated at 80 °C to doses of 165, 300, and 500 kGy, respectively, together with a spectrum of an unirradiated sample, is shown in Figure 4. Triad splittings for the tacticity sequences may be observed, and these tacticities have been indicated on the spectra. The spectrum of the low molecular weight isotactic PMMA (NF656-ISO) in Figure 5 shows that the resonance at 0.817 ppm is more intense than that for the high molecular weight PMMA (ON72-C). Therefore, the resonance due to the α-methyl protons at the chain ends may be assigned to this position. The peak due to the chain ends may be separated from those due to the tacticity triads by using the Peakfit computer software package. The triad distributions obtained from the intensities of the α-methyl proton resonances are given in Table 3.

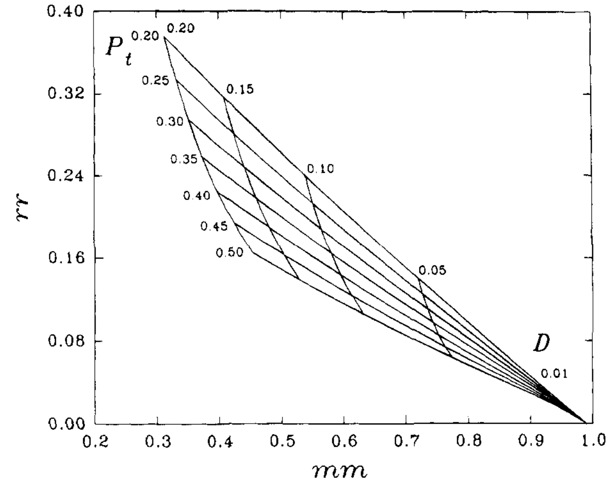


Figure 7. Computer simulations of the tacticity changes with different P_t and D values for isotactic PMMA on γ-irradiation. (The tacticity of the polymer used in the simulation had the same initial triad fractions as the polymer used in the radiation study.)

Table 3. Tacticity Triads after γ-Irradiation at 80 °C for Isotactic PMMA

radiation dose (kGy)	mm	mr	rr
0	0.98	0.02	0.00
165	0.80	0.10	0.10
300	0.69	0.15	0.16
500	0.55	0.22	0.23

It is evident from Figure 4 that, with increasing radiation dose, the isotactic (mm) content of the polymer is decreased, while the syndiotactic (rr) and heterotactic (mr) contents are increased. (Similar significant changes have been obtained in the tacticity sequences for isotactic polypropylene on γ-radiolysis at 200 °C.[21]) The changes in the triad tacticity may be attributed to the recombination of scissioned bonds located on the quaternary carbon during γ-irradiation, so that the configuration for some of the recombined units will be changed.

With a predominance of the stereoregular isotactic sequence comprising the PMMA chain, it may be assumed that for low radiation doses the recombination of a scissioned bond at the quaternary carbon which results in a configurational inversion will most probably occur as an isolated (random) event, such as that shown in Figure 6 in which the Price[22] "0−1" and Bovey[23] "m−r" nomenclatures are used.

From the figure we may predict that one inversion event will result in the loss of 3 mm triads and the formation of 2 mr triads and 1 rr triad. However, the experimental results are not in agreement with these predicted values. The rr triad fraction formed on γ-irradiation is larger than the predicted value, while

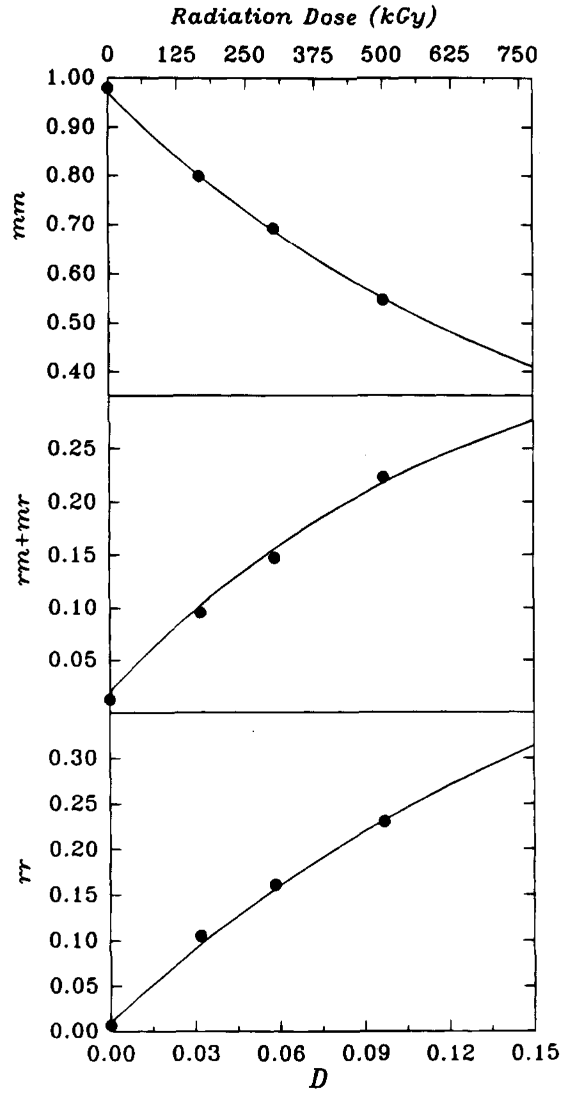


Figure 8. Tacticity changes for isotactic PMMA (ON72-C) on γ-irradiation at 80 °C: (●) experimental; (—) computer simulation.

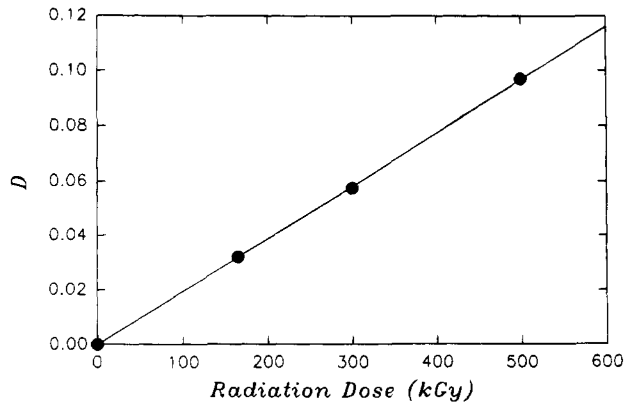


Figure 9. Relationship between experimental absorbed radiation dose and D for the isotactic PMMA on γ-irradiation at 80 °C.

the mr triad is less than the predicted value, on the basis of this model. This suggests that at the doses used in the study the events are not isolated.

It has been assumed in the above model that the recombination of a scissioned bond at the quaternary carbon is an isolated, single (random) event. However, in practice, with an increase in the radiation dose the events will not be isolated, and the radiation history of the polymer will affect the observed results after extensive cleavage and recombination. In addition, a previously scissioned and recombined bond may be recleaved, and the simple assumption of the above model does not account for this situation. Therefore, a Monte Carlo computer simulation, as described above, has been carried out in order to predict the changes in the chain configuration in the process of γ-irradiation. Figure 7 shows the predicted rr and mm triad fractions after γ-irradiation obtained for various values of the simulation parameters D and P_t. This figure shows that, with an increase in D, the mm triad is reduced and the rr triad is increased. However, an increase in the value of P_t will lead to an increase in the mm triad and a decrease in the rr triad.

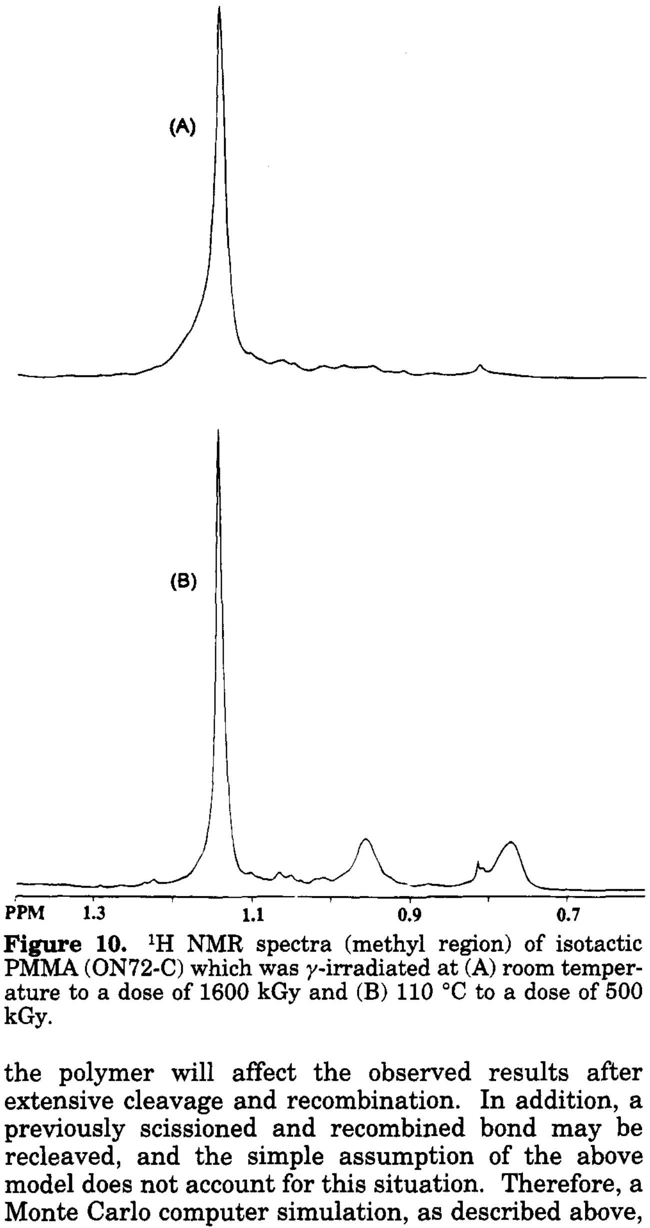


Figure 10. ^{1}H NMR spectra (methyl region) of isotactic PMMA (ON72-C) which was γ-irradiated at (A) room temperature to a dose of 1600 kGy and (B) 110 °C to a dose of 500 kGy.

It has been previously suggested that, for the irradiation of isotactic PMMA at room temperature,[3,4] the probability for a recombined bond to be in the meso configuration is equal to that for the racemic configuration ($P_t = 0.5$). However, it was found that the triad data obtained from the radiation experiments at 80 °C could not be simulated with a value of $P_t = 0.5$.

It is likely that the molecular structure of the polymer would control the configuration of the recombined unit in the chain. Therefore, the value of P_t would depend on the structure of the polymer and may differ significantly from 0.5. For example, in the free-radical polymerization of methyl methacrylate monomer, the probability of generating a meso diad between a growing chain radical and an incoming monomer, P_m, has been found to depend on the polymerization temperature and

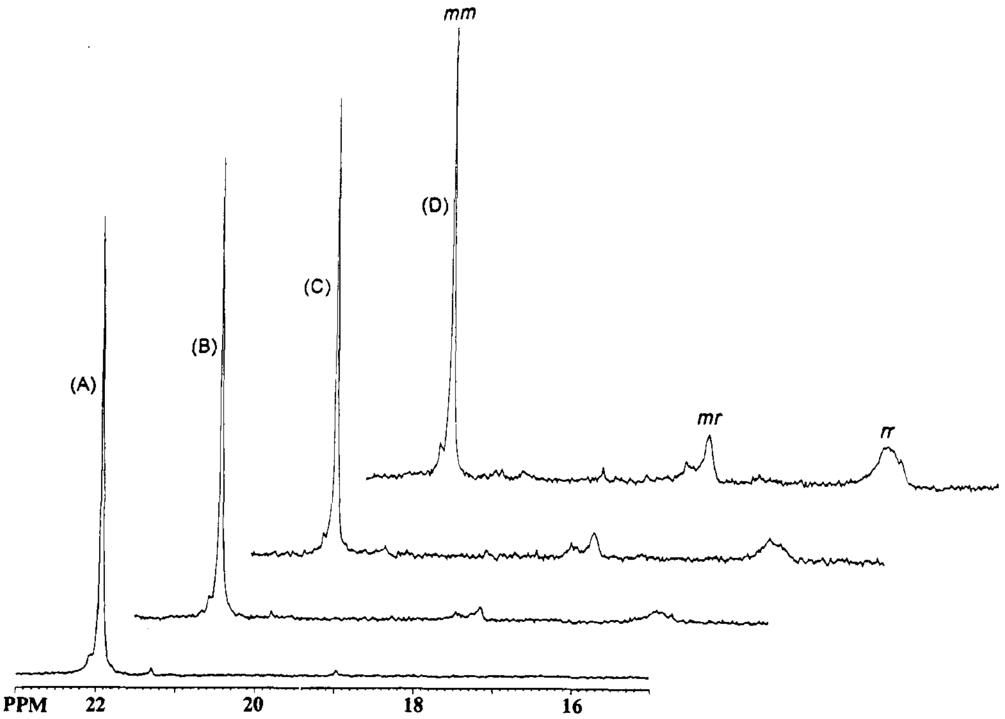


Figure 11. ^{13}C NMR spectra (methyl region) of isotactic PMMA (ON72-C) which was γ-irradiated at 80 °C to doses of (A) 0, (B) 165, (C) 300, and (D) 500 kGy.

has a value much less than 0.5.[24] This means that, in the free-radical polymerization of methyl methacrylate monomer, the tendency is for the PMMA chain to contain more syndiotactic than isotactic triads. The dependence of P_m on temperature has been described approximately by the eq 1[24]

$$\ln \frac{P_m}{1 - P_m} = -\frac{401.1}{T} - 0.217 \qquad (1)$$

where T is the absolute temperature. Thus, if one polymerizes methyl methacrylate monomer at 80 °C, the value of P_m is approximately 0.205.

It may be suggested that, if the irradiation temperature is higher than the glass transition temperature of the polymer, the polymer chain segments experience a high degree of mobility and the recombination of the scissioned bond at the quaternary carbon would have a tendency to adopt the same average tacticity as that observed in the free-radical polymerization of the methyl methacrylate monomer at the same temperature. This would mean that at 80 °C the value of P_t would be the same as that for P_m ($P_m = 0.205$). Using this assumption, the tacticity changes after γ-irradiation may be simulated. Figure 8 shows the experimental and calculated values of the triad fractions for absorbed radiation doses of 165, 300, and 500 kGy at 80 °C.

From Figure 8, the calculated results are in good agreement with the experimental data. In the model the number of bonds which are scissioned and then recombined will have a linear dependence on the absorbed radiation dose. By fitting the calculated triads to the experimental data, we can obtain the value of D which provides the best representation of the experimental triad data. Figure 9 shows the highly linear relationship between the radiation dose and the value of D. From the fit, the G value for temporary chain scission has been calculated to be G(TCS) = 18.6.

The effect of the irradiation temperature has been examined by γ-irradiation of the isotactic PMMA sample at room temperature, 80 and 110 °C. Figure 10 shows the ^1H NMR spectra of the isotactic PMMA (ON72-C) which was γ-irradiated at room temperature to a dose of 1600 kGy and at 110 °C to a dose of 500 kGy, respectively. In the figure the α-methyl proton region from 0.5 to 1.3 ppm is shown. It is evident that the tacticity change of the sample which was γ-irradiated at room temperature is very small compared with that of the samples γ-irradiated at high temperatures. The tacticity triad fractions in the sample which was γ-irradiated at 110 °C have been obtained (rr of 0.18, mr of 0.18, and mm of 0.64). They show that the changes in tacticity are less at 110 °C than the corresponding values for the sample γ-irradiated at 80 °C to the same radiation dose (500 kGy). A computer simulation has been carried out to fit the experimental results at 110 °C. From the simulation, the best fit values for the experimental triad fractions after γ-irradiation to a dose of 500 kGy at 110 °C are $D = 0.070$ and $P_t = 0.230$. These values can be compared with the corresponding D and P_t values obtained at 80 °C ($D = 0.097$, and $P_t = 0.205$) and can be explained by the greater molecular mobility at the higher temperature. This would lead to a reduced probability for recombination of the scissioned bond, so that the D value will decrease as temperature increases. In addition, the increase in the radiation temperature would have a tendency to increase the probability for the recombined bond to adopt a meso configuration, which would be consistent with the situation found in the free-radical polymerization. From eq 1, P_m at 110 °C may be calculated to be 0.22, while the best value for P_t at 110 °C was found to be 0.23. Thus, P_m and P_t are in good agreement and within experimental error.

The ^{13}C NMR spectra have also been used to analyze the tacticity of isotactic PMMA. The tacticity assignments for the resonances have been widely reported in the literature.[25-29] In this work, the triad distribution can been obtained from the methyl carbon and quaternary carbon regions. Figures 11 and 12 show the

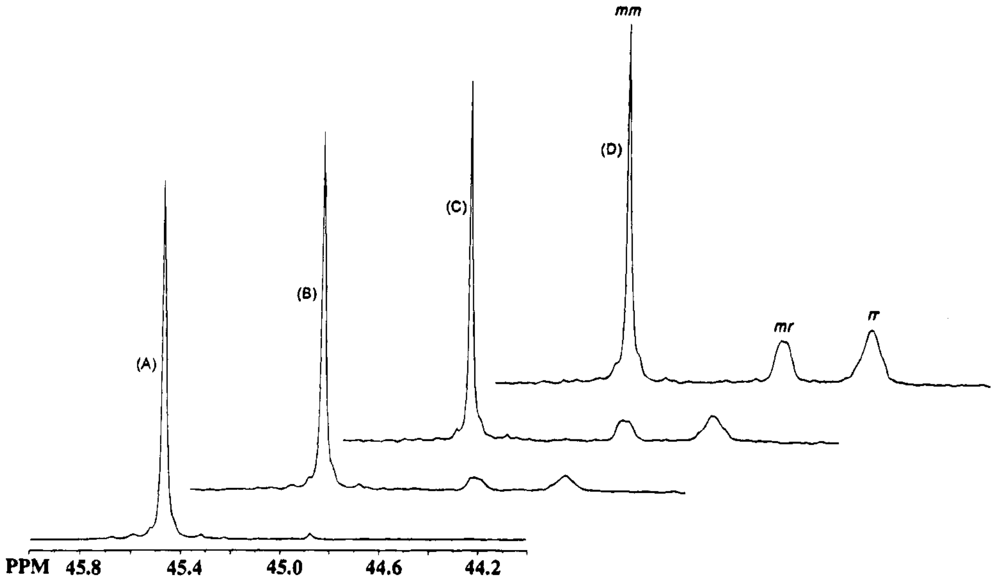


Figure 12. ^{13}C NMR spectra (quaternary carbon region) of isotactic PMMA (ON72-C) which was γ-irradiated at 80 °C to doses of (A) 0, (B) 165, (C) 300, and (D) 500 kGy.

Table 4. Triad Fractions from Resonances in the ^{13}C NMR Spectra due to Quaternary Carbons and Methyl Carbons for 80 °C γ-Irradiation of Isotactic PMMA, together with the Computer Simulation Results[a]

obsd carbon	triad tacticity	irradiation			
		none	165 kGy	300 kGy	500 kGy
quaternary	mm	0.99	0.80	0.69	0.55
	mr	0.01	0.10	0.15	0.22
	rr	0.00	0.10	0.16	0.23
methyl	mm	0.99	0.80	0.67	0.55
	mr	0.01	0.10	0.15	0.22
	rr	0.00	0.10	0.18	0.23
simulation	mm	0.99	0.80	0.69	0.55
	mr	0.01	0.10	0.16	0.22
	rr	0.00	0.10	0.15	0.23

[a] The computer simulation was carried out with P_t of 0.205 and D of 0.000 (no irradiation), 0.0320 (165 kGy irradiation), 0.0575 (300 kGy irradiation), and 0.0970 (500 kGy irradiation).

changes of the resonance intensities with different radiation doses at 80 °C for the methyl carbons and the quaternary carbons, respectively. The triad assignments have been marked on the figures. As with the observations for the ^{1}H NMR spectra of the methyl group, the mm triad fraction is increased with an increase in the radiation dose, while the rr triad fraction is decreased. Table 4 shows the calculated triad fraction values observed from Figures 11 and 12, together with the triad data obtained from the ^{1}H spectra and the computer simulations. The results observed from ^{13}C NMR spectra are in good agreement with those from ^{1}H spectra, within experimental error.

The carbonyl group resonances between 175 and 179 ppm, as shown in Figure 13, may be observed to the pentad level. The pentad fractions for the samples after γ-irradiation at 80 °C with different radiation doses, together with the computer simulation results, are given in Table 5. It is evident that the experimental NMR data are in good agreement with the computer simulation results.

In summary, the temporary chain scission model discussed above can account for the tacticity changes observed on radiolysis of isotactic PMMA. Using this model, the G value for temporary chain scission, G(TCS), is larger than might be expected on the basis of what is presently known for radiolysis reactions which do not involve a chain process. The unexpectedly large value for G(TCS) could indicate that the assumption of a random model for the chain scission and recombination does not apply and that the tacticity changes are clustered, nonrandom events, as suggested by Busfield *et al.*[30] as an explanation for their observed tacticity changes in irradiated isotactic polypropylene. However, on the basis of the experimental data obtained in this work the assumption of an ad hoc, more complicated model involving nonrandom events is not justified. In addition to this, incorporation of nonrandom events in our computer simulation would result in a reduction in the value of P_t, to below the value of P_m for free-radical polymerization. The previous observations from radical yields, volatile product yields, and scission yields would also rule out the simultaneous scission of two or more adjacent polymer units.

The effects of γ-irradiation temperature have also been examined by ^{13}C NMR spectroscopy. Figure 14 shows the ^{13}C NMR Spectrum of the isotactic PMMA after γ-irradiation to a dose of 1600 kGy at room temperature. The changes in the tactic signals are difficult to observe at this temperature and radiation dose. Thus at room temperature, where chain mobility is much less, cage recombination would appear to produce no change in the tacticity of the scissioned unit.

Figure 15 shows the ^{13}C NMR spectrum of the isotactic PMMA sample after γ-irradiation to a dose of 500 kGy at 110 °C. Tacticity changes during γ-irradiation may be observed from this spectrum and provide results which are consistent with those from the ^{1}H NMR spectrum and are also in an agreement with the computer simulation result, as shown in Table 6.

Isotactic PMMA has a T_g of about 38 °C.[31] At room temperature, the amount of thermal energy available for molecular motion in the isotactic PMMA is relatively small. Thus the polymer chains are effectively "frozen", and there is insufficient free volume to allow molecular rotation or translation to take place, so that on scission and recombination a change in the configuration is unlikely to occur. However, above T_g the chain mobility is increased and recombination with a change in tacticity can occur more easily. An increase in temperature will also increase the mobility of the side-chain fragment formed on radiolysis. This would lead to a decrease in

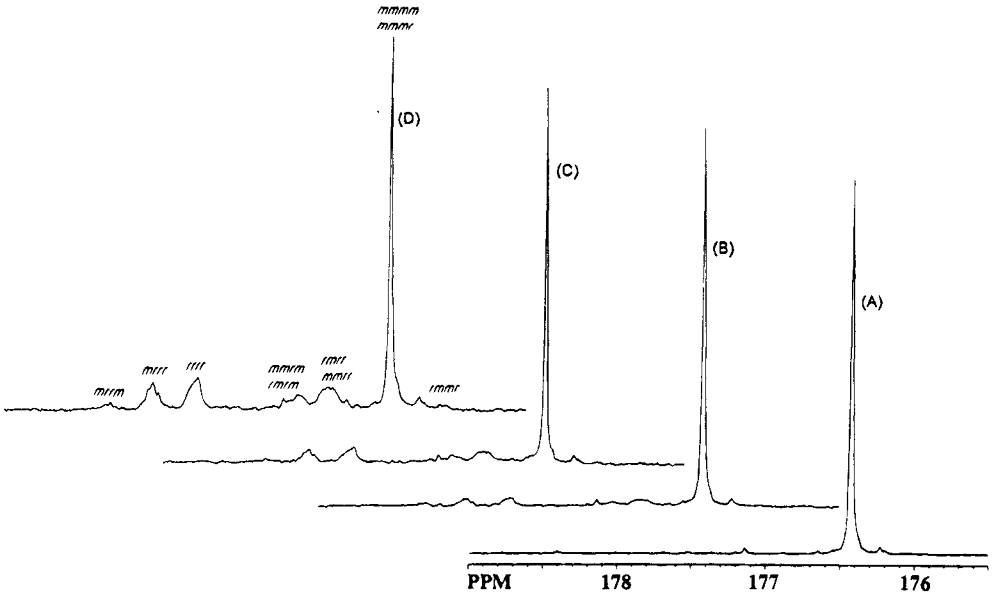


Figure 13. ^{13}C NMR spectra (carbonyl region) of isotactic PMMA (ON72-C) which was γ-irradiated at 80 °C to doses of (A) 0, (B) 165, (C) 300, and (D) 500 kGy.

Table 5. Pentad Fractions from Resonances in the ^{13}C NMR Spectra due to the Carbonyl Groups for γ-Irradiation of Isotactic PMMA at 80 °C, together with the Computer Simulation Results[a]

		no irradiation		165 kGy irradiation		300 kGy irradiation		500 kGy irradiation	
pentad tacticity	NMR peak (ppm)	obsn	simuln	obsn	simuln	obsn	simuln	obsn	simuln
mrrm	178.3	0.00	0.00	0.01	0.02	0.02	0.02	0.02	0.03
mrrr	178.0	0.00	0.00	0.05	0.04	0.08	0.07	0.10	0.10
rrrr	177.7	0.00	0.00	0.04	0.04	0.08	0.06	0.11	0.10
mmrm + rmrm	177.0	0.01	0.00	0.02	0.03	0.06	0.04	0.07	0.06
rmrr + mmrr	176.8	0.00	0.01	0.05	0.07	0.11	0.11	0.14	0.16
mmmm + mmmr	176.4	0.99	0.99	0.81	0.80	0.63	0.68	0.53	0.54
rmmr	176.2	0.00	0.00	0.01	0.00	0.02	0.01	0.02	0.01

[a] The computer simulation was carried out with P_t of 0.205 and D of 0.0000 (no irradiation), 0.0320 (165 kGy irradiation), 0.0575 (300 kGy irradiation), and 0.0970 (500 kGy irradiation).

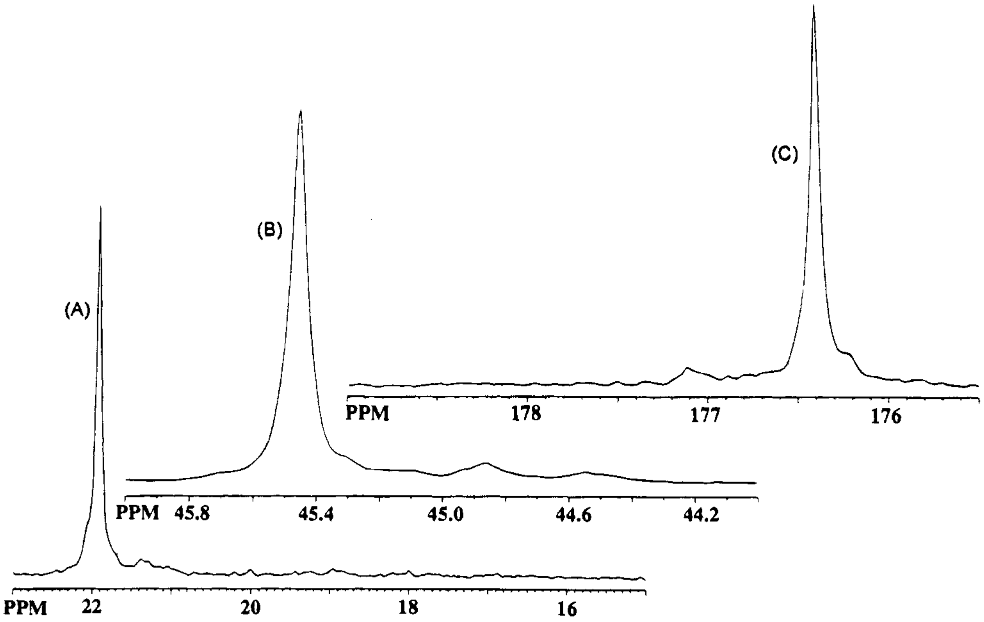


Figure 14. ^{13}C NMR spectra of isotactic PMMA (ON72-C) which was γ-irradiated at room temperature to a dose of 1600 kGy: (A) methyl region, (B) quaternary carbon region; (C) carbonyl region.

the G value for temporary chain scission and an increase in permanent chain scission at higher temperature, since the fragment may diffuse out of the reaction cage. In addition, the tendency for the side-chain fragment to decompose will also increase at higher temperature, thus lowering the probability for the recombination reaction.

Tacticity Changes in γ-Irradiated Syndiotactic PMMA. The same methods as those adopted for isotactic PMMA were used to investigate the radiolysis

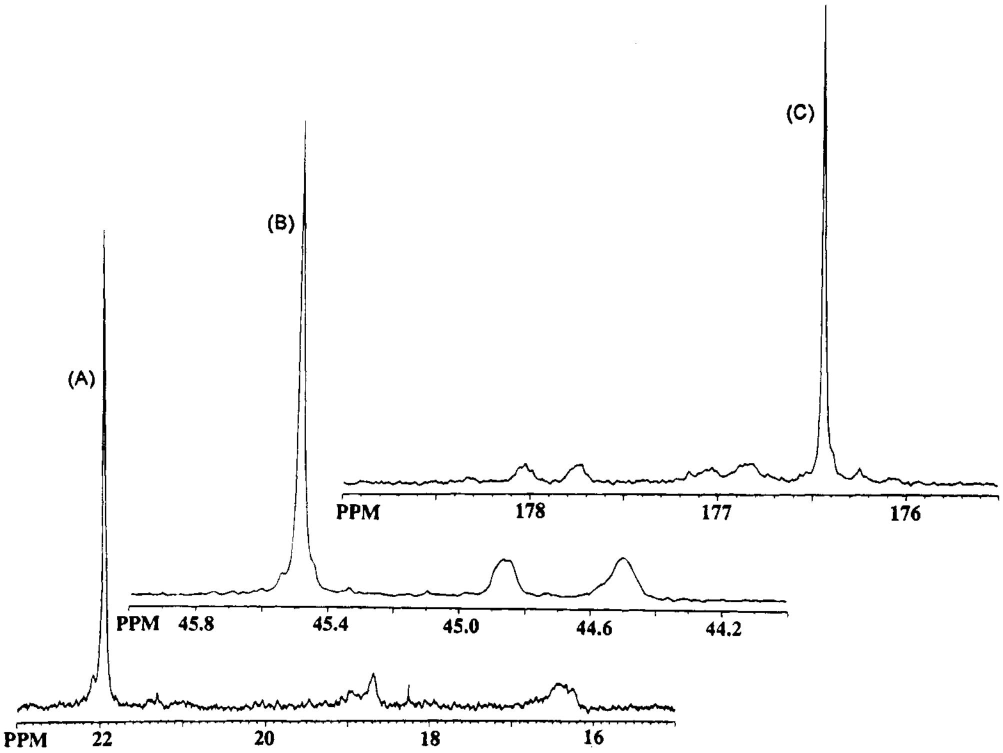


Figure 15. ^{13}C NMR spectra of isotactic PMMA (ON72-C) which was γ-irradiated at 110 °C to a dose of 500 kGy: (A) methyl region; (B) quaternary carbon region; (C) carbonyl region.

Table 6. Pentad Fractions from Resonances in the ^{13}C NMR Spectra due to the Carbonyl Group for γ-Irradiation of Isotactic PMMA at 110 °C to a Dose of 500 kGy, together with the Computer Simulation Results[a]

tacticity	experimental	simulation
mrrm	0.01	0.02
mrrr	0.07	0.08
rrrr	0.07	0.07
mmrm + rmrm	0.07	0.05
rmrr + mmrr	0.13	0.13
mmmm + mmmr	0.61	0.64
rmmr	0.03	0.01

[a] The computer simulation was carried out with $P_t = 0.23$ and $D = 0.0700$.

of syndiotactic PMMA. As observed previously,[19] the new structures and small molecular compounds formed during γ-irradiation of syndiotactic PMMA were similar to those observed for isotactic PMMA.

The α-methyl proton region of the ^{1}H NMR spectrum of syndiotactic PMMA which was γ-irradiated at 80 °C to a dose of 500 kGy, together with a spectrum of an unirradiated sample, is shown in Figure 16. The new structure $-CH(CH_3)-$ which was formed on γ-irradiation may be observed through the methyl proton resonance at 1.0−1.1 ppm. The methyl resonance for this group disturbs the observation of the NMR signal of the α-methyl proton in the methyl methacrylate units which have an mm tacticity. The mm triads formed on radiolysis of syndiotactic PMMA will have a low signal intensity for this α-methyl proton, and it was found that the intensity of these resonances was of the same order as the intensity of the methyl proton resonance from the structure $-CH(CH_3)-$. Because these two resonances are close to each other, an accurate estimate of the tacticity distribution cannot be obtained for syndiotactic PMMA after γ-radiolysis, as shown in Figure 16.

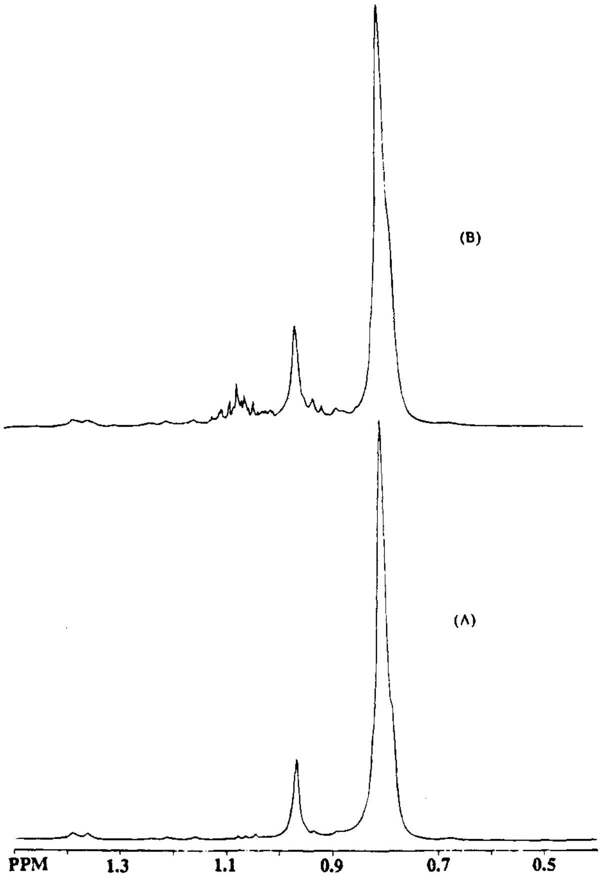


Figure 16. ^{1}H NMR spectra (methyl region) of syndiotactic PMMA (DPI-1): (A) unirradiated; (B) 500 kGy γ-irradiation at 80 °C.

If the probability for a scissioned unit to adopt a meso configuration in syndiotactic PMMA is the same as that found for isotactic PMMA ($P_t = 0.205$ at 80 °C), then a much higher dose would be required to observe tacticity changes in syndiotactic PMMA of the same magnitude as those observed here for isotactic PMMA. In addition,

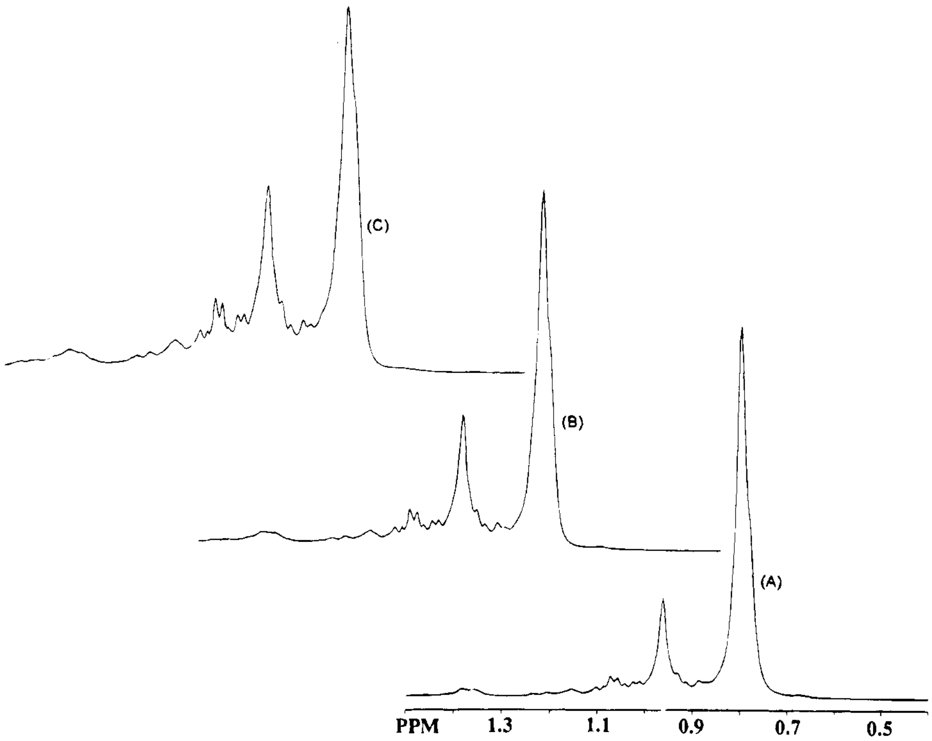


Figure 17. ^{1}H NMR spectra (methyl region) of syndiotactic PMMA (DPI-1) which was γ-irradiated at 110 °C to doses of (A) 165, (B) 300, and (C) 500 kGy.

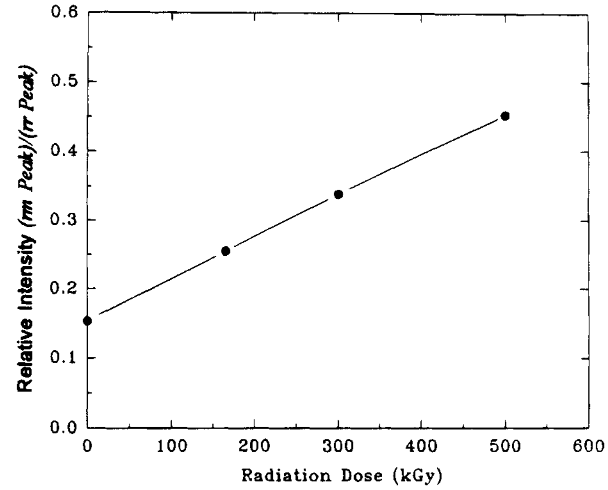
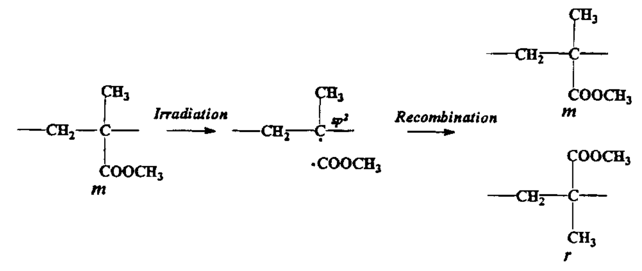


Figure 18. Relationship between the experimental absorbed radiation dose and the relative intensity ratio of the rm and rr peaks for syndiotactic PMMA on the γ-irradiation at 110 °C.

because permanent chain scission and the resultant formation of new structures which interfere with the quantification of the tactic triad fractions also increase with the absorbed dose, the observation and quantification of the tacticity changes in syndiotactic PMMA are much less reliable than they are for isotactic PMMA. However, the spectra of the syndiotactic sample which had been γ-irradiated at 110 °C to different radiation doses show that the rm peak increases in intensity with increasing radiation dose, as shown in Figure 17.

A plot for the changes in the relative intensities of the rm and rr peaks for different radiation doses is given in Figure 18. This figure confirms that configurational inversions do occur during γ-irradiation of the syndiotactic PMMA at 110 °C. Again, these can be attributed to the recombination of the scissioned bonds at the quaternary carbon atom of the main chain.

Mechanism of Tacticity Changes in PMMA Samples on High-Temperature γ-Irradiation. The recombination of a scissioned bond at the quaternary carbon of the main chain is proposed to account for the tacticity changes occurring during the γ-irradiation of PMMA at high temperature. It has been generally accepted that the $-COOCH_3$ side chain is easily scissioned from the main chain during γ-irradiation.[32] David *et al.*[5] have suggested that the main-chain scission could be initiated by the breakage of the $-COOCH_3$ side chain from the main chain, followed by β-scission of a main-chain bond. The following mechanism, based on that proposed by David, can be used to explain the tacticity changes occurring during γ-irradiation.



There has been some argument in the literature as to the degradation mechanism for PMMA on γ-irradiation. Some authors have proposed an alternative model to describe the mechanism for configurational change, in which it has been suggested that the γ-ray can directly break the main chain.[33,34] While this mechanism could also account for the observed tacticity changes in PMMA if recombination occurred within the reaction cage, it cannot account for the observed small-molecule products.[20] It may be proposed that the observed configurational changes may occur through the depolymerization of the polymer and repolymerization of the released monomer. However, recent studies have shown that depolymerization of PMMA only becomes important at temperatures significantly greater than those used here.[35] Also, the new structures cannot be associated with new chain ends, which could be found if a depolymerized methyl methacrylate monomer unit added with a different tacticity to existing free-radical chain ends formed by chain scission. Thus, the above mechanism of David is preferred.

According to the mathematical model presented above, the tacticity changes in isotactic PMMA which had been γ-irradiated at 80 °C could be simulated, assuming recombination of side-chain fragments within the change, and thus the G value of temporary chain scission, G(TCS), was calculated to be 18.6. However, the G value for permanent main-chain scission on γ-irradiation at 80 °C for isotactic PMMA, G(S), has been estimated to be about 2.[36] Thus, the value of G(S) is small compared with that of G(TCS). This means that, during γ-irradiation, the scissioned bonds at the quaternary carbon are approximately 10 times more likely to undergo recombination than to result in permanent main-chain scission. Therefore, it would be expected that reducing the probability for recombination, such as by scavenging the $^{\bullet}COOCH_3$ radical, would increase the yield of permanent chain scission and thus increase the value of G(S) for PMMA on γ-irradiation.

Conclusion

An investigation of the high-temperature radiation properties of PMMA of specific tacticity shows that the tacticity changes in isotactic PMMA may be simulated by a model which allows for recombination of a scissioned bond, with the possibility of the recombined bond being in either the meso or the racemic configurations. The calculated values of P_t were found to be consistent with the tacticity parameter P_m for the free-radical polymerization of a methyl methacrylate monomer. The value of G(TCS) for the isotactic PMMA sample which was γ-irradiated at 80 °C was found to be 18.6, which is much higher than the value of G(S). A mechanism to explain the observed tacticity changes has been proposed.

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