A ^{13}C NMR Study of End Groups and Stereoregularity Changes Induced by γ Irradiation of Molten Polypropylenes

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ABSTRACT: Samples of predominantly isotactic and syndiotactic polypropylenes have been irradiated with gamma rays to high doses in the molten state. Solution state ^{13}C NMR analysis has identified propyl, vinylidene, and isopropyl end groups. The yield of the former shows that the extent of chain scission in isotactic polypropylene is strongly dose dependent with an initial G value of 11.6 reducing to 5.5 at doses greater than 500 kGy. Molecular weight measurements suggest that $G(\text{crosslink})$ is approximately independent of dose with a values of 3.5. The triad sequence contents of the polymers after 2 MGy irradiation in the molten state, show that an equilibrium triad distribution has not been achieved, even though the rates of change of triad sequences are virtually zero by this dose. Initial rate kinetics suggests that this is mainly due to the preferential formation of syndiotactic sequences from isotactic ones.

KEY WORDS Irradiation / Polypropylene / End Groups / Stereoregularity
Changes / ^{13}C NMR / Chain Scission / Crosslinking /

In recent work^{1–3} we have established that irradiation of isotactic polypropylene, PP, with gamma or electron radiation induces relatively large changes in the stereochemistry¹ and that both the size and detailed nature of these changes are morphology² and dose rate³ dependent. For example the G values for the loss of pure isotactic pentad sequences when samples of annealed PP were irradiated with gamma radiation, dose rate 4.4 kGy h^{-1} , at ambient temperature and at 200°C (molten sample) were -94 and -283 , respectively. When the same sample was irradiated in an electron beam, dose rate 720 kGy h^{-1} , at ambient temperature, the corresponding G value was -220 . The first difference suggests that stereochemical change only occurs in the amorphous regions, as the ratio correlates well with the fraction of amorphous component in the solid state. This is reasonable when

considering the conclusions of Keller *et al.*⁴ which suggest that neither crosslinking nor chain scission occur within the crystalline regions of polyethylene when subjected to high energy irradiation. The large dose rate effect on the other hand, was explained by a difference in mechanism. An analysis of the full pentad sequence distributions indicated that the deposition of one quantum of energy at the high dose rate resulted in an average of five inversions on mainly alternate monomer units, whilst at low dose rate an energy quantum promoted an average of two inversions on nearby monomer units. In the latter case the distribution was more random, lying somewhere between adjacent and alternate.

The detailed chemical mechanism of the inversion is unclear. The observed G values are many times greater than those observed for any other irradiation induced chemical effect in PP,

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e.g., $G(\text{H}_2, \text{production})$ is about 2 and $G(\text{chain scission})$ and $G(\text{crosslinking})$ have measured values in the range from 0.1 to 0.9.⁵ Hydrogen atoms are almost certainly produced in the irradiation process so that one possible mechanism is a hydrogen scrambling process in which H atoms become dissociated from the methine position; inversion at the remaining C centred radical occurs by recombination with an H atom in the opposite configuration. This is similar to the mechanism thought to be operative in epimerization studies utilizing a Pd catalyst, in which stereochemical inversion also occurs in molten PP.⁶ This seems reasonable in this case since the Pd catalyst is a ready source of H atoms for the recombination process. However in the irradiation process the dissociated H atom would diffuse well away from the site in the time taken for the inversion and there would be no continuous source of other H atoms as in the epimerization case. In our view a more likely mechanism involves temporary backbone chain scission followed by bond rotation, inversion at the asymmetric chain end C atom and finally recombination. The energy released in the radical recombination process is then responsible for promoting further nearby events. This means of course that irradiation induced chain scission is far more prevalent than previously thought. A large proportion results in recombination with inversion of configuration and, presumably, a further large proportion results in recombination with retention of configuration. Previous measurements of chain scission have all been done on solid samples and the range of G values reported probably reflects the influence of sample morphology on the extent of scission, rather than problems of experimental error. The fact that irradiation of molten PP does not cause gelation, at least up to 2 MGy has provided an opportunity to investigate permanent chain scission utilising solution techniques. However the information relates to amorphous polymer only; on the other hand, morphological problems

due to crystallinity are eliminated. In this work two methods have been used: end group investigation by ^{13}C NMR solution spectroscopy and molecular weight investigation by GPC. The former gives unique information on chain scission whereas the latter relates to both scission and crosslinking. Thus the combination has given information on both.

In previous studies of stereochemical change in molten isotactic PP at very high doses,² the triad sequence content was found to be approaching a constant level after 2 MGy suggesting that the system was close to a state of equilibrium. However the triad content at infinite time, calculated from the exponential equation of best fit for the points, differed significantly from the values derived by both extensive epimerization studies and by rotational isomeric state calculation,⁶ which are themselves in good agreement. A possible reason for the discrepancy is that equilibrium had not been reached in the irradiation study due to the fact that the syndiotactic sequences, which are kinetically favoured during early and intermediate stages of the irradiations, as shown by a study of the full pentad sequence distributions, together with the initially highly isotactic sequences, require very much higher doses to completely break down and equilibrate. Unfortunately it is impractical to carry out the experiments to higher doses as those described required over 2 weeks of irradiation at 200°C. An alternative approach is to investigate the approach to equilibrium from the other side. In this paper, the influence of irradiation to high doses on the stereochemistry of a predominantly syndiotactic sample of PP in the molten state is also described and the results are compared with those of isotactic samples.²

EXPERIMENTAL

Materials

The isotactic sample of polypropylene was kindly donated by Professor A. F. Johnson. It

was prepared by the gas phase process (code GSE 16) and has $\bar{M}_n = 1.1 \times 10^5$, $\bar{M}_w = 5.4 \times 10^5$ and tactic triad contents of $mm = 95\%$, $mr = 3\%$, $rr = 2\%$ (by ^{13}C NMR, our results).

The syndiotactic sample of polypropylene was kindly prepared and donated by Professor P. Ammendola. It was prepared by $\text{VCl}_4/\text{AlEt}_2\text{Cl}$ initiation at -78°C . The tactic triad contents are $mm = 5\%$, $mr = 29\%$, $rr = 65\%$ (by ^{13}C NMR, our results). The sample also contains a small proportion of head-head and tail-tail linkages.

Irradiation

Samples in sealed evacuated glass ampoules were immersed in a block heater at $200 \pm 1^\circ\text{C}$, and irradiated with γ -rays from a ^{60}Co Gammacell 220 source at 4.4 kGy h^{-1} at the ANSTO Lucas Heights facility. Following irradiation the ampoules were annealed for 1 h at 120° to ensure that trapped radicals had decayed to negligible concentration before opening.

NMR Spectra

High resolution ^{13}C NMR spectra of solutions in 1:1 mixture of 1,2-dichlorobenzene and d_5 -nitrobenzene were recorded at 120°C on a Bruker CXP 300 spectrometer. The acquisition details for the conventional one pulse experiment were the same as reported in previous work.¹⁻³ The measurement of spin-lattice relaxation time (T_1 's) was performed with the saturation-recovery technique.^{7,8} Spectral assignment of specific chain end species was aided by a DEPT subspectral editing technique.⁹

Pentad sequences according to the assignments given by Randall¹⁰ and by Cheng and Lee¹¹ were quantitatively assessed from the spectra by application of spectrum simulation programme (LINESIM)¹² assuming pure lorentzian lineshapes.

G values for the production of propyl chain-ends were calculated from the variation of the propyl methyl resonance (14.4 ppm)

expressed as a percentage of the total PP methyl resonance (including chain-ends), with dose.

Molar Mass

The GPC analyses were carried out by RAPRA. Solutions in 1,2-dichlorobenzene stabilized with 2,6-di-*t*-butyl-*p*-cresol were used at 140°C . The analyses were based on calibration with polystyrene standards.

RESULTS AND DISCUSSION

The ^{13}C NMR solution spectra of predominantly isotactic and predominantly syndiotactic polypropylenes before and after 2 MGy of γ irradiation in the molten state are shown in Figure 1. New peaks resulting from the irradiation process are given in Table I along with assignments and relaxation times. The assignments were aided by application of the DEPT pulse sequence technique,⁹ which clearly differentiates CH , CH_2 , and CH_3 assignments, and the empirical additivity rules given by Grant-Paul,¹³ (GP), and Lindeman-Adams,¹⁴ (LA), for aliphatic structures and by Derman *et al.*¹⁵ and Stothers¹⁶ for olefinic structures.

The most conspicuous chain end resonance is a prominent methyl contribution at 14.44 ppm, a chemical shift consistent with the first branch point along the chain being situated γ to it, *i.e.*, on C-4. The C-4 methine carbon yields a resonance of comparable intensity at 30.41 ppm in good agreement with GP and LA predictions. The assignment of these resonances to a propyl end group is in agreement with previous observations¹⁷ relating to the irradiation of ethylene-propylene copolymers. Although the C-2 methylene carbon is obscured by resonance overlap with the main peaks, the C-3 methylene appears as two doublet resonances in the range 39.73–40.82 ppm, see Figure 2. In-chain methylene resonance is inherently sensitive to hexad configurations. The resonance of the C-3 methylene is unusual, because it is attached to a chain end. It is

Figure 1. ^{13}C NMR solution spectra of isotactic (A and B), and syndiotactic (C and D) polypropylene before (A and C) and after (B and D) about 2 MGy gamma irradiation in the molten state.

Notes: The spectrum shown in B was taken with a DEPT pulse sequence. This eliminates the resonance due to quarternary C atoms of the solvent and allows the resonance at 123.4 ppm to be seen.

sensitive to diad splitting, appropriate to the relative arrangement of the first two monomer units, of 0.89 ppm, and subsequent triad splitting appropriate to the arrangement of the third monomer unit relative to the first two.

The size of this five bond splitting (0.2 ppm) is comparable in magnitude to the pentad splittings of in-chain methyl resonances. The assignment of the separate peaks to the triad sequences shown in Table I is based on statistical grounds (for *mm*) and on relaxation times (*mm* and *rr*). Randall's temperature dependent study of T_1 values for methyl pentad resonance¹⁸ consistently showed that resonances due to the pure syndiotactic sequences

possessed the shortest T_1 's.

A propyl end group is likely to be formed by H abstraction following chain scission according to eq 1. Thus one might expect to also observe resonances due to the vinylidene end group. Of the two olefinic resonances observed see Figure 1B, that at 111.50 ppm can confidently be attributed to C-1 of the chain end vinylidene group. The resonance due to C-2 is probably not seen due to spectral overlap with the resonances of the aromatic solvents.

Table I. Assignment of peaks in ^{13}C NMR spectrum of polypropylene after 2 MGy irradiation in the molten state and T_1 relaxation times

Structure	Designation	Predicted chemical shift/ppm			Observed chemical shift ppm	T_1 s	Dept assignment
		GP Rule	LA Rule	Other ^a			
Main-chain CH					28.32	1.28	CH
Main-chain CH_2					46.43	1.26	CH_2
Side-group CH_3					21.83	3.40	CH_3
Propyl	1	14.2	14.35		14.44	7.17	CH_3
$\text{}^5\text{CH}_3$	2	20.6	19.96		(b)	—	—
$\text{—CH—CH}_2\text{—CH}_2\text{—CH}_3$ 4 3 2 1	3	42.1	39.60		39.73–40.82	mr 3.63 mm 3.91 rm 3.17 rr 2.86	CH_2
	4	29.2	30.45		30.41	3.60	CH
	5	21.4	20.12		(b)	—	—
Vinylidene	1			108.7	111.50	2.75	CH_2
$\text{}^3\text{CH}_3$	2			148.5	(c)	—	—
$\text{—CH}_2\text{—C=CH}_2$ 2 1	3			23.6	22.47–23.76	3.58–5.78 ^d	CH_3
Isopropyl	1	22.2	22.6		22.47–23.76	3.58–5.78 ^d	CH_3
$\text{}^5\text{CH}_3$ $\text{}^1\text{CH}_3$	2	26.0	25.9		25.73	4.38	CH
$\text{—CH—CH}_2\text{—CH—CH}_3$ 4 3 2 1	3	51.5	46.3		48.18	—	CH_2
	4	26.7	28.4		(b)	—	—
	5	21.7	20.61		(b)	—	—
Vinylene	—	—	—	—	123.3	—	CH
—CH=CH—							

^a Include model compound comparison, and olefinic empirical rules by Derman *et al.*¹⁵ and Stothers.¹⁶^b Not observed due to spectral overlap from bulk main-chain CH, CH_2 or side-group CH_3 resonances.^c Not observed due to spectral overlap from solvent resonances.^d Calculated from sufficiently resolved peaks in the 22.47–23.76 ppm region.

Correlation with model compounds indicates that the C-3 methyl group should produce a resonance at about 23.6 ppm, *i.e.*, in the region 22.47–23.76 ppm where at least six resonances are observed, see Figure 2. Thus ^{13}C NMR strongly supports the formation of propyl and vinylidene end groups in agreement with the observations of Slovokhotova *et al.*¹⁹ based on IR analysis of PP irradiated at -196°C .

There is also agreement that the yield of vinylidene groups is very much less than the yield of propyl groups. Even after T_1 and NOE considerations are taken into account it is

evident from Figure 1 that the C-1 olefinic methylene resonance is disproportionately low compared with any of the resonances associated with the propyl groups. This may be due to either (i) preferential radical attack of the unsaturated species during prolonged irradiation or (ii) some fraction of radical II abstracting H atoms from nearby polymer and radical I reacting in some other way.

The observation of a methine resonance at 25.73 ppm with a long T_1 value strongly suggests the presence of isopropyl chain end groups. The related C-1 methyl resonances are expected in the cluttered 22.47–23.76 ppm

Figure 2. Scale expansion of the spectra shown in Figures 1B and 1D in the 10–50 ppm range. A, Isotactic PP irradiated to 2.3 MGy; B, Syndiotactic PP irradiated to 2.1 MGy.

region where at least six peaks are observed. They are likely to be sensitive to configurational sequence differences along the end-of-chain monomer units similar to that discussed for the C-3 methylene of the propyl group. Since this region also includes a methyl resonance from the vinylidene group, a detailed assignment is not possible. These isopropyl group assignments are in good agreement with those given by Zambelli *et al.*²⁰ for saturated end groups of model compounds. Isopropyl groups are present in both the unirradiated and irradiated forms of the isotactic PP but only in the irradiated form of syndiotactic PP. An estimate from the peak areas of methine and total methyl resonances suggests that the concentration of isopropyl groups increases from 1.1 to 1.6% in isotactic PP during 2 MGy irradiation. Since this increase is only marginally outside experimental error, the production of isopropyl end groups by irradiation is still subject to

speculation. However the increase is roughly equal to the concentration observed in irradiated syndiotactic PP where no isopropyl groups were observed in unirradiated polymer. A possible mechanism is H abstraction by radical I from either radical II, reaction (2), or from nearby polymer backbone.

Although an olefinic carbon resonance is observed, the absence of an associated methyl resonance expected at <20 ppm suggests that reaction (2) does not occur to any marked extent. The resonance at 123.3 ppm is probably associated with in-chain vinylene unsaturation which has previously been suspected of being produced by irradiation of PP, but never positively observed.²¹

Several attempts have been made to positively identify crosslinks in irradiated polyolefins by NMR techniques^{17,22–25} with a view to establishing both the nature of the crosslink and the mechanism by which it is formed. Although, in this work, conditions which minimised crosslink formation were used, the lack of gelation does not exclude some crosslinks being formed. Theoretically in a system involving completely random scission and crosslinking events, gelation does not occur until $G(\text{crosslink}) > G(\text{scission})/4$. However no unassigned resonances in the 30–55 ppm range of chemical shift were observed indicating that the concentration of branched structures, whose resonances are expected in this range,^{22,23} is below the detection limit of the ¹³C NMR experiment.

The T_1 data for all chain-end and main-chain resonances, see Table I, add further evidence for the validity of the assignments. Since the frictional resistance to crankshaft motion increases with the number of bonds involved,^{26,27} chain-end segmental mobility will be restricted to short range modes only and the average correlation times for chain-end motion will be shorter than those for main chain motion. All methyl species possess an additional component of internal rotation which, when superimposed on existing modes of motion, results in further increased T_1 values compared with those for methylene and methine carbons.

As long as radical II reacts exclusively by abstraction from either radical I or polymer backbone to form a propyl end group and assuming the propyl groups undergo no subsequent reaction during irradiation, then the concentration of propyl end groups is a reliable measure of chain scission. The percentage of propyl based methyl end groups in relation to the total methyl content (backbone+chain-end) is shown for both isotactic and syndiotactic PP's as a function of dose in Figure 3. The curves clearly indicate that the rate of production of propyl end

Figure 3. Propyl end group concentration from ¹³C NMR spectra (A) and reciprocal $\bar{M}_n$ from GPC (B) as a function of dose for irradiated molten polypropylene: isotactic, open circles; syndiotactic, filled circles.

groups is strongly dose dependent, and thus there is no unique value of $G(\text{propyl})$. Black and Lyons²¹ measured the rate of production of vinylidene end groups in irradiated PP and reported similar behaviour. Also, various measurements of MW changes occurring in PP during irradiation^{28–30} including our own study, illustrated in Figure 3, have indicated that chain scission is disproportionately high at low doses. Thus the observed dose dependence of $G(\text{propyl})$ is not new and the result indicates that the trend is independent of the physical state of the polymer. It has been postulated³¹ that the decline in yield with dose is related to the radiation induced decay of unsaturated groups, a phenomenon which has been positively observed in polyethylene.³² However, the fact that the rate of formation of propyl end groups declines with dose suggests that the explanation given for the decline in the rate of formation of unsaturation does not give the full story, since propyl groups are unlikely to be radiation sensitive. Another possible explanation is that, initially, chain scission is high due to the presence of weak links, *i.e.*, species especially sensitive to ra-

diation. When the weak links are exhausted, the rate of scission settles down to a constant value. In this case it is pertinent to express the results as:

$$G(\text{propyl})_{\text{initial}} = G(\text{scission})_{\text{initial}} = 11.6$$

and

$$G(\text{propyl})_{\text{dose} > 500 \text{ kGy}} = G(\text{scission})_{\text{dose} > 500 \text{ kGy}} = 5.5$$

An alternative method of studying chain scission is by observing changes in MW. The data for isotactic PP are presented in Table II and Figure 3. The similarity in form to the propyl end group data is immediately apparent. $\bar{M}_n$ is also influenced by the incidence of crosslinking, and the appropriate equation is:

$$\bar{M}_n^{-1} = (\bar{M}_n)_0^{-1} + 1.04 \times 10^{-5} R[G(S) - G(X)]$$

where $(\bar{M}_n)_0$ is the initial number average MW and $G(S)$ and $G(X)$ are the number of scission and crosslinking events respectively for 100 eV of absorbed radiation and R is the dose in kGy. Thus

$$[G(S) - G(X)]_{\text{initial}} = 8.0$$

and

$$[G(S) - G(X)]_{\text{dose} > 500 \text{ kGy}} = 1.8$$

Comparison of these values with $G(S)$ from

Table II. Molar mass information from GPC as a function of dose for irradiated molten isotactic polypropylene

Dose kGy	$\bar{M}_n$ $\times 10^4$	$\bar{M}_w$ $\times 10^4$	$\bar{M}_z$ $\times 10^4$	M_w/M_n
0	10.7	53.5	193	5.0
86	1.21	4.08	8.43	3.4
184	0.73	2.56	5.49	3.5
356	0.444	1.58	3.59	3.6
529	0.338	1.17	2.85	3.5
731	0.235	0.77	1.85	3.3
1310	0.210	0.646	1.56	3.1
1830	0.185	0.511	1.18	2.8
2300	0.158	0.403	0.86	2.6

the propyl end group measurement for isotactic PP, suggests that $G(X)$ is approximately independent of dose with a value of about 3.5. Values of $G(S)$ and $G(X)$ for the irradiation of solid PP from the literature have generally been found to be approximately equal, even though the absolute magnitude has varied appreciably in the range 0.1 to 0.9 depending on the sample.⁵ The higher values for molten PP compared with those for solid PP reflects two factors. First neither scission nor crosslinking are thought to occur in the crystalline regions.⁴ This approximately accounts for the difference between $G(\text{crosslink})$ values for solid and molten PP's. Secondly, increased backbone motion is likely to cause an increase in the fraction of initial scission events which become permanent.

The extent of temporary scission which leads to configurational inversion in the initial stages of the irradiation of molten isotactic PP, $G(\text{inversion})$, can be estimated from the pentad sequence information, see Table III, if the mechanism of the process occurring within the immediate structural region of the deposited energy quanta is known. This assumes that the

Table III. G values for changes in pentad sequences for two different samples of isotactic polypropylene gamma irradiated in the molten state

Pentad sequence	G values ^a	
	PPA ^b	GSE-16
<i>mmmm</i>	-283	-266
<i>mmmr</i>	49	61
<i>rmmr</i>	10	21
<i>mmrr</i>	65	36
<i>mmrm</i> & <i>rmrr</i> ^c	37	64
<i>rmrm</i>	35	5
<i>rrrr</i>	36	32
<i>mr rr</i>	55	32
<i>mrrm</i>	18	21

^a Calculated from the initial slopes of the line of best fit (single exponential) for the dose/pentad sequence data.

^b From ref 2.

^c Not resolved.

Figure 4. Triad sequence content from ^{13}C NMR methyl resonances as a function of dose in molten state irradiated isotactic (A) and syndiotactic (B) polypropylene. *mm*, circles; *mr*, squares; *rr*, triangles.

events occur within a 5 monomer unit range along the polymer chain. The low yield of *mmmr* pentads compared with that observed for solid isotactic PP¹, together with the relatively high yield of short syndiotactic sequences (containing *rrr* or *rr*) suggests that, on average, 4 or 5 inversions occur per deposition of a quantum of energy over a segment of chain 8 monomer units long. Taking the mean value, 4.5, $G(\text{inversion}) = 283 \times 4.5 / 12 = 106$ for molten isotactic PP. Thus the percentage of initial scission events which lead to permanent scission in irradiated molten isotactic PP is no greater than 11%. This can only be regarded as a maximum value since temporary scission events may occur without inversion of configuration and these of course, are undetectable.

Since the extent of crosslinking is insufficient to cause gelation in the irradiation of molten PP up to at least 2 MGy, the change in microstructure can be followed by ^{13}C NMR to high doses. The triad sequence contents of an initially isotactic and an initially predominantly syndiotactic PP as a function of dose are shown in Figure 4. The isotactic sample was different to that studied in earlier work¹⁻³ in that it had a higher initial isotactic content and was prepared by heterogeneous catalysis in the gas phase. The G values given in Table III and the triad content after high doses given in Table IV indicate that the irradiation effect

Table IV. Triad sequence content of polypropylenes after infinite irradiation dose at 200°C^a and literature equilibrium values

Sample (method)	<i>mm</i>	<i>mr</i>	<i>rr</i>
PPA	31	37	32
GSE-16	30	38	32
S-PP	15	40	45
RIS ^b	23	50	27
Epimerization ^c	23	49	28

^a Calculated from the line of best fit (single exponential) for the dose/pentad sequence data.

^b Rotational isomeric state calculations, ref 6.

^c Epimerization studies at 270°C, ref 6.

on stereochemical inversion is independent of the origin of the PP sample. The data in Table IV together with the ^{13}C NMR spectra of the methyl resonances of the PP samples after 2 MGy of γ irradiation in the molten state (Figure 5) clearly indicate that even after 2 MGy irradiation, when the triad concentrations are approaching plateau values, the tacticity content of the polymer has not reached a state of equilibrium as expected from RIS or epimerization studies.

Assuming that triad transformations are first order processes with the rates directly proportional to dose, then rate constants for each transformation can be calculated from the sets of rate equations relating to initial and equilibrium conditions. The model and typical equation are given below.

Figure 5. ^{13}C NMR spectra of the methyl region of isotactic, PPA (A), GSE 16 (B), and syndiotactic (C) polypropylene after 2 MGy irradiation in the molten state. Pentad assignments: 1, *mmmm*; 2, *mmmr*; 3, *rmmr*; 4, *mmrr*; 5, *mmrm* + *rmrr*; 6, *rmrm*; 7, *rrrr*; 8, *rrrm*; 9, *mrrm*.

The rate equation for isotactic triad is:

$$dx_{mm}/dt = -k_1x_{mm} - k_2x_{mm} + k'_1x_{mr} + k'_2x_{rr}$$

where x is the fraction of the appropriate triad. There are six equations of this type relating to initial conditions, three each for isotactic and syndiotactic PP respectively. The data are shown in Table V. There are a further two independent equations relating to equilibrium conditions, when the rate of change is zero. For the purpose of calculating the rate

Table V. Initial rates of change, R_0 , of triad sequence contents and initial concentrations, x_0 for the irradiation of isotactic and syndiotactic molten polypropylene

Polymer	Triad	x_0	R_0
		%	% MGy $^{-1}$
Iso	<i>mm</i>	94.9	-77
	<i>mr</i>	3.3	43
	<i>rr</i>	2.2	36
Syndio	<i>rr</i>	65.0	-20
	<i>mr</i>	29.2	7
	<i>mm</i>	5.5	15

Table VI. Rate constants for triad transformations occurring during the irradiation of molten polypropylene

	k_1	k'_1	k_2	k'_2	k_3	k'_3
k/MGy^{-1}	0.48	0.35	0.40	0.20	~ 0	0.25

constants, the equilibrium triad sequence content based on purely statistical grounds was used, *i.e.*, $mm = rr = 25\%$, $mr = 50\%$.

The results, see Table VI, show that the transformation of *mm* triads to *rr* triads is disproportionately high and the overall rate of loss of *rr* triads is relatively low. This is in general agreement with the suggestion made previously,² based on the pentad sequence distribution, that, due to the mechanism of the irradiation event, the proportion of syndiotactic sequences formed from isotactic sequences is high and the rate of equilibration of the newly formed syndiotactic sequences is relatively low.

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