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Model linear ethylene–butene copolymers irradiated with γ-rays

Noemí Andreucetti[a], Lilian Fernández Lagos[b], Osvaldo Curzio[a],
Claudia Sarmoria[b], Enrique Vallés[b,]*

[a]*Universidad Nacional del Sur, Departamento de Química e Ingeniería Química, Av. Alem 1253, (8000) Bahía Blanca, Argentina*
[b]*Planta Piloto de Ingeniería Química, UNS-CONICET, CC 717, (8000) Bahía Blanca, Argentina*

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Abstract

Two model linear polyethylenes of different molecular weights and very narrow molecular weight distributions were subject to γ-ray irradiation under vacuum. Irradiations were conducted at two temperatures: 25 and 135°C. Number average and weight average molecular weight of irradiated samples was measured by LALLS and membrane osmometry, and the distribution of molecular weights was studied by GPC. The presence of a low but measurable amount of scission was verified. A mathematical model of the irradiation process was developed, which gave very good predictions of the measured values. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Irradiation; Model; Modification

1. Introduction

The radiation chemistry of polymeric materials has been a field of extensive research. The pioneering investigations of Charlesby [1] and Dole [2] showed that polyolefins exposed to high energy radiation undergo various structural changes. The properties of the irradiated polymer depend on the chemical changes occurring in the molecular structure due to the exposure to radiation. In the case of polyethylene, high energy irradiation promotes especially the crosslinking and scission of chains. Even though numerous studies have been published on the subject, the relative efficiency of these reactions (specially scission) still generates controversy. Most of the past work in this area was performed on commercial polyethylenes made up of mixtures of chemical species and wide molecular weight distributions that cannot be fully characterized. In this work we use narrow distribution model polyethylenes (HPB), obtained from the catalytic hydrogenation of practically monodisperse linear polybutadienes produced by anionic polymerization. These materials have a uniform microstructure, very narrow molecular weight distribution ($M_w/M_n = 1.1$), no terminal vinyl groups and a controlled and homogeneous quantity of short branches. This leads to a low percentage of crystallinity, approximately 30%.

In previous works [3,4] we have verified that the use of this material simplifies the quantitative analysis of the crosslinking and scission reactions. Those results, obtained on HPB samples irradiated with low doses at room temperature under vacuum, have confirmed the presence of a small but measurable amounts of scission.

In this work we extend those results to a wider range of irradiation doses and temperatures. We have measured the number (M_n) and weight average (M_w) molecular weights of the soluble fraction of the samples at different irradiation doses using absolute methods: low angle laser light scattering (LALLS) and membrane osmometry. The measured values of M_n and M_w were compared with the predictions of a probability model of the irradiation process that was specially developed for this purpose.

2. Experimental

Two linear polybutadienes (PB) of different molecular weights were synthesized by anionic polymerization under high purity conditions in a vacuum system. The practically monodisperse homopolymers were then hydrogenated in solution using a 5% palladium on calcium carbonate catalyst, unreduced, from Strem Chemicals Inc. This process converted them into ethylene–butene 1 copolymers. Infrared spectroscopy (IR) was used to determine the double-bond microstructure of the original PB and the degree of unsaturation of the hydrogenated polybutadienes. The

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* Corresponding author. Tel.: +54-91-861535; Fax: +54-91-883764.

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resolution of the instrument allows measurement of unsaturated bonds with a precision better than 0.1% molar. Since no residual unsaturation was detected in the hydrogenated polybutadiene, it was confirmed that the double bonds of PB were completely reacted to obtain ethylene–butene copolymers with composition equivalent to that of linear low density polyethylene (approx. 20 CH_3/1000 C). Details of the synthesis procedure and the characterization techniques of the polymers can be found in previous publications [4,5].

Two samples of linear PB with nominal molecular weights of 50 000 and 100 000 were hydrogenated. The resulting HPB were labeled as polymers B and C. Some of these samples were irradiated at 25°C, and others at 135°C. Samples of copolymers B and C destined for room temperature irradiation were compression molded at 120°C under vacuum. Once cooled back to room temperature the samples were sealed under vacuum in Pyrex tubes. The irradiation of these polymers was performed by a ^{60}Co γ-source. After irradiation, the polymer samples were annealed for 2 h at 140°C to enable residual free radicals to combine completely [6]. The radiation doses applied to polymer B ranged from 5 to 160 kGy and those applied to polymer C from 20 to 100 kGy. Dose was measured with a Fricke dosimeter. Only some samples of polymer C were irradiated at high temperature. Sample preparation was similar to that just described. The samples were not molded, but melted in Pyrex tubes under high vacuum at 120°C until total elimination of air bubbles. The samples were then sealed in those same Pyrex tubes. The irradiation of these samples was performed by a ^{60}Co γ-source at Tokyo University. The dosage ranged from 30 to 100 kGy.

As a final step the Pyrex glass tubes were cut open and the irradiated samples were extracted in soxhlet hot-vapor-jacketed extractors with xylene at 135°C to obtain the soluble fractions. Nitrogen was bubbled continuously in the lower flask of the soxhlet to avoid oxidation of the samples. A control sample of non-irradiated material was simultaneously extracted by the same procedure. The starting sample mass ranged from 0.7 to 1.2 g.

Molecular weights and molecular weight distributions of the soluble fraction of the different polymers were measured by several methods. Gel permeation chromatography (GPC) was performed in a Waters 150 ALC/GPC equipped with five micro styragel columns with nominal pore sizes 10^6, 10^5, 10^4, 10^3, and 500 Å. The hydrogenated PB was run in 1,2,4-trichlorobenzene (TCB) at 140°C. The universal calibration curve was used. The polymer concentration was always less than 0.1%. No branching or column spreading corrections were applied.

Absolute weight average molecular weights were measured by LALLS. The instrument used was a Chromatrix KMX-6. The HPB were run in TCB at 135°C. Number average molecular weights were measured by membrane osmometry (MO). The instrument used in this case was a Knauer model 01.00. The solvent was TCB at 90°C. The molecular weight characterization of the two HPBs before irradiation is reported in Table 1. Not all measurements were performed on all samples, the limitation being the mass available. As mentioned above, initially each sample weighed approx. 1 g. This leaves very little material left for postgel measurements on highly crosslinked samples. GPC and soluble fraction extraction were performed on every sample, while MO and LALLS measurements could be performed on most of them. The information on Table 1 refers only to those samples where the absolute molecular weight measurements could be performed.

Table 1
Molecular weights of the hydrogenated polybutadienes before irradiation

	B polymer			C polymer		
	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
GPC	43 000	50 000	1.16	88 000	96 000	1.09
MO	45 000			102 000		
LALLS		50 000			108 000	

3. Theory

We have modeled the irradiation process assuming that the chains to be irradiated are monodisperse, and that scission is possible. We assume ideal network formation in the sense of Flory [7] and Stockmayer [8,9]: the irradiation process is random, that is, all monomer units are equally likely to be subject to crosslinking and all C–C bonds are equally likely to be subject to scission; all reactions are independent (there is no substitution effect), and there are no intramolecular reactions. The ratio of crosslinking to scission is taken to be constant during the entire irradiation process. We also assume that the crosslinking and scission reactions are independent of each other. Because of that, even though crosslinking and scission take place simultaneously, we may model them as sequential steps. After a given dose of irradiation, the sample will reach a degree of crosslinking, α, and a degree of scission, β. In order to model the process we take the original monodisperse chains and subject them to random breakage until they reach the prescribed degree of scission, β. The resulting mixture, which is not monodisperse, is now made to crosslink randomly until it reaches a degree of crosslinking, α. The result of these two hypothetical steps is the same as that given by the process where crosslinking and scission are simultaneous. The use of two sequential steps is preferred because it is mathematically easier.

We have modeled this two-step process using an extension of the model presented by Miller and Macosko for the homopolymerization of chains with length and site distribution [10,11]. We extended the model so that it could calculate the weight and number average molecular weights of the soluble fraction in samples that were beyond the gel point. Details of the model are given in Appendix A.

4. Results and discussion

Since the polymers used in this work were practically monodisperse, GPC elution curves are very sensitive to changes in the molecular weight distribution induced by the irradiation treatment. According to the GPC analysis performed on the samples irradiated at both temperatures, a low but measurable level of scission was present. In Fig. 1, for example, normalized GPC curves are shown for polymer C irradiated at 25°C (Fig. 1a) and 135°C (Fig. 1b). The irradiation doses applied at each temperature were the same within experimental error. Curves similar to those in Fig. 1 were obtained for polymer B irradiated at room temperature. The ordinate in Fig. 1 indicates the fraction of material of a given molecular weight. Up to the critical gelation dose, which is in the vicinity of 35 kGy (see below), a gradual broadening of the distribution curve with the doses applied was observed, as already reported for room temperature irradiation of these same polymers [3]. Both high molecular weight tails (due to crosslinking) and low molecular weight tails (due to scission) are present. The mass fraction of scissioned material may be estimated from pregel chromatographs close to the gel point. If the total mass for each sample is normalized to unity, the mass (or mass fraction) that lies between any two molecular weights is easily estimated by adding the heights of the graph at the sampling points [12]. The mass fraction of low molecular weight material in excess of what was present in the original material is calculated by subtraction. Using this method we have estimated that the mass fraction

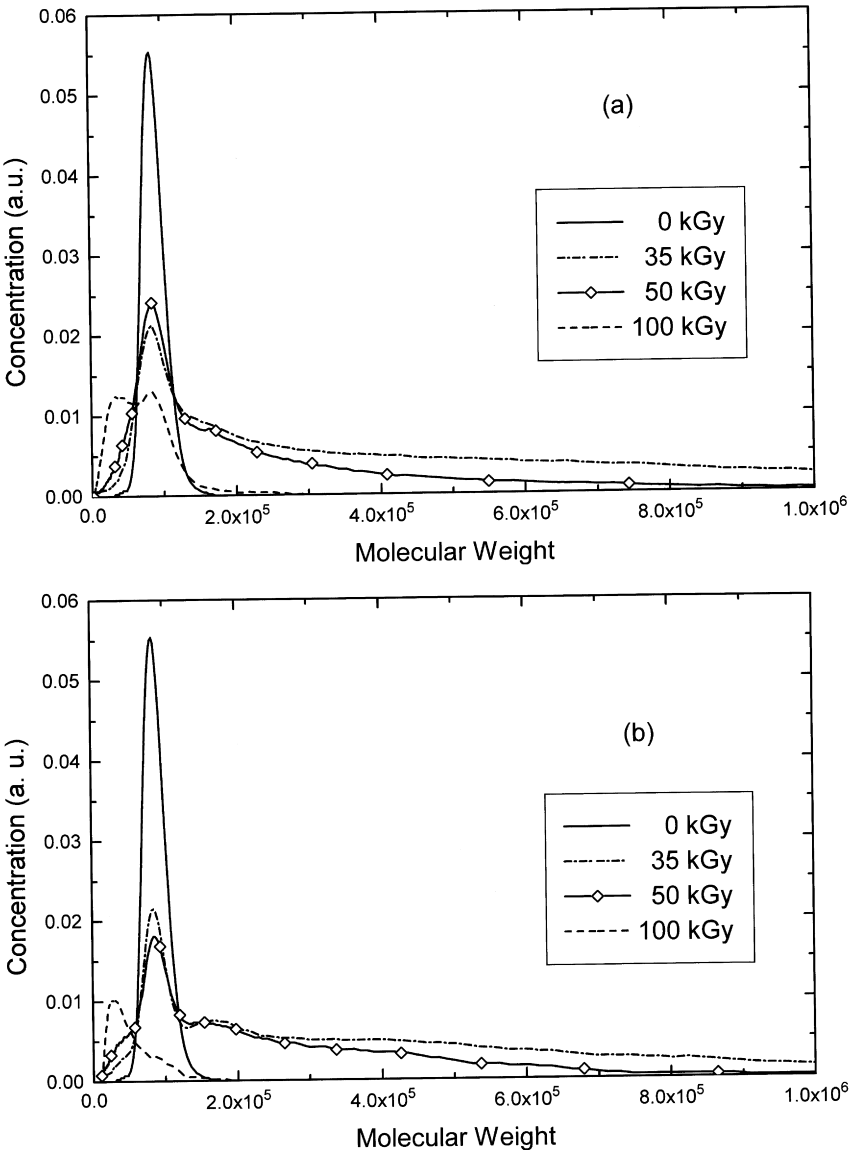

Fig. 1. GPC curves for polymer C. The same irradiation doses (within measurement error) were used at two different temperatures: 25 and 135°C.

of scissioned material amounts to 3% in polymer B and 4% in polymer C (both irradiated at 25°C), and 6% in polymer C irradiated at 135°C. Since the number of bonds in any particular polymer molecule is directly proportional to its mass, and assuming that all bonds are equally likely to be subject to either crosslinking or scission, then the above percentages may be interpreted as a good estimation of the chains scissioned during irradiation.

After the critical gelation dose, only the soluble fraction of the irradiated material may be studied by GPC. Since the gel grows at the expense of the sol by preferentially incorporating the largest molecules, the analyzed fraction is enriched in low molecular weight material. For this reason the postgel GPC curves show broadening only in the low molecular weight region, while the high molecular weight tail decreases. Even though the interpretation of the GPC analysis is mostly qualitative because of chain branching, starting with a practically monodisperse material allows an accurate estimation of the scission levels present in the polymer and the evolution of the polymer gelation process. As shown in Fig. 1, the samples that received 100 kGy evidence a striking displacement of the entire chromatograph towards the low molecular weight region, demonstrating without doubt the presence of scission in these polymers.

Polymer C samples irradiated with doses of 30 and 35 kGy at room temperature and at 135°C gave very similar results by soxhlet extraction, showing that they were both near the critical gelation dose (D_c) at both temperatures. However, analysis of the GPC traces of the samples showed that D_c was smaller for high temperature irradiation. As shown in a previous study [3], the GPC traces show a gradual broadening as the irradiation doses increase, the greatest broadening being found close to the gel point. After the gel point the traces corresponding to the sol fraction start losing their high molecular weight tails. Comparison of the entire set of chromatographs including doses of pre and postgel allow an estimation of the dose range where the gel point is. This, coupled with soxhlet extraction measurements, may be used to give an estimation of the gel dose. Using this experimental information the value of D_c was estimated to be 34 kGy for polymer C samples irradiated at room temperature, and 32 kGy for those irradiated at high temperature. D_c was estimated at 75 kGy for polymer B samples irradiated at room temperature.

Comparison of the GPC traces obtained from polymer C irradiated at different temperatures suggests that there is a higher efficiency in the utilization of energy at high temperature, which results in higher extents of reaction at the same irradiation levels. The differences in the shapes of the GPC curves are consistent with a higher extent of crosslinking achieved in the high temperature samples. As a consequence one should find smaller sol fractions for those samples which become progressively richer in low molecular weight species. Indeed, soxhlet extraction experiments on samples irradiated at 100 kGy show that the high temperature sample contains 2% of soluble material, while the room temperature one contains 5%. Molecular weight measurements on sol fractions of samples irradiated with the same (postgel) dose at different temperatures show that at high temperature the average molecular weights are consistently smaller, as indicated by the data in Table 2. This information tends to support the conclusion that there is a higher efficiency at high temperature, where the polymer samples are in a completely amorphous state.

Table 2
Absolute average molecular weights of polymers irradiated at different temperatures

Polymer	Dose (kGy)	M_n (25°C) (MO)	M_w (25°C) (LS)	M_w (135°C) (LS)
B	0	45 000	50 000	
B	5		54 000	
B	10	52 000	57 000	
B	20		69 000	
B	40	67 000	116 000	
B	60		225 000	
B	75	114 000	3 480 000	
B	80	99 000	2 500 000	
B	118.5	84 000	112 000	
B	160	37 000		
C	0	102 000	108 000	108 000
C	10	139 000	159 000	
C	20	155 000	232 000	
C	30	156 000	631 000	970 000
C	35		2 020 000	860 000
C	40		400 000	
C	45	263 000		
C	50	202 000	360 000	180 000
C	60		190 000	
C	90	69 000	100 000	
C	100			60 000

Absolute measurements of number average and weight average molecular weight were performed on a large number of pregel and postgel samples, using MO and LALLS under the conditions indicated in the experimental section. Only the soluble fraction was analyzed in the postgel region. The measured values are reported in Table 2, where the dose used and the temperature of irradiation for each sample are also indicated. These data were used to estimate the values of the parameters that the theoretical model needs. As explained above, the model may predict molecular weights and sol fractions as functions of the degree of crosslinking, α, and the degree of scission, β. In order to relate the extent of crosslinking, α, with the irradiation dose D the following relationship was used:

$$\frac{\alpha}{\alpha_c} = \frac{D}{D_c} \tag{1}$$

where the subscript ‘c’ indicates the critical value at the gel point. The parameter D_c, the critical gelation dose, must be known in order to use the model. This is the first parameter that requires estimation. The other one is the scission to crosslinking ratio.

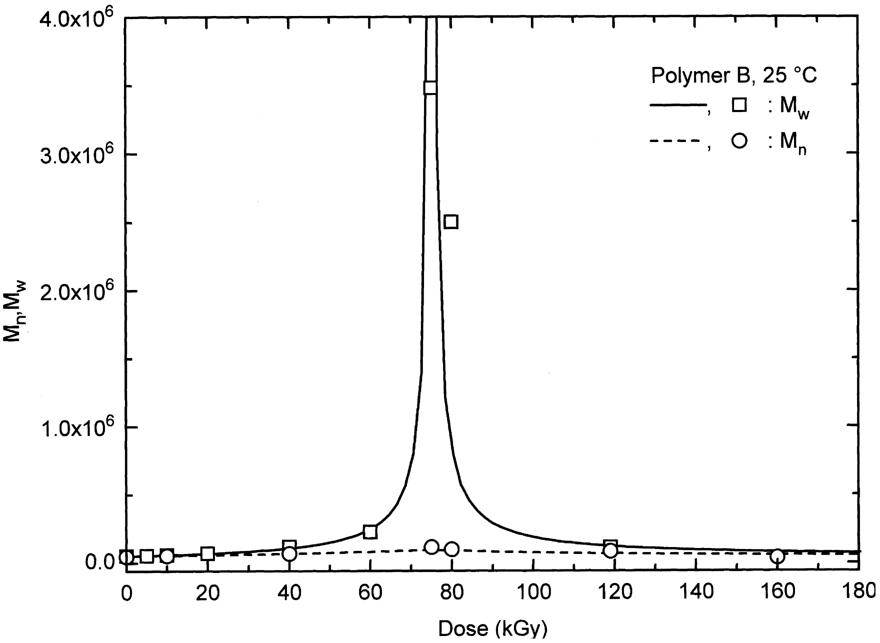

Fig. 2. Number average and weight average molecular weight of samples of polymer B irradiated at room temperature. 2.8% scission and $D_c = 75.3$ kGy were used for the model. Symbols indicate experimental measurements, lines correspond to theoretical predictions.

We used the Levenberg–Marquardt method for finding the best values of critical gel dose and percentage of scission that would minimize the objective function:

$$f = \sum_{i=1}^{n} \left(M_w^{\exp} - M_w^{\text{theo}}\right)_i^2 + \left(M_n^{\exp} - M_n^{\text{theo}}\right)_i^2 \quad (2)$$

where n is the number of experimental observations, $M_n^{\exp}$ is the absolute number average molecular weight measured by membrane osmometry, $M_w^{\exp}$ is the absolute weight average molecular weight measured by LALLS, M_n^{theo} and M_w^{theo} are the theoretical values of the number and weight average molecular weights calculated according to the model. Both pregel and postgel data were used; molecular weights were measured on the complete sample in the pregel, and on the soluble fraction in the postgel. For polymer C irradiated at 135°C we only have $M_w^{\exp}$ data. For those samples we also performed a least squares minimization with the Levenberg–Marquardt method, this time with the objective

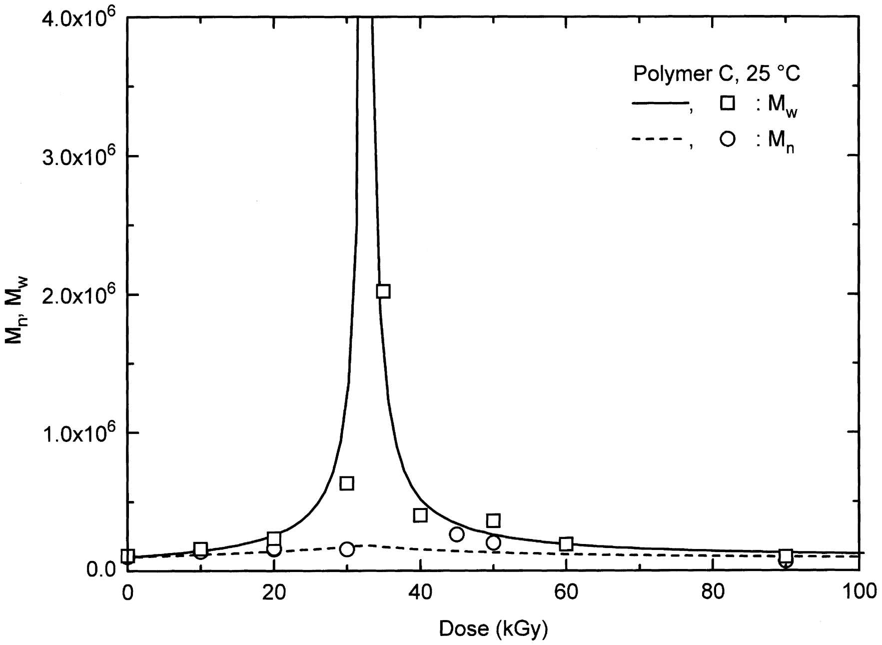

Fig. 3. Number average and weight average molecular weight of samples of polymer C irradiated at room temperature. The model used 4.9% scission and $D_c = 32.7$ kGy. Symbols indicate experimental measurements, lines correspond to theoretical predictions.

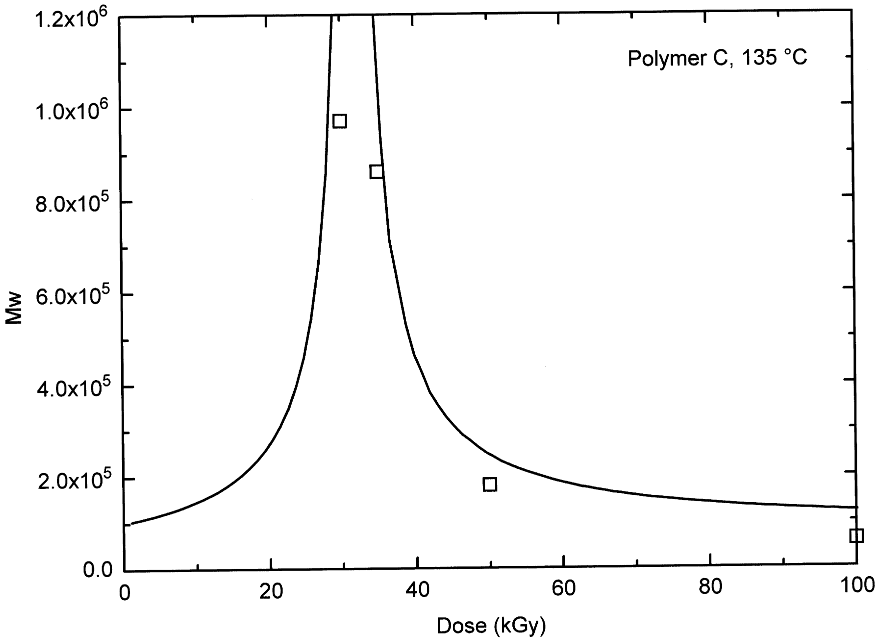

Fig. 4. Weight average molecular weight of samples of polymer C irradiated at 135°C compared with the theoretical predictions with a 6.2% scission level and $D_c = 31.7$ kGy. Symbols indicate experimental measurements, lines correspond to theoretical predictions.

function:

$$f = \sum_{i=1}^{n} \left(M_w^{\text{exp}} - M_w^{\text{theo}}\right)_i^2 \tag{3}$$

This particular set of data contains only four points.

The optimal parameters found for polymer B were 2.8% scission and 75.3 kGy critical gel dose. For polymer C irradiated at 25°C the optimal parameters were 4.9% scission and 32.7 kGy critical gel dose, while for polymer C irradiated at 135°C those parameters were 6.2% scission and 31.7 kGy critical gel dose. These results are consistent with the experimental estimations obtained from GPC and gel fraction data that were already discussed. Theoretical predictions of molecular weights evaluated using those optimal parameters were compared with the experimental values. Results for room temperature irradiation are shown

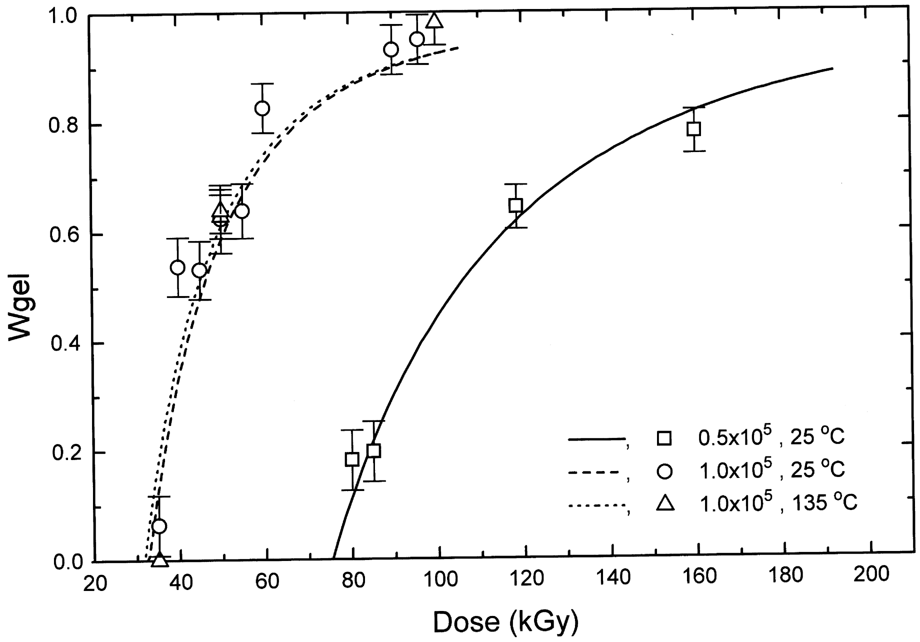

Fig. 5. Gel fraction vs irradiation dose for all polymer samples compared with the theoretical predictions. Critical gelation doses and scission levels used in the model are the same as those used for the corresponding molecular weight curves. Symbols indicate experimental measurements, lines correspond to theoretical predictions.

in Fig. 2 and Fig. 3, and for high temperature irradiation in Fig. 4.

Aside from experimental scatter, the agreement between theory and experiment is very good. Data are more scattered in the postgel region, which is to be expected due to the amount of manipulation that is needed in the process of sol extraction.

The weight fraction of gel for all the samples measured in this work are shown in Fig. 5 as a function of irradiation dose. The error bars indicate our estimation of the experimental error. The multiple manipulations necessary during gel extraction and the small mass of the samples contribute to the relatively large errors that we report. Data for room temperature irradiation have been previously reported [3]. High temperature irradiation data were obtained from six samples, four of which were beyond the gel point. Notice that data for polymer C samples irradiated at 25°C and 135°C fall very close together. All experimental values are compared in Fig. 5 with the theoretical prediction given by Eq. (A1) using the optimal parameters for β and D_c found from the molecular weight data, as explained above. The agreement is good for all samples. Results for polymer C tend to fall above the theoretical curves. However, taking into consideration both the inherent error in the measurements and the fact that the same parameters used to fit M_n and M_w are used unchanged to predict gel fraction, the agreement between theory and experiment can be considered good, even for that set of data.

5. Conclusions

We have irradiated model, practically monodisperse polyethylenes of two molecular weights at room temperature using doses lower and higher than the critical gelation dose. One of the polyethylenes was also irradiated at 135°C. Gel fraction was measured by extraction; M_n, M_w and GPC distribution curves were measured on the soluble fractions. We found that scission is present in all irradiated samples, at a level below 8%. Theoretical calculations agreed with the experiments both before and after the gel point. M_n values were the most sensitive to the presence of scission. Irradiation at 135°C, where the polymer is completely amorphous, seems to result in a higher efficiency in the utilization of the irradiation energy.

Acknowledgements

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Appendix A Derivation of the mathematical model of simultaneous crosslinking and scission

We start the process with monodisperse long chains. These chains have L repeat units, L being a deterministic quantity. If these chains are subject to scission until a proportion β of the bonds are broken, a new length distribution of chains L^β results. L^β is not deterministic, but a random variable. What we have now is a collection of chains with different lengths. The collection of all chains may be described by the probability distribution of L^β, $P(L^\beta = l)$, $l = 1, 2\ldots$, that is, the probability that a randomly chosen chain has a length $L^\beta = l$. 'Randomly' chosen may mean different things. If all chains are equally likely to be chosen, then what results is the number distribution of L^β, $P_n(L^\beta = l)$. If all units of mass are equally likely to be chosen, then the mass distribution of L^β is what results, $P_m(L^\beta = l)$. Taking expectations of those distributions the number average length and the weight average length may be found as:

$$E_n(L^\beta) = \sum_{l=1}^{\infty} l\, P_n(L^\beta = l) \tag{A1}$$

$$E_m(L^\beta) = \sum_{l=1}^{\infty} l\, P_m(L^\beta = l) \tag{A2}$$

For the purposes of the model we need to find the probability generating functions of the weight and number distributions of L^β. According to Miller and Macosko [11] we find, for chains that are originally monodisperse with length L,

$$\phi_{L^\beta,n}(z) = \frac{\xi^L(1-\xi-\beta)^2 + \xi(2\beta(1-\xi)-\beta^2) + \beta^2\xi(1-\xi)(L-1)}{(1+\beta(L-1))(1-\beta)(1-\xi)^2} \tag{A3}$$

$$\phi_{L^\beta,m}(z) = \frac{z\beta^2}{(1-\xi)^2} + \frac{2\beta\xi(1-z)}{L(1-\xi)^3}(1-\xi^L) + \frac{(1-z)^2(1-\beta)}{(1-\xi)^2}\xi^L \tag{A4}$$

where

$$\xi = (1-\beta)z \tag{A5}$$

The mean values of the number and weight distributions are [11]:

$$E_n(L^\beta) = \frac{L}{1+\beta(L-1)} \tag{A6}$$

$$E_m(L^\beta) = \frac{2-\beta}{\beta} - \frac{2(1-\beta)}{\beta^2 L}\left(1-(1-\beta)^L\right)$$

This ends the scission step. Now we want this collection of chains to be crosslinked until they reach a degree of crosslinking α. For such a collection of chains Miller and Macosko [10,11] derived the formulas to calculate the weight average molecular weight of the crosslinked chains, the gel point, the sol fraction, the fraction of elastically active and pendant material, the number of elastically active junctions and the number of elastically active network chains. Applying these formulas to the collection of chains that result from the hypothetical scission step we find, for example,

$$M_w = m_0 \left(E_m(L^\beta) + \frac{\alpha \left(E_m(L^\beta) \right)^2}{1 - \alpha \left(E_m(L^\beta) - 1 \right)} \right) = \tag{A7}$$

$$\frac{m_0(1+\alpha)\left[(1-\beta)^{L+1} + \beta + \beta L - \beta^2 L/2 - 1\right]}{\beta^2 L(\alpha + 1/2) - \alpha(1-\beta)^{L+1} + \alpha(1-\beta) - \alpha\beta L}$$

where m_0 is the mass of a repeat unit. This expression is entirely equivalent to the one previously reported by Andreucetti et al. [3] All other parameters may also be calculated. Of special interest in this work is the sol fraction, which may be calculated as

$$w_s = \sum_{f=0}^{\infty} P_m(L^\beta = f)\left(P\left(F_A^{out}\right)\right)^f \tag{A8}$$

where $P(F_A^{out})$ is the probability of finding a finite end looking out of an *A*-site. This probability is the smallest solution of the algebraic equation [11]:

$$P\left(F_A^{out}\right) = 1 - \alpha + \alpha \frac{\phi_{L^\beta,m}\left(P\left(F_A^{out}\right)\right)}{P\left(F_A^{out}\right)} \tag{A9}$$

$\phi_{L^\beta,m}$ was defined in Eq. (A4). This ends the crosslinking step. At this point the calculated parameters correspond to chains that have been subject to a degree of scission, β, and a degree of crosslinking, α.

In order to model our experimental data we needed to calculate the number and weight average molecular weights of the sol fraction. Those quantities were not calculated in Miller and Macosko's work on crosslinking of chains [10,11], so we extended the model to be able to evaluate them.

The sol fraction diminishes as the conversion increases beyond the gel point. The average molecular weights of the sol fraction also diminish progressively as conversion advances. Flory showed [7] that the average molecular weights of the sol fraction at a given conversion, α, beyond the gel point are equal to the average molecular weights of the system at another conversion α', where $\alpha' < \alpha_{gel} < \alpha$. The particular relationship between α and α' varies with the chemical system under consideration. Therefore, the problem of finding the average molecular weights of the sol fraction leads to the problem of finding the equivalent conversion in the sol, α'. The conversion, α, may be interpreted as the probability that a given site has reacted. Now, if we are interested in evaluating molecular weights for the soluble fraction only, every time we check to see whether a site reacted we also have to make sure that it did not react with the gel. Those two events have to be simultaneous, and therefore the important probability is:

$$\alpha' = \alpha G_R(0) \tag{A10}$$

where $G_R(0)$ is the probability that a repeat unit has zero paths to the gel. Miller and Macosko [11] have given an expression for $G_R(0)$ that we may adapt to our particular system. The resulting expression is:

$$G_R(0) = \frac{\phi_{L^\beta,m}\left(P\left(F_A^{out}\right)\right)}{P\left(F_A^{out}\right)} \tag{A11}$$

where $\phi_{L^\beta,m}$ was defined in Eq. (A4).

From Eqs. (A9)–(A11) we find the equivalent extent of reaction in the sol, α'. Then, the weight average molecular weight in the sol is found to be:

$$M_w^{sol} = m_0 \left(E_m(L^\beta) + \frac{\alpha' \left(E_m(L^\beta) \right)^2}{1 - \alpha' \left(E_m(L^\beta) - 1 \right)} \right) \tag{A12}$$

The expression for the number average molecular weight in the pregel region is the well known result [3]:

$$M_n = \frac{m_0 L}{1 - \alpha \dfrac{L}{2} + \beta L} \tag{A13}$$

In the sol fraction, we again replace α by α' to get:

$$M_n^{sol} = \frac{m_0 L}{1 - \alpha' \dfrac{L}{2} + \beta L} \tag{A14}$$

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