Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 45 (2004) 5661–5669
polymer
www.elsevier.com/locate/polymer

# Model for a scission-crosslinking process with both H and Y crosslinks

Claudia Sarmoria*, Enrique Vallés

*Planta Piloto de Ingeniería Química (PLAPIQUI—UNS—CONICET), Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina*

Received 7 April 2004; received in revised form 3 June 2004; accepted 5 June 2004

Available online 25 June 2004

**Abstract**

We present a mathematical model that may predict average molecular weights and weight fraction of solubles for polymer chains subjected to irradiation, where both scission and crosslinking are present. Two types of crosslinks are allowed: four-armed or H crosslinks, and three-armed or Y crosslinks. This is a departure from the more traditional models for irradiation, where only H crosslinks are allowed. The model is valid both in the pregel and postgel regions, and may be applied to chains with any known distribution of molecular weights. We compare predictions from the model with experimental data on polydimethylsiloxane treated with electron beams at different doses, and show that the introduction of Y crosslinks leads to a marked improvement in the quality of the predictions as compared with a more traditional model where only H type crosslinks are allowed.


*Keywords:* Polymer science; Crosslinking process; Scission

## 1. Introduction

Even though the irradiation of polymers is a relatively old process, interest has not decayed. Irradiation of several different polymers have been studied in the past [1–12] and continue to be studied. By now it has been established that the net effect of irradiation on any polymer is a combination of chain scission and chain crosslinking. Which one of the two reactions predominates depends on the polymer and the operating conditions. For example, if polyethylene is irradiated with γ-rays under vacuum crosslinking predominates, but if the process is carried out with polypropylene then the predominant reaction is scission. Polydimethylsiloxane (PDMS) mainly crosslinks under those same conditions.

Irradiation may be performed by γ-rays or by electron beam attack. The latter delivers more energy per unit time, and has smaller penetration than the former. In thin films, the mechanism is assumed to be the same for both methods. The presence of oxygen makes a difference in γ-ray irradiation, but not as much in electron beam attack due to its velocity.

From the very beginning of the studies of the effects of irradiation on polymers, mathematical models of the process have been developed. Saito [13] reviewed them in 1972. That review already contained works that considered the simultaneous crosslinking and scission of polymer chains. Later works have continued to deal with this problem using either a kinetic or a probabilistic approach [6,14–20]. Several variations of the simultaneous crosslinking and scission problem were considered: monodisperse or polydisperse starting chains where crosslinking is defined as the joining of two chains, forming a four-functional crosslink [6,14–20]; crosslinking due to scission [14], where the only crosslinks allowed are those formed by newly cut chains that attack a monomer on a different chain, and other variations that involve adaptations to specific polymers or different mathematical methods used to solve the problem.

A few years ago we published a mathematical model that was very successful in calculating average molecular weights and postgel parameters (sol and gel fraction, molecular weights of the soluble fraction, fraction of trapped entanglements, etc.) for practically monodisperse low density polyethylene irradiated by γ-rays under vacuum [19,20]. It was relatively easy to extend the model so that it could handle both monodisperse and polydisperse polymers. When we applied this mathematical model to polydisperse PDMS irradiated with electron beam, we could not reproduce the molecular weights of the soluble fraction in

* Corresponding author. Tel.: +54-291-4861700; fax: +54-291-4861600.
*E-mail address:* csarmoria@plapiqui.edu.ar (C. Sarmoria).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.06.006

the postgel. Polydispersity itself was not to blame: if we decomposed the polydisperse distribution into 10 monodisperse fractions that would add up to the original distribution, applied the 'monodisperse' model to each of the monodisperse fractions, and combined the results, we obtained essentially the same molecular weights as with the model that accounted for polydispersity.

A recent work by Hill et al. [10] suggests that the crosslinks in irradiated PDMS could be of both the H-type (with four arms) and the Y-type (with three arms). Our mathematical model only considered H-type crosslinks. Therefore we modified it to include both types of crosslinks. In what follows, we show the new model and the improvements in prediction of postgel sol fraction molecular weights that may be achieved with it.

## 2. Mathematical model

As in our previous models, we assume that crosslinking and scission are independent reactions. Since they are independent, they do not influence each other in any way, and that gives us the freedom of achieving given degrees of crosslinking and scission following any path we wish. Taking advantage of this, we model crosslinking and scission as sequential steps, even though in practice they are simultaneous. The end result is the same, but the mathematics are much simpler following this path. The starting polymer chains are polydisperse.

In order to be able to model H and Y crosslinks, we picture the starting chains as containing only one type of reactive site, named A. All bonds in a chain are considered reactive A-sites. All A-sites are equally likely to be subject to scission. Now, the scission reaction generates sites at the split ends that have a different reactivity, and we name them B. The process is schematically illustrated in Fig. 1. Notice that any chain may have at most two B-sites.

When the crosslinking step is considered, we propose that the only possible reactions are A–A and A–B. The A–A reaction gives H-crosslinks, while A–B reaction results in Y-crosslinks. We do not consider B–B reactions since they do not generate new crosslinking points, and also because the probability of that occurrence is much lower than for the other two reactions. Fig. 2 shows an example of a branched molecule formed in this type of process. Both crosslinking reactions are random: all A–A pairs are equally likely, as are all A–B pairs. However, the A–A and A–B reactions have a different likelihood, and the relative proportion of each is one of the parameters of the model. We also assume that all groups react independently of one another (no substitution effect) and that there is no intramolecular reaction in finite species. In short, we adhere to the ideal crosslinking assumptions as defined by Flory and Stockmayer, except two different crosslinking reactions are present.

Our model uses the recursive formalism developed by Miller and Macosko in their 1987 and 1988 papers on crosslinking of chains with length and site distribution [21, 22]. It requires us to describe in detail the statistical characteristics of the long chains that will be processed. Each chain is composed of a discrete number of repeat units. The number of repeat units in the chain is the random variable $L$. All units are considered to be reactive, in the sense that all of them may be subject to scission and crosslinking. Therefore, each repeat unit contains one A-site, and the functionality of the chain in A-sites is the random variable $F_A$. It is obvious that $L = F_A$, but the notation is useful in the derivation of the model. The complete set of starting chains may be described by the probability distribution of $L$. This is indicated as $P(L = l)$, $l = 1, 2, 3, \ldots \infty$, and it is the probability that a randomly chosen chain will have $l$ repeat units.

The crosslinking and scission reactions occur at random, and while calculating molecular weights we will need to choose chains randomly. This 'randomness' may mean different things depending on what characteristic of the chain is being weighted. If all chains are equally likely to be chosen, the number distribution results, $P_n(L = l)$. If all units of mass are equally likely to be chosen, then the resulting distribution is the mass distribution $P_m(L = l)$. We may also choose using other criteria. For example, if we choose by reactive site of type A, we get a site A distribution, $P_{SA}(L = l)$. In the particular case we describe here, where all bonds are reactive, $P_{SA}(L = l) = P_m(L = l)$.

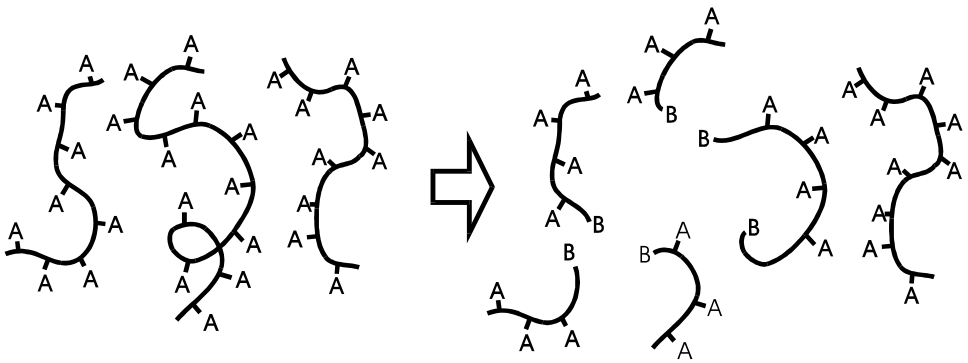

Fig. 1. Schematic representation of the result of the scission step on the collection of chains.

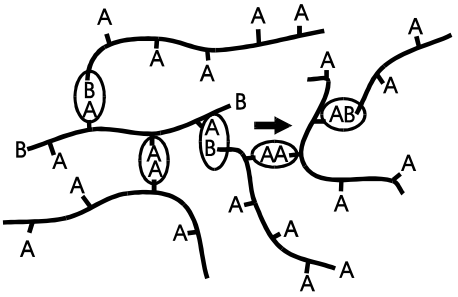


Fig. 2. A molecule formed during the scission-crosslinking process.

For each of these distributions, an expected chain length may be calculated. $E_m(L)$ is the mass-average length, $E_n(L)$ is the number average length, $E_{SA}(L)$ is the site A average length. Those quantities may be calculated as:

$$E_i(L) = \sum_{l=0}^{\infty} lP_i(L = l) \qquad i = \mathrm{n, m, SA} \tag{1}$$

Since $P_{SA}(L = l) = P_m(L = l)$, then $E_m(L) = E_{SA}(L)$.

With the same reasoning we may calculate number, weight, or A-site averages of any quantity we need.

The weight of each chain is represented by the random variable $M = m_0 L$, where $m_0$ is the weight of each repeat unit. Average weights are calculated as

$$E_i(M) = m_0 E_i(L) \tag{2}$$

since all repeat units weigh the same.

As explained above, we simulate the simultaneous process of crosslinking and scission as a two-step process that starts with scission. We now have to take the number of B-sites, the 'split ends', into consideration. The random variable $F_B$ is introduced for that purpose. After the original set of chains has been subjected to a degree of scission $\beta$, the chain length distributions change. Let $L^\beta$ denote the length of a randomly chosen chain after undergoing scission. The description of the chains after the scission step now requires knowledge of the probabilities $P_n(L^\beta = l)$, $P_m(L^\beta = l)$, $P_{SA}(L^\beta = l)$, $P_{SB}(L^\beta = l)$, $l = 1\ldots\infty$. It is possible to establish the distribution of $L^\beta$ from that of $L$. Montroll [23] and Miller and Macosko [22] give the equations for $P_n(L^\beta = l)$, $P_m(L^\beta = l)$, $l = 1\ldots\infty$, and their corresponding expectations. Other distributions may be calculated from them. Details are given in Appendix A.

The complete set of chains could in principle be described by the joint probability distribution of $L^\beta$ and $F_B$. This is indicated as $P(L^\beta = l,\ F_B = f_B)$, $f_B = 0, 1, 2$; $l = 1, 2, 3, \ldots\infty$, and it is the probability that a randomly chosen chain will have $l$ repeat units and $f_B$ B-sites. Since scission occurs randomly, however, the length of a chain and the number of B-sites it contains are independent variables, and so the joint probability distribution just mentioned may be expressed as a product, $P(L^\beta = l,\ F_B = f_B) = P(L^\beta = l) \times P(F_B = f_B)$, $f_B = 0, 1, 2$; $l = 1, 2, 3, \ldots\infty$.

If we want to calculate the average molecular weight of a polymer that has reached a degree of crosslinking $\alpha$ and a degree of scission $\beta$, we pick a unit of mass at random and evaluate what is the expected weight attached to it. The unit of mass will be on a chain with a random mass $M$, a random number $F_A = M$ of A-sites and a random number $F_B$ of B-sites. The weight attached to an A-site, such as the one indicated with an arrow in Fig. 2, will be zero if the site is unreacted. The chance of that happening is $1 - \alpha$. If the A-site reacted, it may have done so with either an A or a B-site. If the site reacted with another A-site, the weight attached will be the weight looking into an A-site, $W_A^{in}$. If it reacted with a B-site, the weight will be that looking into a B-site, $W_B^{in}$. The probabilities of those two events are $\alpha(1 - \gamma)$ and $\alpha\gamma$, respectively, where $\gamma$ is the probability that an A-site reacted with a B-site rather than with another A-site. This can be expressed in a compact form as:

$$\gamma = \frac{\#\text{ A-sites involved in A–B reactions}}{\begin{pmatrix}\#\text{ A-sites involved}\\ \text{in A–A reactions}\end{pmatrix} + \begin{pmatrix}\#\text{ A-sites involved}\\ \text{in A–B reactions}\end{pmatrix}} \tag{3}$$

$$W_A^{out} = \begin{cases} 0 & \text{A unreacted} \quad P = 1 - \alpha \\ W_A^{in} & \text{A reacted with A} \quad P = \alpha(1 - \gamma) \\ W_B^{in} & \text{A reacted with B} \quad P = \alpha\gamma \end{cases} \tag{4}$$

where $P$ is the probability of each event. Similarly, the weight to be found looking out of a B-site may be expressed as

$$W_B^{out} = \begin{cases} 0 & \text{B unreacted} \quad P = 1 - \delta \\ W_A^{in} & \text{B reacted} \quad P = \delta \end{cases} \tag{5}$$

It is more convenient to express the B-site conversion, $\delta$, in terms of $\alpha$, $\beta$ and $\gamma$. In order to do that, one must recall that by definition,

$$\delta = \frac{\#\text{ sites involved in A–B reaction}}{\text{total \# of B-sites}} \tag{6}$$

$$\alpha = \frac{\begin{pmatrix}\#\text{ sites involved}\\ \text{in A–B reaction}\end{pmatrix} + \begin{pmatrix}\#\text{ sites involved}\\ \text{in A–A reaction}\end{pmatrix}}{\text{total \# of A-sites}} \tag{7}$$

If the stoichiometric imbalance is defined as

$$r = \frac{\text{total \# of A-sites}}{\text{total \# of B-sites}} \tag{8}$$

then one may easily show that

$$\frac{\alpha}{\delta} = \frac{1}{r}\frac{\begin{pmatrix}\text{\#A-sites involved in}\\ \text{A–A reactions}\end{pmatrix} + \begin{pmatrix}\text{\#A-sites involved in}\\ \text{A–B reactions}\end{pmatrix}}{\text{\#B-sites involved in A–B reactions}} = \frac{1}{r}\frac{1}{\gamma} \tag{9}$$

where the second equality arises from the definition of $\gamma$ in Eq. (3) and the fact that the same number of A-sites and B-sites is involved in A–B reactions. In this system, the stoichiometric imbalance $r$ is not constant, since the number of B-sites increases with time while the number of A-sites decreases. Since each bond in a chain is an A-site, and each scission reaction destroys one A-site and generates two B-sites, we may express $r$ as

$$r = \frac{E_m(L) - E_m(L)\beta}{2E_m(L)\beta} = \frac{1-\beta}{2\beta} \tag{10}$$

With this expression, we find that

$$\delta = \frac{\alpha\gamma(1-\beta)}{2\beta} \tag{11}$$

If we take expectations of the random events indicated in Eqs. (4) and (5), and substituting Eq. (11) into the result, we find

$$E(W_A^{out}) = 0(1-\alpha) + E_{SA}(W_A^{in})\alpha(1-\gamma) + E_{SB}(W_B^{in})\alpha\gamma \tag{12}$$

$$E(W_B^{out}) = 0\left(1 - \frac{\alpha\gamma(1-\beta)}{2\beta}\right) + E_{SA}(W_A^{in})\frac{\alpha\gamma(1-\beta)}{2\beta} \tag{13}$$

The expectations looking into various sites are taken by A site or by B site depending on the type of site that has reacted with the starting one. We now turn to the calculation of $E_{SA}(W_A^{in})$ and $E_{SB}(W_A^{in})$. The weight looking into an A site is the expected weight of the chain plus the weights that are attached to the remaining A sites and all the B sites. Mathematically this is expressed as

$$E_{SA}(W_A^{in}) = E_{SA}(M) + (E_{SA}(F_A) - 1)E(W_A^{out}) + E_{SA}(F_B)E(W_B^{out}) \tag{14}$$

Similarly we find that

$$E_{SB}(W_B^{in}) = E_{SB}(M) + (E_{SB}(F_B) - 1)E(W_B^{out}) + E_{SB}(F_A)E(W_A^{out}) \tag{15}$$

Eq. (12) through (15) may be solved for $E(W_A^{out})$ and $E(W_B^{out})$. Considering that in our particular case expectations by A-site are the same as expectations by mass, and that $M = m_0L^\beta$, the result is

$$E(W_A^{out}) = -\alpha m_0\Big\{2\beta[E_m(L^\beta)(\gamma-1) - \gamma E_{SB}(L^\beta)] + \alpha\gamma^2[E_m(L^\beta)(1 - E_{SB}(F_B)) + E_{SB}(L^\beta)E_m(F_B) + \beta(E_m(L^\beta)(E_{SB}(F_B) - 1) - E_m(F_B)E_{SB}(L^\beta))]\Big\}/D \tag{16}$$

$$E(W_B^{out}) = \alpha\gamma m_0(\beta-1)[\alpha\gamma E_{SB}(L^\beta) - E_m(L^\beta)]/D \tag{17}$$

$$D = 2\beta + 2\alpha\beta(1 - E_m(L^\beta)) - \alpha\gamma E_m(F_B) + 2\alpha\beta\gamma(E_m(L^\beta) - E_{SB}(L^\beta) - 1) + \alpha\beta\gamma E_m(F_B) + \alpha^2\beta^2\gamma[1 - E_{SB}(F_B) + E_m(L^\beta)(E_{SB}(F_B) - 1) - E_m(F_B)E_{SB}(L^\beta)] + \alpha^2\gamma^2[E_m(L^\beta) - 1 + E_m(F_B)E_{SB}(L^\beta) + E_{SB}(F_B)(1 - E_m(L^\beta))] \tag{18}$$

The weight average molecular weight is then

$$M_w = m_0E_m(L^\beta) + E_m(F_A)E(W_A^{out}) + E_m(F_B)E(W_B^{out}) \tag{19}$$

The evaluation of the different expectations is shown in Appendix A. They may all be expressed in terms of the moments of the distribution of the untreated chains, the degree of scission $\beta$ and the degree of crosslinking $\alpha$, all of which are knowable quantities. The starting chains may be either monodisperse or polydisperse.

Eq. (19) is only valid in the pregel region, where $\alpha < \alpha_c$. The gel point $\alpha_c$ may be found by making $D = 0$ in Eq. (18), a condition that causes the theoretical $M_w$ in Eq. (19) to become infinite. Beyond this conversion we may still calculate several parameters, including the weight average molecular weight of the soluble fraction, but for that it is necessary to be able to distinguish the sol from the gel. That requires looking out of a reactive site and evaluating the probability that all paths in that direction are finite. Since there are two different types of reactive sites, two such probabilities must be evaluated: the probability that the path will be finite looking out of an A or a B site, $P(F_A^{out})$ and $P(F_B^{out})$. These probabilities may be calculated by conditioning:

$$P(F_A^{out}) = (1-\alpha)P(F_A^{out}|\text{A unreacted}) + \alpha P(F_A^{out}|\text{A reacted}) = 1 - \alpha + \alpha P(F_A^{out}|\text{A reacted}) \tag{20}$$

Since the A site may react either with another A site or

with a B site,

$$P(F_A^{out}|\text{A reacted}) = (1-\gamma)P(F_A^{out}|\text{A reacted with A}) + \gamma P(F_A^{out}|\text{A reacted with B}) = (1-\gamma)P_{SA}(F_A^{in}) + \gamma P_{SB}(F_B^{in}) \quad (21)$$

$$P_{SA}(F_A^{in}) = P_m(F_A^{in}) = \sum_{l=1}^{\infty}\sum_{f_B=0}^{2} P_m(F_A^{in}|L^\beta = l, F_B = f_B)P_m(L^\beta = l)P_m(F_B = f_B) = \sum_{l=1}^{\infty}\sum_{f_B=0}^{2} P(F_A^{out})^{l-1}P(F_B^{out})^{f_B} P_m(L^\beta = l)P_m(F_B = f_B) \quad (22)$$

where the probabilities of the different functionalities may be expressed as a product because $L^\beta$ and $F_B$ are independent. Because of that independence the summations may be rearranged as

$$P_m(F_A^{in}) = \sum_{l=1}^{\infty} P(F_A^{out})^{l-1} P_m(L^\beta = l)\sum_{f_B=0}^{2} P(F_B^{out})^{f_B} P_m(F_B = f_B) \quad (23)$$

The summations in Eq. (23) may be expressed in terms of probability generating functions (pgfs). By definition, the pgf $\phi_{A,b}(z)$ is

$$\phi_{A,b}(z) = \sum_{a=0}^{\infty} z^a P_b(A = a) \quad (24)$$

where $z$ is the dummy variable of the transformation, A is a random variable and $b$ specifies the type of probability distribution of A that is used. Using this definition, Eq. (23) may be expressed as

$$P_m(F_A^{in}) = \frac{\phi_{L^\beta,m}(P(F_A^{out}))}{P(F_A^{out})}\phi_{F_B,m}(P(F_B^{out})) \quad (25)$$

Since according to Eq. (A4) in Appendix A $P_m(F_B = f_B) = P_n(F_B = f_B)$, we find that

$$P_m(F_A^{in}) = \frac{\phi_{L^\beta,m}(P(F_A^{out}))}{P(F_A^{out})}\phi_{F_B,n}(P(F_B^{out})) \quad (26)$$

In order to calculate Eq. (23), we still need to evaluate $P_{SB}(F_B^{in})$

$$P_{SB}(F_B^{in}) = \sum_{l=0}^{\infty}\sum_{f_B=1}^{2} P_{SB}(F_B^{in}|L^\beta = l, F_B = f_B) P_{SB}(L^\beta = l)P_{SB}(F_B = f_B) = \sum_{l=0}^{\infty}\sum_{f_B=1}^{2} P(F_A^{out})^l P(F_B^{out})^{f_B-1} P_{SB}(L^\beta = l)P_{SB}(F_B = f_B) = \sum_{l=0}^{\infty} P(F_A^{out})^l \sum_{f_B=1}^{2} P(F_B^{out})^{f_B-1} P_{SB}(L^\beta = l)P_{SB}(F_B = f_B) \quad (27)$$

Applying again the definitions of probability generating functions,

$$P_{SB}(F_A^{in}) = \phi_{L^\beta,n}(P(F_A^{out}))\frac{\phi_{F_B,SB}(P(F_B^{out}))}{P(F_B^{out})} \quad (28)$$

where we have used the result that $P_{SB}(L^\beta = l) = P_n(L^\beta = l)$, obtained in Appendix A (Eq. (A14)).

Substitution of Eqs. (21), (26) and (28) into Eq. (20) yields

$$P(F_A^{out}) = 1 - \alpha + \alpha(1-\gamma)\frac{\phi_{L^\beta,m}(P(F_A^{out}))}{P(F_A^{out})} \times \phi_{F_B,n}(P(F_B^{out})) + \alpha\gamma\phi_{L^\beta,n}(P(F_A^{out}))\frac{\phi_{F_B,SB}(P(F_B^{out}))}{P(F_B^{out})} \quad (29)$$

The probability of finding a finite end looking out of a B-site, $P(F_B^{out})$, is also found by conditioning. The result is

$$P(F_B^{out}) = 1 - \frac{\alpha\gamma(1-\beta)}{2\beta} + \frac{\alpha\gamma(1-\beta)}{2\beta} \times \frac{\phi_{L^\beta,m}(P(F_A^{out}))}{P(F_A^{out})}\phi_{F_B,n}(P(F_B^{out})) \quad (30)$$

Eqs. (29) and (30) must be solved iteratively. A simple bisection search scheme works very well. The various pgfs may be calculated by definition. Expressions of pgfs for common chain length distributions have been reported in the literature [22].

Once the probability of finite ends looking out of both types of sites is known, we are ready to calculate the probability of choosing a site and finding that it has no paths leading to the gel along the chain. In the notation of Miller and Macosko [22] this is $G_R(0)$. For this process we pick units of mass at random. We will pick an A-site with

probability

$$P_{\mathrm{m}}(\text{A-unit}) = \frac{N_{\mathrm{C}}E_{\mathrm{m}}(L)m_0 - N_{\mathrm{C}}\beta E_{\mathrm{m}}(L)m_0}{N_{\mathrm{C}}E_{\mathrm{m}}(L)m_0 + N_{\mathrm{C}}\beta E_{\mathrm{m}}(L)m_0} = \frac{1-\beta}{1+\beta} \quad (31)$$

where $N_{\mathrm{C}}$ is the total number of chains. Given that an A site has been selected, the probability of finding no paths to the gel along the chain is

$$G_R(0|\text{A-site}) = \sum_{f_{\mathrm{B}}=0}^{2}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{j+k} P(F_{\mathrm{B}}^{\mathrm{out}})^{f_{\mathrm{B}}}$$

$$P_{\mathrm{SA}}(F_1 = j, F_2 = k) P_{\mathrm{SA}}(F_{\mathrm{B}} = f_{\mathrm{B}}) = \sum_{f_{\mathrm{B}}=0}^{2} P(F_{\mathrm{B}}^{\mathrm{out}})^{f_{\mathrm{B}}}$$

$$P_{\mathrm{m}}(F_{\mathrm{B}} = f_{\mathrm{B}}) \sum_{j=0}^{\infty}\sum_{k=0}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{j+k} P_{\mathrm{n}}(F_{\mathrm{A}} = j+k+1)/E_{\mathrm{n}}(F_{\mathrm{A}}) \quad (32)$$

Combining the indices of the last two summations,

$$G_{\mathrm{R}}(0|\text{A-site}) = \sum_{f_{\mathrm{B}}=0}^{2} P(F_{\mathrm{B}}^{\mathrm{out}})^{f_{\mathrm{B}}}$$

$$P_{\mathrm{n}}(F_{\mathrm{B}} = f_{\mathrm{B}}) \sum_{f_{\mathrm{A}}=1}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{f_{\mathrm{A}}-1} P_{\mathrm{n}}(F_{\mathrm{A}} = f_{\mathrm{A}})/E_{\mathrm{n}}(F_{\mathrm{A}})$$

$$= \phi_{F_{\mathrm{B}},\mathrm{n}}(P(F_{\mathrm{B}}^{\mathrm{out}})) \sum_{f_{\mathrm{A}}=1}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{f_{\mathrm{A}}-1} P_{\mathrm{SA}}(F_{\mathrm{A}} = f_{\mathrm{A}})$$

$$= \phi_{F_{\mathrm{B}},\mathrm{n}}(P(F_{\mathrm{B}}^{\mathrm{out}})) \frac{\phi_{F_{\mathrm{A}},\mathrm{m}}(P(F_{\mathrm{A}}^{\mathrm{out}}))}{P(F_{\mathrm{A}}^{\mathrm{out}})} \quad (33)$$

Similar reasoning leads to the probability of finding no paths to the gel along the chain given a B-site was chosen

$$G_{\mathrm{R}}(0|\text{B-site}) = \sum_{f_{\mathrm{B}}=0}^{2}\sum_{l=0}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{l} P(F_{\mathrm{B}}^{\mathrm{out}})^{f_{\mathrm{B}}-1}$$

$$P_{\mathrm{SB}}(L = l) P_{\mathrm{SB}}(F_{\mathrm{B}} = f_{\mathrm{B}})$$

$$= \sum_{f_{\mathrm{B}}=0}^{2} P(F_{\mathrm{B}}^{\mathrm{out}})^{f_{\mathrm{B}}-1} \frac{f_{\mathrm{B}} P_{\mathrm{n}}(F_{\mathrm{B}} = f_{\mathrm{B}})}{E_{\mathrm{n}}(f_{\mathrm{B}})} \sum_{l=0}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{l} \quad (34)$$

$$P_{\mathrm{n}}(L^{\beta} = l) = \frac{\phi'_{F_{\mathrm{B}},\mathrm{n}}(P(F_{\mathrm{B}}^{\mathrm{out}}))}{E_{\mathrm{n}}(f_{\mathrm{B}})} \phi_{L^{\beta},\mathrm{n}}(P(F_{\mathrm{A}}^{\mathrm{out}}))$$

where the prime indicates the first derivative of the probability generating function with respect to its dummy argument.

Since a B-site is chosen with probability

$$P_{\mathrm{m}}(\text{B-unit}) = 1 - P_{\mathrm{m}}(\text{A-unit}) = \frac{2\beta}{1+\beta} \quad (35)$$

then the total probability of finding no paths to the infinite network is

$$G_{\mathrm{R}}(0) = \frac{1-\beta}{1+\beta} G_{\mathrm{R}}(0|\text{A-site}) + \frac{2\beta}{1+\beta} G_{\mathrm{R}}(0|\text{B-site}) \quad (36)$$

Following the arguments of Flory [24] and other authors [20,25], one may define an extent of reaction valid only for the sol fraction in the postgel region, which is equivalent to an extent of reaction in the pregel region. In our case,

$$\alpha_{\mathrm{s}} = \alpha G_{\mathrm{R}}(0|\text{A-site}) \quad (37)$$

We have used the probability of no connections to the gel given the choice of an A-site because the conversion $\alpha$ refers to A-sites only. Substitution of $\alpha_{\mathrm{s}}$ in place of $\alpha$ in the expressions for the average molecular weights in the pregel region yields the average molecular weights of the sol fraction in the postgel region.

In order to find the sol fraction, we must again pick units of mass at random. Then,

$$w_{\mathrm{s}} = P_{\mathrm{m}}(\text{A-site}) P_{\mathrm{m}}(\text{soluble}|\text{A-site}) + P_{\mathrm{m}}(\text{B-site}) P_{\mathrm{m}}(\text{soluble}|\text{B-site})$$

$$= \frac{1-\beta}{1+\beta} \sum_{f_{\mathrm{A}}=1}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{f_{\mathrm{A}}}$$

$$P_{\mathrm{m}}(F_{\mathrm{A}} = f_{\mathrm{A}}) + \frac{2\beta}{1+\beta} \sum_{f_{\mathrm{B}}=0}^{2} P(F_{\mathrm{B}}^{\mathrm{out}})^{f_{\mathrm{B}}} P_{\mathrm{m}}(F_{\mathrm{B}} = f_{\mathrm{B}})$$

$$= \frac{1-\beta}{1+\beta} \sum_{l=1}^{\infty} P(F_{\mathrm{A}}^{\mathrm{out}})^{l} \quad (38)$$

$$P_{\mathrm{m}}(L^{\beta} = l) + \frac{2\beta}{1+\beta} \sum_{f_{\mathrm{B}}=0}^{2} P(F_{\mathrm{B}}^{\mathrm{out}})^{f_{\mathrm{B}}} P_{\mathrm{n}}(F_{\mathrm{B}} = f_{\mathrm{B}})$$

$$= \frac{1-\beta}{1+\beta} \phi_{L^{\beta},\mathrm{m}}(P(F_{\mathrm{A}}^{\mathrm{out}})) + \frac{2\beta}{1+\beta} \phi_{F_{\mathrm{B}},\mathrm{n}}(P(F_{\mathrm{B}}^{\mathrm{out}}))$$

All the equations presented may be calculated for any known starting distribution of chains.

## 3. Results and discussion

The model just described was implemented in Fortran code and run for several cases. The quantities needed for input are the starting molecular weights and type of molecular weight distribution, the gel point (expressed as dose at the critical point), the maximum dose used, the level of scission (expressed as a fraction of the crosslinking conversion $\alpha$) and the proportion of all crosslinks that are of the Y type. All this information can be obtained from standard experimental techniques such as size exclusion chromatography (SEC), sol extraction measurements from the crosslinked polymer, and nuclear magnetic resonance

(NMR) determinations to evaluate the fraction of Y and H type crosslinked points. The model assumes that the ratio $\alpha/\beta$ is constant throughout the reaction, and that the energy expended on the sample is directly proportional to the sum of conversions $\alpha + \beta$. The output is the number and weight average molecular weights, both before and after the gel point, and the soluble fraction. Results are obtained as functions of conversion. Since experimental information is available in terms of applied dose, results are converted using the expression

$$\frac{D}{D_c} = \frac{\alpha + \beta}{\alpha_c + \beta_c} \tag{39}$$

where $D$ is the dose, and the subscript c indicates the critical point or gel point. In order to compare theoretical predictions with experimental data, a reasonably good estimate of the experimental gel point $D_c$ is needed in order to be able to use Eq. (39). The values of $\alpha_c$ and $\beta_c$ will vary with the $\alpha/\beta$ ratio and must be calculated theoretically. They are evaluated as those conversions at which the weight average molecular weight diverges.

As an example, Fig. 3 shows a comparison between model results and experimental data obtained on a commercial PDMS (supplier: Petrarch Systems, currently United Chemical Technologies, $M_w = 70,100$ and $M_n = 41,800$) irradiated using electron beams in air at room temperature. The starting distribution was assumed to be a Negative Binomial with parameters chosen so that the experimentally measured $M_n$ and $M_w$ could be reproduced. For details on this distribution as applied to polymer chains, see Miller and Macosko [22]. The level of scission was estimated to be 20% of the overall crosslinking conversion. The full line shows predictions when 25% of the crosslinks are of the Y type,

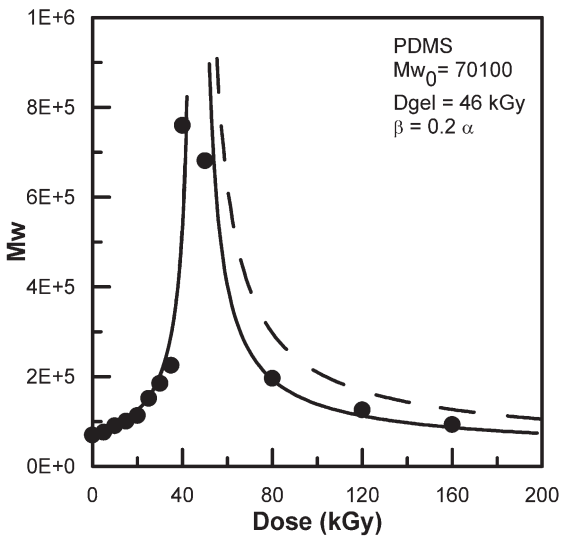


Fig. 3. Model predictions for a commercial PDMS treated with electron beams using different proportions of H and Y crosslinks and a constant degree of scission compared with experimental data. Filled circles: experimental data; dashed line: 100% H crosslinks; full line: 25% Y crosslinks, 75% H crosslinks.

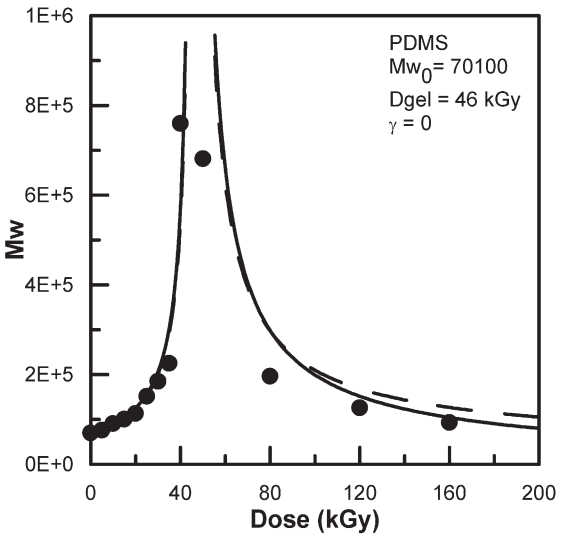


Fig. 4. Model predictions for a commercial PDMS treated with electron beams using different levels of scission and 100% H crosslinks compared with experimental data. Filled circles: experimental data; dashed line: $\beta = 0.2\alpha$; full line: $\beta = \alpha$.

while the dashed line corresponds to 100% H type crosslinks. Consideration of the Y type crosslinks affords a definite improvement in the agreement with experimental data. If Y type crosslinks are not allowed, the only other parameter that could possibly lower $M_w$ in the postgel region is the level of scission. However, it was impossible to fit the experimental $M_w$ data solely by increasing this level. Fig. 4 shows that even if one assumes that $\beta = \alpha$, a gross overestimation of the possible level of scission for this particular system, the predicted $M_w$ does not fit well the experimental values if Y type crosslinks are not allowed. The level of Y crosslinks that gives a good fit in Fig. 3 is in the range of those reported by Hill et al. [10] for a PDMS system.

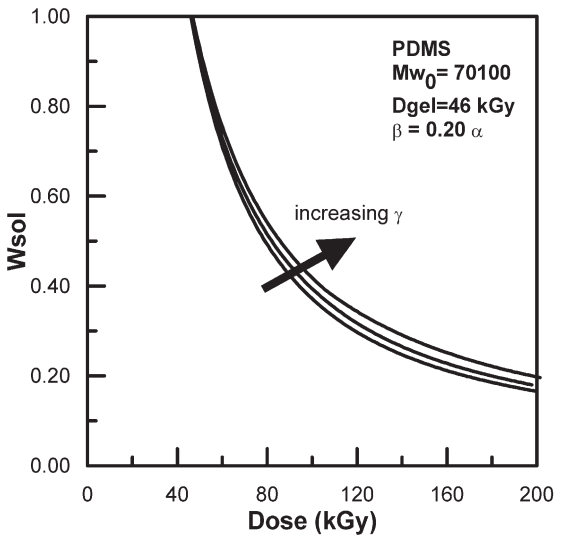


Fig. 5. Influence of the proportion of Y crosslinks on the sol fraction. Curves correspond to $\gamma = 0$, $\gamma = 0.25$, $\gamma = 0.5$.

The proportion of Y crosslinks also affects the prediction of the sol fraction. An example is shown in Fig. 5, where we have plotted the predicted weight fraction of solubles for three different proportions of Y crosslinks (the arrow points in the direction of increasing $\gamma$). Comparison with Fig. 3 suggests that the sol fraction is less sensitive to the parameter $\gamma$ than the weight average molecular weight. Similar results are obtained with other sets of data, and will be shown in a forthcoming publication [26].

## 4. Conclusions

We have presented a mathematical model for the simultaneous crosslinking and scission of polymeric chains that takes both H and Y crosslinks into account. The starting chains may be either monodisperse or polydisperse. The model allows fitting $M_w$ data that was impossible to fit otherwise, with a level of trifunctional crosslinks comparable to that reported in the literature for PDMS systems [10]. The model is a tool that will allow the study of other irradiated systems. Coupled with a multiparameter optimization algorithm, and experimental data obtained under different conditions, it could allow to find out whether the proportions of H and Y crosslinks depend solely on the chemistry of the chains, or whether the irradiation conditions are important. Work is under way in this direction [26].

## Acknowledgements

The authors wish to thank Universidad Nacional del Sur and CONICET for financial support.

## Appendix A

### *A.1. Probability distributions that describe the polymer chains*

Let the number chain length distribution of a polymer $P_n(L=l)$ be known. The remaining distributions needed in the model may be calculated from it as follows:

$$P_m(L=l) = \frac{m_0 l P_n(L=l)}{m_0 \sum_{l=0}^{\infty} l P_n(L=l)} = \frac{l P_n(L=l)}{E_n(L)} \tag{A1}$$

The number of B-sites per chain may be 0, 1 or 2. A B-site appears on a chain end every time a scission reaction occurs. Since this reaction is postulated to take place randomly, the B-sites are randomly distributed among all chains. We assume that the B-sites follow a Binomial distribution with probability $P_n(\text{B-site})$ and two trials (one for each end). The resulting distribution is

$$P_n(F_B = f_B) = \sum_{f_B=0}^{2} \binom{2}{f_B} P_n(\text{B-site})^{f_B} \times (1 - P_n(\text{B-site}))^{2-f_B} \tag{A2}$$

The probability $P_n(\text{B-site})$ is the number probability of finding a B-site. Since they are found only at chain ends, the relevant probability is calculated as the ratio of new ends created by scission to total number of chain ends. At a degree of scission $\beta$, the total number of new chain ends that has been formed from $N_0$ starting chains is $2N_0E_m(L)\beta$, since each cut generates two B-sites. Then,

$$P_n(\text{B-site}) = \frac{2N_0E_m(L)\beta}{2N_0 + 2N_0E_m(L)\beta} = \frac{E_m(L)\beta}{1 + E_m(L)\beta} \tag{A3}$$

Now we can calculate probabilities associated with the number of B-sites per chain.

$$P_m(F_B = f_B) = \frac{l P_n(F_B = f_B)}{\sum_{f_B=0}^{2} l P_n(F_B = f_B)} = \frac{P_n(F_B = f_B)}{\sum_{f_B=0}^{2} P_n(F_B = f_B)} = P_n(F_B = f_B) \tag{A4}$$

where the last equality results from the fact that the denominator is unity.

$$P_{SB}(L=l) = \frac{f_B P_n(L=l)}{\sum_{l=0}^{\infty} f_B P_n(L=l)} = P_n(L=l) \tag{A5}$$

$$P_{SB}(F_B = f_B) = \frac{f_B P_n(F_B = f_B)}{\sum_{f_B=0}^{2} f_B P_n(F_B = f_B)} = \frac{f_B P_n(F_B = f_B)}{E_n(F_B)} \tag{A6}$$

The corresponding expectations, as defined in Eq. (1), are

$$E_m(L) = \sum_{l=0}^{\infty} l P_m(L=l) = \sum_{l=0}^{\infty} \frac{l^2 P_n(L=l)}{E_n(L)} = \frac{E_n(L^2)}{E_n(L)} \tag{A7}$$

The quantities $E_n(L^2)$ and $E_n(L)$ are easily calculated by definition for most common chain length distributions. Several examples may be found in the works of Miller and Macosko [21,22].

$$E_{SB}(F_B) = \sum_{f_B=0}^{2} \frac{f_B^2 P_n(F_B = f_B)}{E_n(F_B)} = \frac{E_n(F_B^2)}{E_n(F_B)} \tag{A8}$$

where the expectations $E_n(F_B^2)$ and $E_n(F_B)$ are calculated by definition.

As a consequence of Eqs. (A4) and (A5),

$$E_{\mathrm{m}}(F_{\mathrm{B}}) = E_{\mathrm{n}}(F_{\mathrm{B}}) \tag{A9}$$

$$E_{\mathrm{SB}}(L) = E_{\mathrm{n}}(L) \tag{A10}$$

After the scission step, at a given degree of scission $\beta$, the probabilities that describe the resulting chains may be calculated. It follows from Montroll [23] and Miller and Macosko [22] that

$$P_{\mathrm{n}}(L^{\beta} = l) = \frac{P_{\mathrm{n}}(L = l)(1-\beta)^{l-1} + \sum_{i=l+1}^{\infty} P_{\mathrm{n}}(L = i)(1-\beta)^{i-1}[2 + \beta(i - l - 1)]}{1 + \beta(E_{\mathrm{n}}(L) - 1)} \tag{A11}$$

and the corresponding expectation is [22]:

$$E_{\mathrm{n}}(L^{\beta}) = \frac{E_{\mathrm{n}}(L)}{1 + \beta(E_{\mathrm{n}}(L) - 1)} \tag{A12}$$

Similarly, Miller and Macosko [22] show that the mass expectation is

$$E_{\mathrm{m}}(L^{\beta}) = \frac{2 - \beta}{\beta} - \frac{2(1-\beta)}{\beta^2 E_{\mathrm{n}}(L)}(1 - \phi_{L,\mathrm{n}}(1-\beta)) \tag{A13}$$

where $\phi_{L,\mathrm{n}}(1-\beta)$ is the probability generating function defined in Eq. (24) for the dummy argument $1-\beta$.

Following a procedure analogous to that used in Eqs. (A5) and (A10), we may find that

$$P_{\mathrm{SB}}(L^{\beta} = l) = P_{\mathrm{n}}(L^{\beta} = l) \tag{A14}$$

$$E_{\mathrm{SB}}(L^{\beta}) = E_{\mathrm{n}}(L^{\beta}) \tag{A15}$$

## References


[1] Halley PJ, Mackay ME. Polymer 1994;35:2186–91.
[2] Sen K, Kumar P. J Appl Polym Sci 1995;55:857–63.
[3] Smirnov VV, Nevzorov VV, Kirpichenko YE. Translation from Khimiya Vysokikh Energii 1992;26:429–32.
[4] Torikai A. Ang Makromol Chem 1994;216:225–41.
[5] Lyons BJ. Radiat Phys Chem 1993;24:197–205.
[6] Andreucetti NA, Curzio OA, Vallés EM, Carella JM. Radiat Phys Chem 1988;31:663–70.
[7] David C, Baeyens-Volant D. Eur Polym J 1978;14:29–38.
[8] Jones RA, Cail JI, Stepto RFT, Ward IM. Macromolecules 2000;33:7337–44.
[9] Hill DJT, Thurecht KJ, Whittaker AK. Radiat Phys Chem 2003;67:729–36.
[10] Hill DJT, Preston CML, Salisbury DJ, Whittaker AK. Radiat Phys Chem 2001;62:11–17.
[11] Yagoubi N, Peron R, Legendre B, Grossiord JL, Ferrier D. Nucl Instrum Meth Phys Res B 1999;151:247–54.
[12] Sayyah SM, Sabbah IA, Ayoub MMH, Barsoum BN, Elwy E. Polym Degrad Stabil 1997;58:1–9.
[13] Saito O, (The radiation chemistry of macromolecules) In: Dole M, editor. vol. I. New York: Academic Press; 1972. p. 224–60. and references cited therein.
[14] Demjanenko M, Dušek K. Macromolecules 1980;13:571–9.
[15] Dušek K, Demjanenko M. Radiat Phys Chem 1986;28:479–86.
[16] Galiatsatos V, Eichinger BE. J Polym Sci B 1988;26:595–602.
[17] Shyichuk AV, Lutsjak VS. Eur Polym J 1995;31:631–4.
[18] Shyichuk AV. Eur Polym J 1998;34:113–5.
[19] Andreucetti NA, Sarmoria C, Curzio OA, Vallés EM. Radiat Phys Chem 1998;52:177–82.
[20] Andreucetti N, Fernández Lagos L, Curzio O, Sarmoria C, Vallés E. Polymer 1999;40:3443–50.
[21] Miller DR, Macosko CW. J Polym Sci B 1987;25:2441–69.
[22] Miller DR, Macosko CW. J Polym Sci B 1988;26:1–54.
[23] Montroll E. J Am Chem Soc 1941;63:1215–20.
[24] Flory PJ. Principles of polymer chemistry. Ithaca: Cornell University Press; 1953.
[25] Miller DR, Vallés EM, Macosko CW. Polym Engng Sci 1979;19:272–83.
[26] Ressia JA, Satti A, Villar MA, Vallat MF, Sarmoria C, Vallés EM. In preparation.