On Establishing Mechanisms of Radiation-Induced Network Formation in High Polymers

J. G. SPIRO and C. A. WINKLER, *Department of Chemistry, McGill University, Montreal, Canada*

Synopsis

In an effort to develop new techniques for studying the effects of irradiation on high polymers, the influence of molecular weight distribution has been investigated. From general mathematical expressions obtained by Saito, equations have been developed to be used for polymers of Schulz-Zimm distributions, and their mixtures. According to the computations, it should be possible to distinguish between crosslinking and endlinking as alternative mechanisms of network formation, by comparing gelling doses for samples of different initial distributions. From gelling dose determinations for polystyrene samples of different polydispersities, it was confirmed that network formation in irradiated polystyrene takes place through crosslinking, in agreement with mechanisms suggested by several authors. It is believed that the simple technique described should be useful for studying radiation processes in polymers that form networks, especially since the method is insensitive to the extent of degradation.

Introduction

Network formation in irradiated polymers is usually attributed to cross-linking, i.e., the formation of tetrafunctional branch units linking two chains together side by side. However, there is little direct evidence that crosslinking is, in fact, responsible for the changes observed in many irradiated polymers, and the mechanisms suggested are largely based on analogies with the vulcanization of rubber, "dimer" formation in irradiated alkanes, and other related processes. Moreover, serious objections can be raised to this mechanism for hydrocarbon polymers, on the basis of discrepancies between hydrogen evolution and crosslink formation. For example, Charlesby and Davison[1] reported that the G values for both hydrogen evolution and formation of *trans* unsaturation were practically independent of the temperature in irradiated polyethylene, while crosslink yields increased with temperature, and Turner's data indicate a similar effect with irradiated natural rubber.[2] Again, Burlant, Neerman, and Serment[3] found the value of G (crosslink) for polystyrene to be essentially independent of the temperature in the range -196 to $65°C.$, while $G(H_2)$ decreased by over 40% when the temperature was lowered over the same range. Recent investigations of Turner[4] indicate that G(crosslink) as well as $G(H_2)$ is largely independent of the temperature when polyethylene and

rubber are irradiated, and that previous data[1,2] were due to increased degradation at low temperatures. However, it is difficult to believe that the yield of main chain scissions should increase at low temperatures. Thus it is doubtful that the wide acceptance of crosslinking during irradiation of polymers is yet justified.

The most plausible alternative to crosslinking during the radiation-induced network formation in polymers would seem to be the endlinking mechanism first suggested by Charlesby.[5] In endlinking, as in degradation, the basic process is rupture of the polymer chains. Network formation is then attributed to trifunctional links formed between the broken chains and other polymer molecules through the active ends of fragments. Processes analogous to endlinking are thought to be responsible for the formation of certain hydrocarbons in the radiolysis of alkanes.

In spite of the considerable differences between crosslinking and endlinking, Charlesby[5] has shown that it is difficult to choose between the two mechanisms when polymers of initially random distribution are studied. Charlesby's results have been confirmed by the more general mathematical analyses of Saito.[6,7]

The present work is concerned mainly with polymers of nonrandom initial distribution. It will be demonstrated that differences in the effects of distribution on changes produced through the two mechanisms provide a basis for distinguishing between crosslinking and endlinking in polystyrene. It is expected that the technique used will also be applicable to a variety of other polymers.

Theoretical

The ingenious mathematical techniques of Saito[6,7] have opened up new methods for studying irradiated polymers. Kotliar and Anderson[8] demonstrated the advantages of using the Schulz-Zimm distribution function in Saito's treatment, but they have not treated the problem of endlinking. Therefore, in the present study of the differences between crosslinking and endlinking, new formulae were developed on the basis of Saito's analyses.

In actual computations, the emphasis was placed on quantities that can be determined experimentally with comparative ease: the critical or gelling dose, the number-average molecular weight, and the weight-average molecular weight. The investigations were limited to the effect of doses not exceeding the gelling dose, since it is doubtful that cyclization may be neglected after the gel point,[7] and the mathematical difficulties become considerable.

The role of the initial distribution is not pronounced in crosslinking without degradation, and simple formulae have been developed which are valid for arbitrary initial distribution.[9] Hence, the following paragraphs deal only with endlinking and crosslinking with degradation.

Many of Saito's results, valid for any distribution, involve the quantity here denoted by $u_2'(\tau)$, the weight-average degree of polymerization after τ main chain scissions per monomer unit. The importance of the quantity

$u_2'(\tau)$ is a consequence of the generally employed mathematical approach, whereby linking and degradation are considered independent of each other, and are treated as if they occurred consecutively, rather than simultaneously. To study the effect of molecular weight distribution, a simplified expression was developed for $u_2'(\tau)$, to be used with distributions of the Schulz-Zimm type and their superpositions.

A normalized form of the Schulz function is

$$n(u) = [A_0/\Gamma(\lambda)](\lambda/u_1)^\lambda u^{\lambda-1} \exp \{-\lambda u/u_1\} \qquad (1)$$

where $n(u)$ is the number of molecules of degree of polymerization u, A_0 is the total number of molecules, λ is a positive parameter, giving the sharpness of the distribution, and u_1 is the number-average degree of polymerization. It will be noted that the commonly employed random, or exponential, or most probable distribution can be considered as merely a special case of the Schulz-Zimm distributions, corresponding to $\lambda = 1$.

The parameter λ is related to the number-average and weight-average molecular weights by the formula

$$\lambda = \bar{M}_n/(\bar{M}_w - \bar{M}_n) \qquad (2)$$

Therefore the parameters of the Schulz function for a given polymer sample can be readily computed from experimental data. In actual calculations it is often convenient to consider only integral values of λ. This is no serious restriction for narrow distribution samples and their mixtures, because the possible error introduced by rounding off λ will be less than the experimental error associated with the determination of molecular weights.

For mixtures, eq. (1) can be immediately extended to

$$n(u) = \sum_i [A_{0i}/\Gamma(\lambda_i)](\lambda_i/u_{1i})^{\lambda_i} u^{\lambda_i-1} \exp \{-\lambda_i u/u_{1i}\} \qquad (3)$$

which represents a sum of generalized exponential distributions. The subscript i refers to the ith component of a given mixture.

For polymer samples of distributions given by eq. (3), $u_2'(\tau)$ may be computed from a simplified expression derived by Saito[6]

$$u_2'(\tau) = (2/\tau) - (2/N\tau^2) \int_0^\infty n(u)(1-e^{-u\tau})du \qquad (4)$$

where N is the total number of monomer units in the sample. The combination of eqs. (3) and (4) leads to the expression

$$u_2'(\tau) = \frac{2}{\tau} - \frac{2}{\tau^2} \left\{ \frac{\sum_i A_{0i} \left[1 - \left(\dfrac{\lambda_i}{\lambda_i + u_{1i}\tau}\right)^{\lambda_i} \right]}{\sum_i A_{0i} u_{1i}} \right\} \qquad (5)$$

By using eq. (5), it was possible to simplify some of the formulae of Kotliar and Anderson,[8] and their computations were readily extended to endlinking.

TABLE I

Results of Gelling Dose Calculations for Schulz-Zimm Distributions

λ	Crosslinking (number of crosslinked units per primary weight-average molecule at gel point for various β/α)								Endlinking (number of trifunctional branch units per primary weight-average molecule at gel point for various $\bar{\sigma}$)							
	$\beta/\alpha =$ 0.10	$\beta/\alpha =$ 0.20	$\beta/\alpha =$ 0.30	$\beta/\alpha =$ 0.40	$\beta/\alpha =$ 0.50	$\beta/\alpha =$ 0.75	$\beta/\alpha =$ 1.00	$\beta/\alpha =$ 1.75	$\bar{\sigma} =$ 0.0	$\bar{\sigma} =$ 0.1	$\bar{\sigma} =$ 0.2	$\bar{\sigma} =$ 0.3	$\bar{\sigma} =$ 0.4	$\bar{\sigma} =$ 0.5	$\bar{\sigma} =$ 0.6	$\bar{\sigma} =$ 0.7
1	1.053	1.111	1.176	1.250	1.333	1.600	2.000	8.003	1.333	1.385	1.455	1.556	1.714	2.000	2.667	6.000
2	1.047	1.098	1.155	1.219	1.292	1.519	1.854	6.565	1.067	1.108	1.162	1.241	1.365	1.587	2.101	4.637
3	1.044	1.092	1.145	1.204	1.271	1.480	1.785	5.968	0.974	1.011	1.061	1.132	1.244	1.445	1.906	4.162
4	1.042	1.088	1.139	1.196	1.259	1.457	1.745	5.643	0.927	0.962	1.009	1.077	1.183	1.372	1.807	3.919
5	1.041	1.085	1.135	1.190	1.251	1.442	1.719	5.440	0.898	0.932	0.977	1.043	1.146	1.328	1.746	3.772
7	1.039	1.082	1.130	1.182	1.241	1.424	1.687	5.200	0.865	0.897	0.941	1.004	1.103	1.277	1.677	3.601
10	1.038	1.080	1.125	1.176	1.233	1.409	1.661	5.016	0.839	0.871	0.913	0.975	1.070	1.239	1.624	3.472
15	1.037	1.077	1.122	1.171	1.226	1.396	1.640	4.870	0.820	0.850	0.892	0.952	1.044	1.209	1.583	3.371
20	1.036	1.076	1.120	1.169	1.223	1.390	1.628	4.796	0.810	0.840	0.881	0.940	1.032	1.194	1.562	3.320

From the point of view of distinguishing between crosslinking and end-linking, the most interesting results were obtained when gelling doses were calculated for different mechanisms, distributions, and extents of degradation. These computations were based on Saito's formulae,[6,7] from which the gelling doses are given by the roots of the equations

$$1 - \frac{\tau}{\beta/\alpha} u_2'(\tau) = 0 \tag{6}$$

and

$$[1 + (2\bar{\sigma} - 1)u_1\tau]^2 - 2(1 - \bar{\sigma})^2 u_1 \tau^2 (1 + u_1\tau)u_2'(\tau) = 0 \tag{7}$$

In eq. (6), the extent of degradation is expressed as the number of scissions per crosslinked unit (β/α), while for endlinking [eq. (7)], it is given as the fraction $\bar{\sigma}$ of ends produced by scissions that do not form new links. In eq. (7), u_1 is the initial number-average degree of polymerization.

Computations were performed on high speed digital computers of the McGill University Computing Center. Typical results are given in Table I, in terms of the number of crosslinked units or trifunctional branch units per primary weight-average molecule. Both quantities are directly proportional to the radiation dose, which in the present instance is the gelling dose.

It is evident from the data of Table I that while the critical dose in crosslinking is more or less independent of the initial distribution, in endlinking the gelling dose for narrow distribution samples should be considerably lower than for more polydisperse samples of the same weight average-molecular weight. Moreover, except for very pronounced degradation (approaching the degree where gel formation is no longer possible), the above effect is essentially independent of the proportion of scissions and linkages. Thus, it appears that by comparing samples of a given polymer differing in polydispersity, it should be comparatively easy to decide whether endlinking has a significant role in the radiation-induced changes. As will be illustrated later, this technique is also readily applicable when samples of narrow molecular weight distribution are mixed.

It should perhaps be emphasized that the theoretical basis of the above method for distinguishing between crosslinking and endlinking is general, and does not depend on specific reactions involved. Therefore, application of this technique should lead to reliable conclusions for a variety of polymers. In particular, it should be applicable to a study of endlinking in polymers such as irradiated poly(vinyl alcohol), where this mechanism has been suggested to occur in aqueous solution.[10]

Application to Polystyrene

The radiation chemistry of polystyrene is of considerable interest. The extremely high resistance of this polymer to radiation effects apparently cannot be explained merely on the basis of the protective action of benzene

TABLE II
Number-Average and Weight-Average Molecular Weights of Anionic Polystyrene Samples

Sample	$\bar{M}_n$	$\bar{M}_w$
S102	78,500	82,500
S105	147,500	153,500
S108	247,000	267,000

rings,[11] and there is considerable evidence[3,12] that the hydrogen yields are lower than they should be for the "usual" crosslinking processes. As mentioned previously, temperature effects are also difficult to explain in terms of simple crosslinking. From the point of view of the suggested technique for establishing the mechanism, this polymer has the advantage that samples of narrow and consequently well defined distribution can be obtained by anionic polymerization.[13] Accordingly, it was decided to apply to polystyrene the previously outlined technique.

The narrow range polymers used in this work were generously donated by Dr. H. W. McCormick of the Dow Chemical Company, and had the molecular weights listed in Table II. Samples for irradiation were prepared by dissolving suitable amounts of polystyrene in benzene, and recovering the polymer by freeze-drying.

As a result of preliminary computations, the following two samples were used in the experimental study: (1) pure S105, designated sample I; (2) A mixture of S102 and S108 in the molar ratio 4:1, designated sample II ($\bar{M}_n = 112,200$, $\bar{M}_w = 164,000$). Ratios of the gelling doses predicted for each mechanism and different degrees of degradation are given in Table III. The expected value of R_g^{II}/R_g^{I} for endlinking exceeds the ratio anticipated for a crosslinking mechanism by nearly 30%, and therefore it is apparent that no very great accuracy was required to choose between the two mechanisms.

To determine the gelling doses, S105 and S102/S108 samples were irradiated by γ-rays from a Co[60] source, and the relative viscosities of their solutions in toluene were measured at 25°C. at a concentration of 0.6 g./100 ml. A Craig and Henderson suspended-level viscometer was used. The critical doses were determined by extrapolating the viscosity–dose curves to "infinite" viscosity, as shown in Figure 1. It is very likely that systematic errors involved in such procedures cancel out when the ratio of gelling doses is calculated, thereby increasing the accuracy of the technique.

From osmotic measurements the extent of degradation, assuming a crosslinking mechanism, was found to be $\beta/\alpha = 0.14$. The theoretical value of R_g^{II}/R_g^{I} corresponding to $\beta/\alpha = 0.14$ is 0.96, while the experimental value from Figure 1 is $R_g^{II}/R_g^{I} = 0.95$. This result confirms that crosslinking is the predominant mechanism in the irradiation of polystyrene, and thereby supports previous hypotheses.

TABLE III
Results of Gelling Dose Calculations for Samples S105 and S102/S108

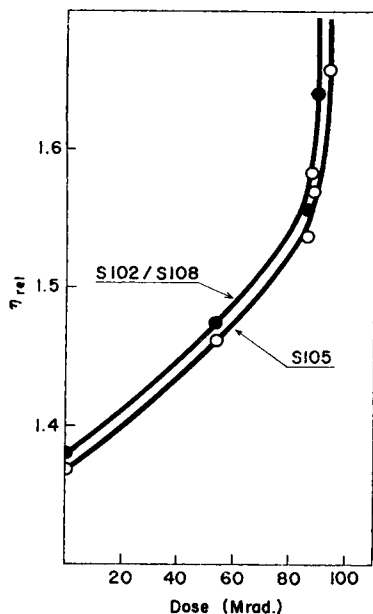|	Crosslinking (number of crosslinked units per primary weight-average molecule at gel point for various β/α)					Endlinking (number of trifunctional branch units per primary weight-average molecule at gel point for various $\bar{\sigma}$)					
	$\beta/\alpha = 0.0$	$\beta/\alpha = 0.14$	$\beta/\alpha = 0.20$	$\beta/\alpha = 0.25$	$\beta/\alpha = 0.33$	$\bar{\sigma} = 0.0$	$\bar{\sigma} = 0.1$	$\bar{\sigma} = 0.2$	$\bar{\sigma} = 0.3$	$\bar{\sigma} = 0.4$	$\bar{\sigma} = 0.5$
Sample I	1.00	1.05	1.07	1.09	1.13	0.80	0.83	0.87	0.93	1.02	1.18
Sample II	1.00	1.07	1.10	1.13	1.18	1.05	1.09	1.14	1.22	1.35	1.57
R_g^{II}/R_g^{I}	0.94	0.96	0.96	0.97	0.98	1.22	1.23	1.23	1.23	1.23	1.24

Fig. 1. Determination of the gelling dose for samples S105 and S102/S108: (O) experimental points for S105; (●) for S102/S108.

Although the excellent agreement between theory and experiment with polystyrene might be fortuitous, there is every reason to believe that the technique should be suitable for distinguishing between crosslinking and endlinking as basic mechanisms of network formation. It is more difficult to predict the effect of initial distribution when both crosslinking and endlinking are involved. However, the data of Table I indicate that the differences between the two mechanisms are so pronounced that it should be possible to detect processes where one of the mechanisms is responsible for only a fraction of the total effect. The insensitivity of the suggested technique to degradation should be of particular advantage in studies of the latter type.

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Résumé

En vue du développement de nouvelles techniques, pour étudier les effets des irradiations sur les hauts polymères, on a étudié l'influence de la distribution des poids moléculaires. Au départ des expressions mathématiques générales obtenues par Saito, on a adopté des équations applicables aux polymères répondant aux distributions Schultz-Zimm ainsi que leurs mélanges. En concordance avec ces calculs, il est possible de distinguer entre le pontage et le lien final comme étant des mécanismes alternatifs de la formation de réseau, en comparant les doses de gélification pour des échantillons de distributions initiales différentes. Au départ de déterminations des doses de gélification pour des échantillons de polystyrène de différentes polydispersités, on a confirmé que la formation d'un réseau lors de l'irradiation du polystyrène se fait par pontage, en accord avec les mécanismes suggérés par différents auteurs. Il est à croire que cette technique simple décrite sera utilisable pour l'étude des processus d'irradiation de polymères formant des réseaux, spécialement puisque cette méthode est insensible à l'étendue de la dégradation.

Zusammenfassung

Im Rahmen der Entwicklung neuer Methoden zur Untersuchung der Wirkungen von Strahlung auf Hochpolymere wurde der Einfluss der Molekulargewichtsverteilung untersucht. Aus allgemeinen, von Saito entwickelten mathematischen Ausdrücken wurden Gleichungen für die Anwendung auf Polymere mit Schulz-Zimm-Verteilung und deren Mischungen hergeleitet. Gemäss den Berechnungen sollte durch Vergleich der Gelbildungsdosis von Proben mit verschiedener anfänglicher Verteilung eine Unterscheidung zwischen den beiden möglichen Mechanismen der Netzwerkbildung, nämlich Vernetzung und End-zu-Endverknüpfung, möglich sein. Auf Grund der Bestimmung der Gelbildungsdosis von Polystyrolproben verschiedener Polydispersität wurde festgestellt, dass die Netzwerkbildung in bestrahltem Polystyrol durch Vernetzung stattfindet. Dies steht mit dem von einigen Autoren vorgeschlagenen Mechanismus im Einklang. Die beschriebene einfache Methode dürfte für die Untersuchung von Strahlungsprozessen in zur Netzwerkbildung fähigen Polymeren nützlich sein, besonders weil diese Methode unempfindlich gegenüber dem Ausmass des Abbaues ist.