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Fast Neutron Irradiation Effects on Polymers. 2. Cross-Linking and Degradation of Polystyrene

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ABSTRACT: Irradiation effects of fast neutrons on polystyrene were compared with those of ^{60}Co γ-rays from the viewpoint of linear energy transfer (LET). For in vacuo irradiations, the G values of cross-links and main-chain scissions, $G(\mathrm{X})$ and $G(\mathrm{S})$, are 0.036 and 0.022, respectively, for γ-rays of low LET (ca. 0.02 eV/Å). Fast neutrons of high LET (ca. 3.7 eV/Å) increase not only the $G(\mathrm{X})$ value to 0.14–0.26, depending on the initial molecular weight of polystyrene, but also the $G(\mathrm{S})$ value to 0.22. For in air irradiations, oxygen increases the $G(\mathrm{S})$ value by a factor of about 7 without affecting the $G(\mathrm{X})$ value appreciably for γ-rays, whereas for fast neutrons oxygen decreases both the $G(\mathrm{X})$ and $G(\mathrm{S})$ values to about $^1/_3$ and $^1/_2$ those obtained in vacuo, respectively. As to the change in the molecular weight distribution by irradiation, the M_z/M_w ratio of polystyrene irradiated with fast neutrons in vacuo increases much more rapidly than that with γ-rays as the number of cross-linked units increases, suggesting the nonrandom cross-linking at high LET. All of these findings are explained qualitatively by a difference in the spatial distribution of microscopic energy deposition and the resulting reactive species between fast neutrons and γ-rays. The computer simulation shows that nonrandom cross-linking actually takes place at high LET, and it is caused by the microscopic inhomogeneity of energy deposition.

In a previous paper,[2] we reported the study on the fast-neutron irradiation effects of poly(methyl methacrylate) (PMMA). The study demonstrated that the G value of main-chain scissions due to fast neutrons is different from that due to ^{60}Co γ-rays because of a difference in linear energy transfer (LET), and furthermore the degradation does not take place at random especially for fast-neutron irradiation due to the increased inhomogeneity of energy deposition on a microscopic scale.

These LET effects may be observed more clearly for cross-linking polymers than for predominantly degrading polymers such as PMMA, since the difference in LET will have a more striking influence on the bimolecular reaction of cross-linking rather than on the essentially unimolecular reaction of degradation. From these points of view, we studied the fast-neutron and ^{60}Co γ-ray irradiation effects on polystyrene concerning the G values of cross-links and main-chain scissions and the change in the molecular weight distribution and were able to find clearly the LET effects caused by the two types of radiation.[3] The present paper mainly describes the LET effects and the interpretation made on the same basis as previously mentioned for the degradation of PMMA.[2]

Experimental Section

Two samples of monodisperse polystyrene powder with molecular weights of 1.1×10^5 and 3.9×10^5 (Pressure Chemical Co.) were used without further purification, and the irradiation procedure was the same as that previously described.[2] The fast-neutron reactor used here and the procedure of the in-reactor dosimetry were the same as those described in previous papers.[2,4] The ^{60}Co γ-ray irradiations were made at room temperature at a dose rate of about 0.6 Mrad/h. For in-reactor irradiations, the sample temperature was kept below 33 °C during irradiation, and the dose rates due to fast neutrons and the concomitant γ-rays were 1.30 (86%) and 0.22 Mrad/h (14%), respectively.

Measurements of molecular weight distribution were carried out with the same gel-permeation chromatography (GPC) apparatus and procedures as previously described.[2] The solid curve in Figure 1 shows the GPC calibration curve obtained from eight standard samples of monodisperse linear polystyrene (Pressure Chemical Co.). The GPC calibration curve for cross-linked polystyrene was calculated according to the method described by Drott and Mendelson[5] for branched polymers. The calculation was made by assuming that the number of branch points per molecule is equal to that of cross-link points per molecule and that the number of macromolecules subjected to both cross-linking and main-chain scission is negligibly small at low absorbed doses in the pre-gel region. Then the number of branch points per molecule was estimated simply by dividing the molecular weight of cross-linked polystyrene by the initial molecular weight and subtracting 1 from the quotient. The GPC calibration curves thus determined for cross-linked polystyrene whose initial molecular weight is 1.1×10^5 and 3.9×10^5 are shown in Figure 1 by the broken and dash-dot curves, respectively. Using these calibration curves, we calculated the molecular weight distribution and the number-, weight-, and z-average molecular weights, M_n, M_w, and M_z, from the GPC chromatogram.

Results

1. *G* Values of Cross-Links and Main-Chain Scissions. Typical examples of the molecular weight distributions obtained after irradiation with ^{60}Co γ-rays and fast neutrons are shown in Figure 2a,b, respectively, by the solid (in vacuo) and dash-dot curves (in air) together with that before irradiation (broken curve) for the polystyrene sample with an initial molecular weight of 3.9×10^5 ($M_w/M_n = 1.10$). It is seen from Figure 2a that cross-linking predominates over degradation for polystyrene irradiated with γ-rays in vacuo, whereas in air the predominance is reversed. In fact, gelation took place at about 47 Mrad in vacuo, but in air it was not observed even at 120 Mrad. For fast-neutron irradiations, on the other hand, cross-linking predominates in both cases as seen from Figure 2b, and gelation was actually observed both in vacuo (at about 21 Mrad) and in air (at about 35 Mrad). The results obtained from the polystyrene sample with an initial molecular weight of 1.1×10^5 ($M_w/M_n = 1.06$) were essentially the same as those described above.

When the molecular weight distribution before irradiation is adequately approximated by the Schultz–Zimm distribution,[6,7] the G values of cross-links and main-chain scissions, $G(\mathrm{X})$ and $G(\mathrm{S})$, can be determined at the same time by solving the following two simultaneous equations which were derived by Saito[8] on the assumption that cross-linking and main-chain scission take place at random

$$\frac{M_n^{\,0}}{M_n} = 1 + u\tau - u\chi \tag{1}$$

$$\frac{M_n^{\,0}}{M_w} = (u\tau)^2/2[u\tau - 1 + (1 + u\tau/b)^{-b}] - 2u\chi \tag{2}$$

where $u\chi$ and $u\tau$

$$u\chi = \frac{M_n{}^0}{0.965 \times 10^6} G(\mathrm{X})D \tag{3}$$

$$u\tau = \frac{M_n{}^0}{0.965 \times 10^6} G(\mathrm{S})D \tag{4}$$

are parameters standing for the numbers of cross-linked units and main-chain scissions per initial number-average molecule, respectively, $M_n{}^0$ is the number-average molecular weight before irradiation, u is the degree of polymerization of $M_n{}^0$, b is a parameter indicating the narrowness of the Schultz–Zimm distribution breadth, and D is the absorbed dose in Mrad.

Simultaneous eq 1 and 2 in $u\chi$ and $u\tau$ were solved by using a computer for each irradiated sample whose M_n and M_w values were available from the GPC chromatogram. The $u\chi$ and $u\tau$ values thus determined were first converted to the values corresponding to $G(\mathrm{X})D$ and $G(\mathrm{S})D$ by using eq 3 and 4, respectively, and then the $G(\mathrm{X})D$ and $G(\mathrm{S})D$ values were plotted as a function of D. As to samples irradiated in the reactor, the $G(\mathrm{X})D$ and $G(\mathrm{S})D$ values corrected for the concomitant γ-ray contributions were plotted as a function of the absorbed dose due to fast neutrons, D_n. This correction was made by subtracting the γ-ray contributions, $G_\gamma(\mathrm{X})D_\gamma$ and $G_\gamma(\mathrm{S})D_\gamma$, using the $G_\gamma(\mathrm{X})$ and $G_\gamma(\mathrm{S})$ values determined here for ^{60}Co γ-ray irradiation and the D_γ value measured by the in-reactor dosimetry.[4] Examples of the plots obtained in this way are shown in Figure 3a,b for polystyrene ($M_n{}^0 = 3.9 \times 10^5$) irradiated in air with ^{60}Co γ-rays and fast neutrons, respectively. The slopes of these linear plots and the least-squares method give the $G(\mathrm{X})$ and $G(\mathrm{S})$ values and their 95% confidence limits, which are collected in Table I together with the values of $2G(\mathrm{X}) + G(\mathrm{S})$ and $G(\mathrm{S})/G(\mathrm{X})$. The value of $2G(\mathrm{X}) + G(\mathrm{S})$ corresponds to the G value of the polymeric intermediates which either form intermolecular cross-links by the combination or dissociate spontaneously into two macromolecules.

2. Change in Molecular Weight Distribution. The change in the molecular weight distribution by irradiation can be followed by plotting the ratios of M_w/M_n and M_z/M_w as a function of $u\chi$, i.e., the number of cross-linked units per initial number-average molecule. The plots obtained for the polystyrene sample with an initial molecular weight of 3.9×10^5 are shown in Figure 4. The plots for in air irradiation (Figure 4b) demonstrate that both the M_w/M_n and M_z/M_w ratios increase with $u\chi$ more rapidly for fast neutrons than for γ-rays, and that these ratios for γ-rays appear to level off at $u\chi$ values of 1.0 or above. This finding corresponds to the fact that gelation does not take place in polystyrene irradiated in air with γ-rays but does take place even in air with fast neutrons. On the other hand, the plots for in vacuo irradiation (Figure 4a) indicate that the M_z/M_w ratio increases with $u\chi$ much more rapidly for fast neutrons than for γ-rays, although the M_w/M_n ratio increases similarly for both types of radiation.

These characteristics of the M_w/M_n and M_z/M_w changes with $u\chi$ were essentially the same for the polystyrene sample with an initial molecular weight of 1.1×10^5.

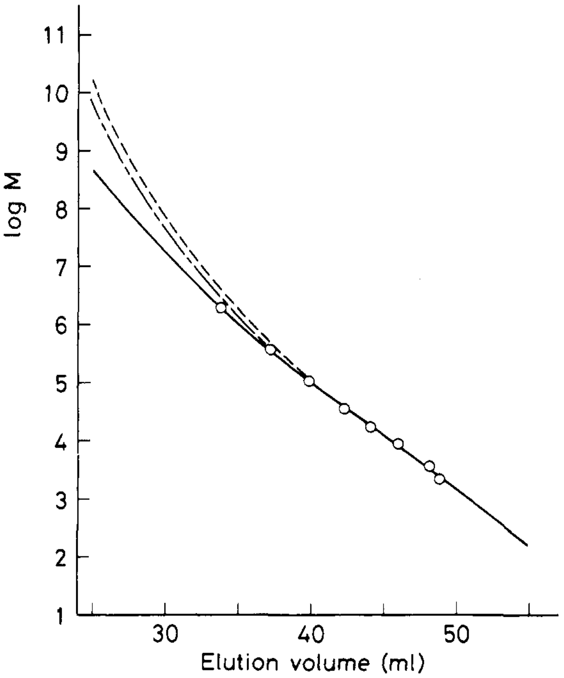

Figure 1. GPC calibration curves of the elution volume vs. the molecular weight for linear polystyrene (solid curve) and for branched polystyrene which is produced by cross-linking of monodisperse polystyrene with an initial molecular weight of 1.1×10^5 (broken curve) or 3.9×10^5 (dash-dot curve).

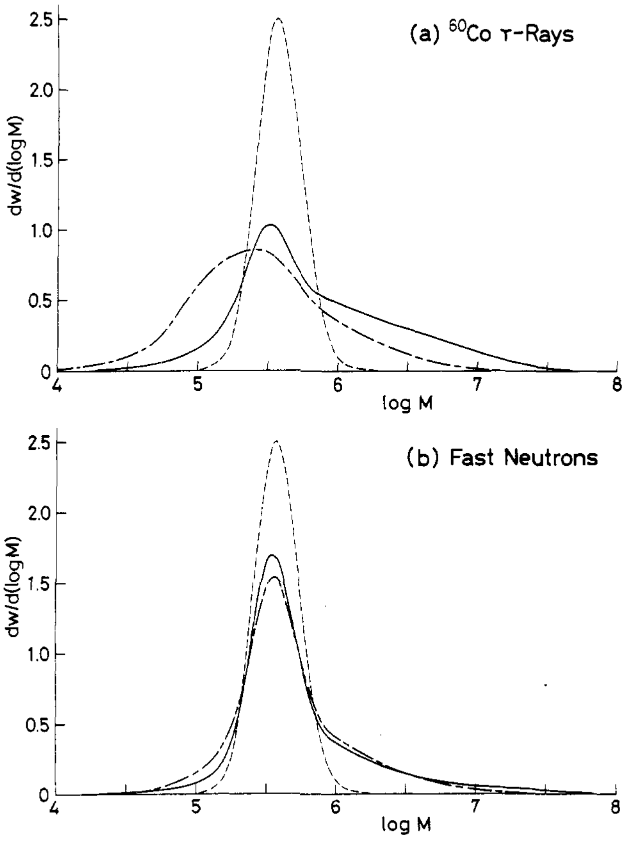

Figure 2. Molecular weight distributions of polystyrene before (broken curve) and after irradiations in a ^{60}Co γ-ray source (a) and in the fast-neutron reactor (b) in vacuo (solid curve) and in air (dash-dot curve). Absorbed doses (Mrad) are as follows: 25.8 (in vacuo) and 38.9 (in air) for (a); 6.3 (in vacuo) and 12.5 (in air) for (b).

Discussion

1. Accuracy of $G(\mathrm{X})$ and $G(\mathrm{S})$. Our $G(\mathrm{X})$ and $G(\mathrm{S})$ values in Table I were evaluated from eq 1 and 2 which have been derived by assuming that cross-linking and main-chain scission take place at random.[8] However, our previous work on the degradation of PMMA[2] demonstrated that the main-chain scission does not take place at random for fast-neutron irradiation because of the microscopic inhomogeneity of energy deposition, and that the inhomogeneity makes the M_w value somewhat higher than that predicted by the random degradation theory. For the exact evaluation of $G(\mathrm{X})$ and $G(\mathrm{S})$, therefore, eq

Table I
G Values of Cross-Links and Main-Chain Scissions of Polystyrene for ^{60}Co γ-Rays and Fast Neutrons

		in vacuo		in air	
	initial mol wt	γ-rays	neutrons	γ-rays	neutrons
$G(X)$	1.1×10^5	0.036 ± 0.001	0.264 ± 0.079	0.031 ± 0.006	0.085 ± 0.019
	3.9×10^5	0.033 ± 0.007	0.142 ± 0.040	0.034 ± 0.004	0.055 ± 0.009
$G(S)$	1.1×10^5	0.019 ± 0.007	0.209 ± 0.093	0.150 ± 0.051	0.089 ± 0.020
	3.9×10^5	0.030 ± 0.021	0.225 ± 0.057	0.143 ± 0.020	0.111 ± 0.026
$2G(X) + G(S)$	1.1×10^5	0.091 ± 0.009	0.737 ± 0.251	0.212 ± 0.063	0.259 ± 0.058
	3.9×10^5	0.096 ± 0.035	0.509 ± 0.137	0.211 ± 0.028	0.221 ± 0.044
$G(S)/G(X)$	1.1×10^5	0.54	0.79	4.93	1.05
	3.9×10^5	0.92	1.59	4.17	2.04

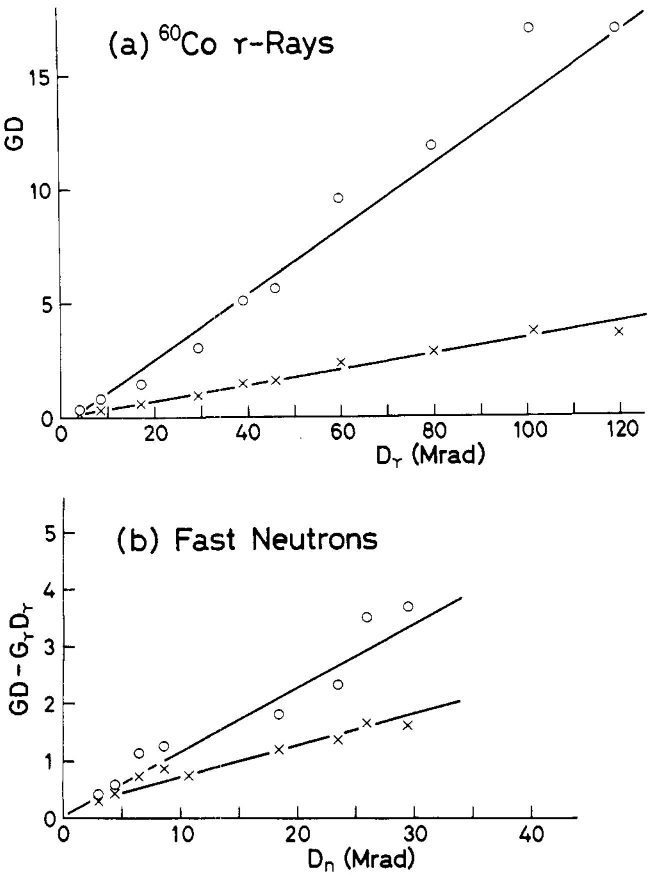

Figure 3. Plot of the number of cross-links (×) or main-chain scissions (○) vs. the absorbed dose D_γ due to ^{60}Co γ-rays (a) and D_n due to fast neutrons (b) for polystyrene with an initial molecular weight of 3.9×10^5 irradiated in air. For (b), corrections are made for the concomitant γ-rays by the term $G_\gamma D_\gamma$ (see text).

2 which expresses the M_w change must be modified to hold even for nonrandom cross-linking and degradation by introducing a parameter expressing the degree of the microscopic inhomogeneity of energy deposition, i.e., $\Delta D/x$ in our previous paper.[2] Even if the modified equation should be obtained, however, the additional parameter of $\Delta D/x$ will make it too complex to be used for the evaluation of G values. For this reason, we used eq 2 without modification as an approximation in the evaluation of the $G(X)$ and $G(S)$ values.

Our $G(X)$ values for γ irradiation in vacuo are within the variation in the reported values of 0.019–0.051.[9-17] However, our $G(X)$ values for fast-neutron irradiation in vacuo are slightly higher than the reported value of 0.096.[12] Our $G(S)$ values, on the other hand, are considerably higher compared with the reported values of 0.00086 and 0.022 for in vacuo and in air γ irradiation,[16,18] respectively, and are so compared with the reported value of 0.027 for fast neutrons in vacuo.[12] Nevertheless, $G(S)$ values similar to ours, 0.019[14] and 0.010–0.051,[17] are also reported for γ irradiation in vacuo. The wide variation in the $G(X)$ and $G(S)$ values among workers seems to arise mainly from differences in the sample preparation, the irradiation conditions, and the method used to evaluate the G values. In this connection, it should be noted that the $G(S)/G(X)$ ratios in Table I are smaller than 4 for all cases except for the in air γ irradiation which produces no observable gel in the present work. This result is consistent with Saito's theoretical finding that the gel formation occurs only when

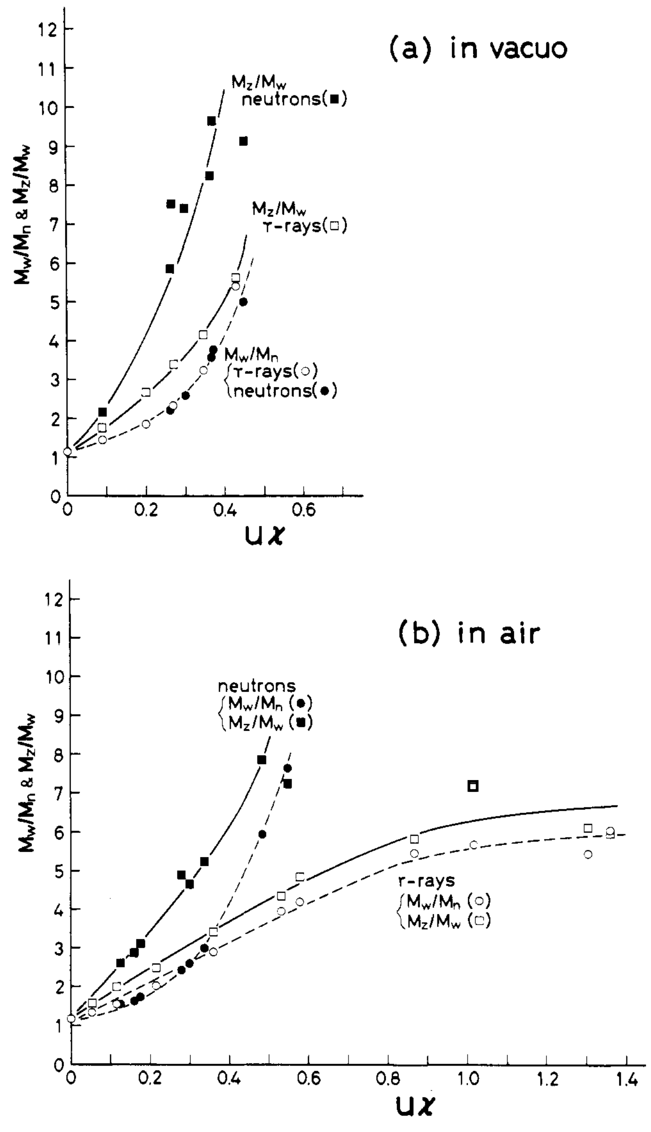

Figure 4. Plot of the M_w/M_n (○, ●) and M_z/M_w (□, ■) ratios for in vacuo (a) and in air irradiations (b) with ^{60}Co γ-rays (open points) and fast neutrons (solid points) as a function of the number of cross-linked units per initial number-average molecule, $u\chi$, for polystyrene with an initial molecular weight of 3.9×10^5.

the $G(\mathrm{S})/G(\mathrm{X})$ ratio is smaller than 4,[8] indicating that our method to evaluate the $G(\mathrm{X})$ and $G(\mathrm{S})$ values is not erroneous. In addition, the G values in Table I were obtained by using the same polystyrene sample and similar irradiation conditions between fast neutrons and γ-rays. Therefore, it is reasonable to discuss the effects of LET and oxygen on $G(\mathrm{X})$ and $G(\mathrm{S})$, using the G values obtained in the present work.

2. LET Dependence of $G(\mathrm{X})$ and $G(\mathrm{S})$. The ^{60}Co γ-rays and fast neutrons incident upon polystyrene produce secondary electrons and recoil protons whose over-all LET is estimated to be ca. 0.02 and ca. 3.7 eV/Å, respectively.[2] The increase in LET enhances the value of $2G(\mathrm{X}) + G(\mathrm{S})$ by a factor of 5.3–8.1 for in vacuo irradiation, as seen from Table I. If both cross-links and main-chain scissions result from macroradicals, this finding means that the number of macroradicals produced by the same amount of energy deposition is much larger for fast-neutron than for γ-ray irradiation. The higher yield of macroradicals for fast neutrons can be explained qualitatively by the same mechanism as Burns and Jones used to account for the LET effect in aromatic substances such as benzene, biphenyl, and orthoterphenyl.[19] They found that the G values of hydrogen formation and decomposition of these molecules increase with LET and interpreted the LET effect by the mechanism involving the competition between the deactivation of an excited molecule M* by the collision with a ground state molecule M (eq 5) and the

$$\mathrm{M}^* + \mathrm{M} \rightarrow 2\mathrm{M} \qquad (5)$$

$$\mathrm{M}^* + \mathrm{M}^* \rightarrow \text{radicals} \qquad (6)$$

radical formation by the bimolecular reaction of the excited molecules (eq 6). This mechanism will apply for the γ-ray and fast-neutron irradiations of polystyrene also. In this case, it is a monomer unit of the polymer that acts as M or M*, and the resulting radicals will be mainly hydrogen atoms and the side-group macroradicals. The excited monomer units of polystyrene will be produced more closely to one another for fast-neutron than for γ-ray irradiation, since the microscopic energy deposition of high LET radiation is more inhomogeneous compared with that of low LET ones.[20,21] Therefore, the higher yield of macroradicals for fast neutrons should be attributed to the bimolecular reaction of the excited monomer units (eq 6) at the expense of the competing unimolecular reaction (eq 5).

The results of in vacuo irradiations listed in Table I demonstrate that the increase in LET enhances the $G(\mathrm{X})$ and $G(\mathrm{S})$ values at the same time by factors of 4.3–7.3 and 7.5–11, respectively. If cross-link formation and main-chain scission of polystyrene proceed by the combination and dissociation[11] of the side-group macroradicals, respectively, and furthermore if these two types of reaction are simply competitive, then the $G(\mathrm{S})/G(\mathrm{X})$ ratio is expected to be decreased by high LET radiations which favor the bimolecular reaction of macroradicals resulting in increased $G(\mathrm{X})$ and decreased $G(\mathrm{S})$ values. However, this expectation is incompatible with our result that the $G(\mathrm{S})/G(\mathrm{X})$ ratio for in vacuo irradiation with fast neutrons is slightly higher than that with γ-rays, as shown in Table I. This unexpected result can be explained by considering two types of cross-linking, viz., intermolecular cross-linking between two macromolecules and intramolecular cross-linking between two monomer units of the same macromolecule. Only the former is responsible for the observable change in the M_n and M_w values, and consequently our $G(\mathrm{X})$ values are merely for this type of cross-linking. If therefore the intramolecular cross-linking is favored at high LET, the G value of the competing intermolecular cross-linking, $G(\mathrm{X})$, may be decreased so as to result in a higher ratio of $G(\mathrm{S})/G(\mathrm{X})$ for fast-neutron than for γ-ray irradiation.

This idea may be reasonably accepted by taking into consideration the fact that the probability of simultaneous ionization and/or excitation of several segments in the same polymer chain is increased by high LET radiations.[22] Furthermore, the evidence supporting the idea was actually obtained in the present work. The results of in vacuo irradiations in Table I show that the $G(\mathrm{X})$ value for fast neutrons decreases from 0.264 to 0.142 with an increase in the initial molecular weight of polystyrene from 1.1×10^5 to 3.9×10^5, while the $G(\mathrm{X})$ value for γ-rays decreases only slightly from 0.036 to 0.033. The $G(\mathrm{X})$ dependence on the initial molecular weight has already been reported by Charlesby[15] for monodisperse polystyrene samples irradiated with ^{60}Co γ-rays in vacuo. He derived the following semiempirical relationship between $G(\mathrm{X})$ and the initial number-average molecular weight $M_n{}^0$ by taking into consideration the increasing contribution of intramolecular cross-linking with the increasing molecular size of polymers.

$$G(\mathrm{X}) = 0.047/(1 + 6.4 \times 10^{-4}(M_n{}^0)^{1/2}) \qquad (7)^{23}$$

The $G(\mathrm{X})$ values calculated from this equation for $M_n{}^0 = 1.1 \times 10^5$ and 3.9×10^5 are 0.039 and 0.034, respectively, which are in fair agreement with those obtained by γ irradiation in the present work. If the contribution ratio of intermolecular to intramolecular cross-linking is independent of LET, the rate of decrease in $G(\mathrm{X})$ when $M_n{}^0$ is increased from 1.1×10^5 to 3.9×10^5 will be the same between the γ-ray and fast-neutron irradiations. However, the rate of decrease observed here is considerably higher for fast neutrons (46%) than for γ-rays (6%). This finding can be taken as the evidence indicating that the intramolecular cross-linking is favored at high LET since the decrease in $G(\mathrm{X})$ is just equal to the increase in the G value of intramolecular cross-linking. Accordingly, the higher ratio of $G(\mathrm{S})/G(\mathrm{X})$ for fast neutrons than for γ-rays is most likely ascribed mainly to the intramolecular cross-linking which is enhanced by high LET radiations at the expense of the competing intermolecular cross-linking.

Several authors[24] have suggested that high LET radiations will produce localized regions of high temperatures (thermal spikes) along the tracks, and the temperature in the spikes will get temporarily much higher than the over-all temperature of a material under irradiation. If this suggestion holds true of polystyrene irradiated with fast neutrons, the higher ratio of $G(\mathrm{S})/G(\mathrm{X})$ for fast neutrons than for γ-rays may be ascribed in part to the thermal spikes, since it is reported that the $G(\mathrm{S})/G(\mathrm{X})$ ratio of polystyrene irradiated with ^{60}Co γ-rays in vacuo increases with an increase in irradiation temperature of 30 to 100 °C.[17] However, the temperature in the thermal spikes may be much higher than those mentioned above. Further studies are therefore required for a detailed discussion of the thermal spike contribution to the $G(\mathrm{S})/G(\mathrm{X})$ ratio.

3. Influence of Oxygen on $G(\mathrm{X})$ and $G(\mathrm{S})$. Comparison of the $G(\mathrm{X})$ and $G(\mathrm{S})$ values obtained in vacuo with those in air (Table I) demonstrates that the presence of oxygen increases the $G(\mathrm{S})$ value by a factor of 5–8 for γ-rays, whereas for fast neutrons it decreases both the $G(\mathrm{X})$ and $G(\mathrm{S})$ values to about $^1/_3$ and $^1/_2$ those obtained in vacuo, respectively.

The increase in the $G(\mathrm{S})$ value for in air irradiation with γ-rays is most likely ascribed to the spontaneous dissociation of the peroxidic macroradical intermediate (oxidative degradation).[25] If therefore the peroxidic macroradical is formed by the reaction of oxygen with a side-group macroradical, the presence of oxygen will prevent the combination of the side-group macroradicals resulting in a decreased G(X) value. However, the G(X) value observed for γ irradiation in air is practically the same as that in vacuo, as shown in Table I. This fact suggests another mechanism for the peroxidic macroradical formation, for instance

$$\mathrm{M^* + O_2 \rightarrow \text{peroxidic macroradical}} \qquad (8)$$

where M* stands for an excited monomer unit of polystyrene. If this reaction actually occurs at low LET, it would increase the G(S) value alone without significant influence on the G(X) value.

For fast neutrons of high LET, on the other hand, another reaction mechanism of oxygen must be taken into account in order to explain the simultaneous decrease in G(X) and G(S) by the presence of oxygen, for instance

$$\mathrm{M^* + M^* + O_2 \rightarrow 2M + O_2^*} \qquad (9)$$

where oxygen acts as a quencher of excited monomer units M*. This reaction would compete with the macroradical formation (eq 6), decreasing the yield of macroradicals which either form cross-links or undergo main-chain scissions. This mechanism would explain not only the simultaneous decrease in G(X) and G(S) by the presence of oxygen but also relatively small differences in the G(S)/G(X) ratio between the in vacuo and in air irradiations with fast neutrons (Table I). However, no evidence supporting these postulated reactions of oxygen (eq 8 and 9) is available at the present stage. Further studies are therefore required for a detailed discussion of the reaction mechanism of oxygen during irradiation of polystyrene.

4. LET Dependence of Change in Molecular Weight Distribution. It is clear that the characteristics of the M_w/M_n and M_z/M_w changes with $u\chi$ shown in Figure 4 are related primarily to a difference in the G(S)/G(X) ratio which arises as a result of the LET effects due to fast neutrons and γ-rays. For in air irradiations, in fact, the G(S)/G(X) ratio (Table I) differs by a factor of 2–5 between fast neutrons and γ-rays. Therefore, the difference in the M_w/M_n and M_z/M_w changes with $u\chi$ between the two types of radiation (Figure 4b) should be ascribed mainly to the difference in the G(S)/G(X) ratio. For in vacuo irradiations, on the other hand, the G(S)/G(X) ratio differs only by a factor of 1.5–1.7 between fast neutrons and γ-rays. This result suggests that the more rapidly increasing ratio of M_z/M_w with $u\chi$ for fast neutrons than for γ-rays (Figure 4a) should be ascribed to factors other than the G(S)/G(X) ratio.

The molecular weight distributions after in vacuo irradiations with fast neutrons and γ-rays are compared in Figure 5 when the number of cross-linked units per initial number-average molecule is the same for both types of radiation ($u\chi = 0.26$). These distributions are normalized so as to become unity when integrated by molecular weight M from zero to infinity, and hence it can be seen that the distribution for fast neutrons (solid curve) has a higher weight fraction than that for γ-rays (dash-dot curve) in the molecular weight region of initial polystyrene (broken curve) and above ca. 6×10^6. These characteristics in the molecular weight distribution change (Figure 5) and in the M_z/M_w change with $u\chi$ (Figure 4a) are considered to be ascribed to the same factor which causes the nonrandom degradation of PMMA,[2] i.e., the inhomogeneous energy deposition of fast neutrons on a microscopic scale.

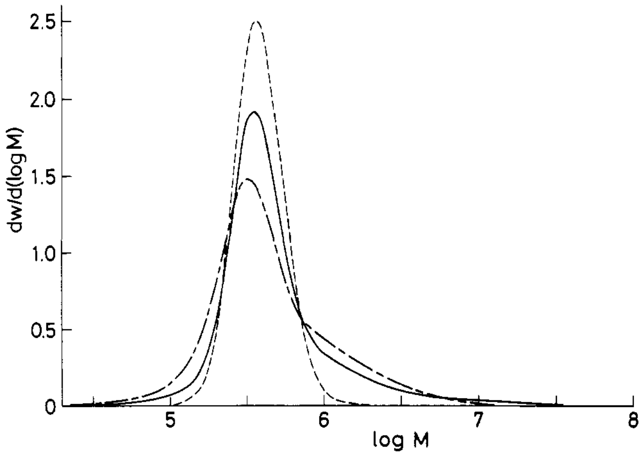

Figure 5. Comparison of the molecular weight distributions changed by in vacuo irradiations with ^{60}Co γ-rays (dash-dot curve) and fast neutrons (solid curve) to the same $u\chi$ value of 0.26 for polystyrene with an initial molecular weight of 3.9×10^5 (broken curve). See the text for $u\chi$.

In order to confirm this view, we carried out the computer simulation of the nonrandom cross-linking on the same basis as previously described for the nonrandom degradation of PMMA.[2] When the total absorbed dose in a polymer system is increased by ΔD, let the increment be absorbed exclusively in a small part whose fraction to the whole system is x. In this case, the increment of absorbed dose within the small part becomes $\Delta D/x$, which is taken as a parameter expressing the degree of the microscopic inhomogeneity of energy deposition. We assume further that this process of energy deposition has been repeated independently N times when the total dose in the whole system is D, i.e., $D = \Delta DN$. When $x \ll 1$ and $\Delta D \ll D$, the following Poisson distribution gives the probability that the absorbed dose within the small part of x is $k\Delta D/x$

$$P(k,\mu) = \mu^k e^{-\mu}/k! \qquad (10)$$

where μ is the mean value of the Poisson distribution, i.e., $\mu = Nx$ or $D/(\Delta D/x)$. The molecular weight distribution $w'(M,D)$ when the above-mentioned process is repeated independently N times can be calculated from the following equation on the assumption that the cross-linking within the small part of x is at random

$$w'(M,D) = \sum_{k=0}^{N} P(k,D/(\Delta D/x))w(M,k\Delta D/x) \qquad (11)$$

where $w(M,k\Delta D/x)$ is obtained by solving the following integrodifferential equation of random cross-linking[8] numerically, using the Runge–Kutta method,

$$\frac{1}{p}\,\frac{\partial w(p,\chi)}{\partial \chi} = -2w(p,\chi) + \int_0^p w(l,\chi)\mathrm{w}(p-l,\chi)\,\mathrm{d}l \qquad (12)$$

where p and l stand for the degree of polymerization which is treated as continuous, χ is the density of cross-links defined by eq 3, and $w(p,\chi)$ represents the weight fraction of macromolecules having p monomer units.

An example of the molecular weight distribution thus obtained from the computer simulation of the nonrandom cross-linking is illustrated in Figure 6 for $\Delta D/x = 3.0$ and $u\chi = 0.2$ (solid curve) together with the Schultz–Zimm distribution as the initial value of the computation (broken curve). Comparison of the simulated distribution with that of the random cross-linking at the same $u\chi$ value (dash-dot curve in the same figure) demonstrates that the weight fraction in the molecular weight region above ca. 3×10^6 is higher for the nonrandom cross-linking than for the random one. This result means that the inhomogeneous energy deposition causes cross-linking to proceed more

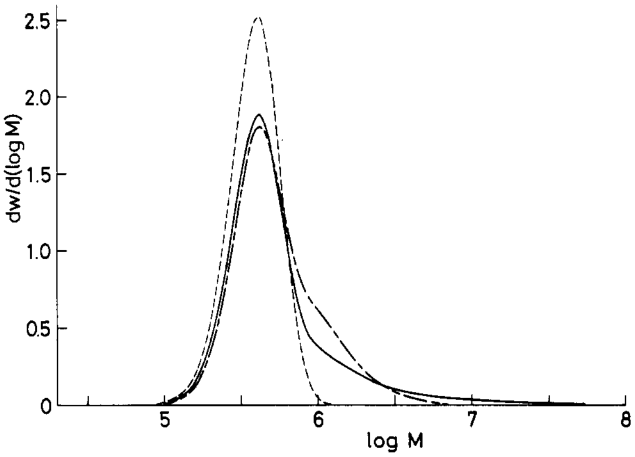

Figure 6. Comparison of the molecular weight distributions obtained from the computer simulation of the random (dash-dot curve) and nonrandom cross-linking (solid curve) for the initial Schultz–Zimm distribution (broken curve).

rapidly than the random cross-linking in certain localized regions of the polymer at the expense of cross-linking in the other regions, forming considerably highly- and only slightly-cross-linked polymers at the same time, even at relatively low total doses. The highly-cross-linked polymers, although small in the weight fractions, will increase the M_z/M_w ratio more highly than those in the random cross-linking. These characteristics in the computer simulation of the nonrandom cross-linking are in fact observed for fast-neutron irradiated polystyrene both in the molecular weight distribution (Figure 5) and in the plot of M_z/M_w vs. $u\chi$ (Figure 4a). It is concluded, therefore, that the actual cross-linking of polystyrene does not take place at random for fast-neutron irradiation, and the nonrandom cross-linking is caused by the microscopic inhomogeneity of energy deposition.

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Crossover Effects on the Sedimentation Velocity Scaling Laws in Semidilute Solutions of Polymers

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ABSTRACT: Measurements of the sedimentation constants in the semidilute regime have been performed in an extended range of concentration, made experimentally available by the use of high molecular weight polystyrene in bromobenzene, a good solvent with a small refraction index increment. The blob hypothesis is confirmed in the sense that the concentration dependence of S is independent of M, but the exponent in the apparent scaling law is shown to be concentration dependent. This can be rationalized considering the size of the blob compared to the radius of gyration of a chain of N_c segments, N_c being the number characteristic of the polymer solvent system, above which the pair correlation function changes from Gaussian to excluded-volume statistics.

The treatment of polymer solutions as critical systems has considerably renewed our picture of polymer solutions.[1,2] The Daoud–Jannink diagram[3] clearly describes the domains corresponding to different scaling laws for the monomer–monomer pair correlation function in the concentration–temperature plane. For a polymer with a given degree of polymerization N, the crossover from one domain to the other is a function of two characteristic quantities.[4,5]

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