Radiation-Induced Network Formation in Polymers

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SYNOPSIS

The topological approach to radiation crosslinking of polymers is based on research of the transition from one topological form of macromolecules to another form, especially from a branched to a network form. The different types of transition and different threshold doses are considered. On the basis of the statistical physics of macromolecules, a conclusion about the network formation through cycles of definite size was made. The dependence of properties of radiation-crosslinked polymers on characteristics of topological forms was studied. The characteristics of topological forms for some polymers [poly(vinylchloride), block copolymers, and polyethylene] were determined. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The process of radiation crosslinking of polymers is a basis for a series of radiation-chemical technologies. As a result of radiation crosslinking, the linear macromolecules convert to branched and cyclic (network) forms according to the scheme: linear form → branched form → network form. These topological forms of macromolecules are the subject matter of statistical physics of macromolecules.[1,2] Every next topological form is forming in an environment of previous form; therefore, these forms can coexist during some dose region. A late form can partly turn into the preceding form as a result of the radiation scission proceeding simultaneously with crosslinking, e.g., branched form ↔ network form.

The theory of radiation crosslinking of polymers, elaborated on the basis of the probabilistic approach,[3] characterizes the process of a transition from a linear form to a branched form of macromolecules. The principal characteristics of the probabilistic approach, e.g., the gel dose R_g and the scission-crosslinking ratio Δ (other notations are β/α or p/q) were used in many works in the area of the radiation chemistry of polymers.

In the dose region above R_g, the radiation crosslinked polymer contains the network form simultaneously with the branched form; therewith, a fraction of the network form increases as a result of the irradiation of the polymer. For this form, the probabilistic approach[3] is not suitable. The investigation of the transition from a branched structure to a network one is an important problem, because it makes it possible to study a structural mechanism of the crosslinking of polymers and to prognosticate the properties of polymers crosslinked by irradiation in a wide dose range. For this purpose, the relationship of elastic active and inactive network chains was used in the polymers crosslinked by the non-radiation method.[2,4] Also, for the polymers crosslinked by irradiation, analogous work was done.[5]

In the present work, we consider an approach based on the notion of the threshold doses. The theoretical results are applied to several polymers.

THEORETICAL BACKGROUND

In a general case, the transition from linear macromolecules to the continuous network structure as a result of irradiation takes place through the following topological forms: linear macromolecules (1) → branched macromolecules (2) → branched macromolecules with individual two-dimensional cycles (3) → branched macromolecules with fragments of three-dimensional network (4) → three-dimensional network (5) (Scheme 1).

The experimental evidence of the existence of the intermediate forms in crosslinked polymers are given in Refs. 2, 6, and 7. The intermediate form (4) can be absent and then the process of a transition from form (3) to form (5) can take place.

It is known[3] that the gel dose R_g corresponds to the mass-average molecular mass of irradiated polymer $\bar{M}_w \rightarrow \infty$; it is equivalent to a formation of branched macromolecules with very large molecular mass, i.e., the branched form becomes a continuous one at the gel dose (the first threshold dose).

It is possible to assume that the network form becomes as continuous one at the network formation dose R_n (the second threshold dose). On the basis of Ref. 8, it is possible to make the conclusion that at doses $R > R_n$ the equilibrium modulus E_∞ of the irradiated polymer is larger than zero, and at doses $R < R_n$, the value E_∞ is equal to zero.

We shall consider the continuous intermediate forms in Scheme 1. The continuous form (2) corresponds to the crosslinked polymers above the dose R_g. The continuous form (3) is, in essence, form (2) containing intramolecular loops. These loops function much like specific branches and do not make a contribution to the equilibrium modulus.[9] The accumulation and linking of intramolecular two-dimensional cycles (form 3) can result in the formation of the continuous form (5).

In a case of form (4), the bond between fragments of a three-dimensional network and different branched macromolecules can take place. Then, the heterogeneous network with the wide molecular mass distribution of interjunction network chains can be formed. For this network, the elastic properties are described by the series Takayanagi model with a continuous branched form.[9] In this case, the threshold dose R_n corresponds to a beginning of the continuous heterogeneous network formation.

Hence, it is possible to consider form (5) as the continuous homogeneous network. The heterogeneous network (form 4) can convert to homogeneous one, in the limit. We shall consider the homogeneous network formation on a basis of the notions of the statistical physics of macromolecules.[1]

The radiation crosslinking of polymers takes place as a result of collisions of reactionable macromolecular units (e.g., macroradicals) during irradiation of polymers. In the equilibrium state, the conformation of the flexible macromolecule is a Gaussian coil. The average unit-concentration C of the definite (marked) linear macromolecule decreases as a result of an increase of the macromolecular chain length:

$$C \sim N^{-1/2} \tag{1}$$

where N is the number of chain units. Therefore, the probability of collisions of marked units with units of other macromolecules increases. It results in an increase of the probability of intermolecular crosslinking.[3] As a result of the irradiation of these entangling coils, the random branched macromolecule is forming with the average unit-concentration:

$$C \sim N^{1/4} n^{-3/4} \tag{2}$$

where N is the number of chains units, and n, the average number of units between branches.

Therefore, the units-concentration of a definite branched macromolecule increases as a result of an increase of an unit-quantity N or molecular mass, i.e., for the branched macromolecule, the intramolecular crosslinking is a principal process. However, it is necessary to take into account also a change of parameter n. The values of parameters N and n of a branched (irradiated) polymer can be expressed in terms of the degree of polymerization of an unirradiated polymer by using the equivalent relative parameter Z/M, where Z is N or n, and M is the degree of polymerization of an unirradiated polymer. The value of Z/M is proportional to a value of N or n. In Figure 1, values of the factors of eq. (2) expressed in terms of the parameter Z/M are shown in dependence on this parameter.

The factors including parameters N and n change in opposite directions as a result of a change of the parameter Z/M. Therewith, there is one point of
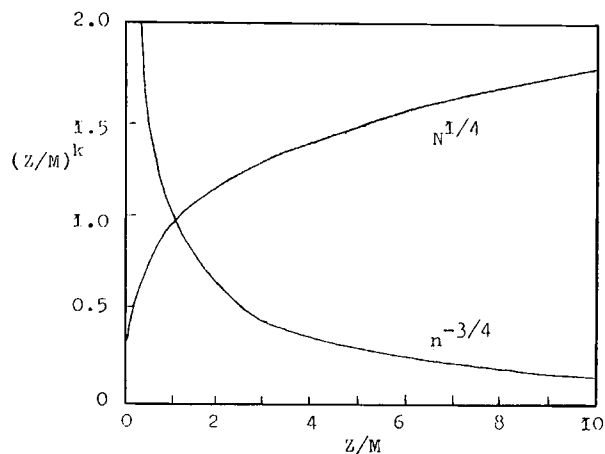

Figure 1 Dependence of factors in eq. (2) for the random branched macromolecule on the relative parameter (k is equal to $\frac{1}{4}$ for the factor containing N and $-\frac{3}{4}$ for the factor containing n).

intersection of curves corresponding to factors in eq. (2). This point corresponds to the maximum concentration of units in a random branched macromolecule and the maximum probability of cycle formation as a result of irradiation. For this point, $Z/M = 1$, i.e., the value of parameter Z (N or n) is commensurable with the degree of polymerization of the unirradiated polymer. Hence, the homogeneous network formation takes place through cycles with a molecular mass of interjunction chains $\bar{M}_c \approx \bar{M}_n$ (number-average molecular mass of unirradiated polymer), i.e., at the threshold dose R_n $\bar{M}_c \approx \bar{M}_n$.

The problem is a determination of the dose R_n and the relationship between doses R_g and R_n. For the homogeneous network formation, the threshold dose[10,11] is

$$R_n = 2k/\bar{M}_nG_c(1 + S_n - 2\Delta) \qquad (3)$$

where $\bar{M}_n$ is the number-average molecular mass of the unirradiated polymer; G_c, the radiation-chemical yield of crosslinking (crosslinked units per 100 eV absorbed); S_n, the sol-fraction at R_n; Δ, the ratio of yields of scission and crosslinking, and $k = 0.96 \times 10^4$ if the dose is measured in MGy. Using the equation[3] for R_g, it is possible to obtain an equation for the ratio:

$$R_n/R_g = 2K(1 - 0.5\Delta)/(1 + S_n - 2\Delta) \quad (4)$$

where K is the polydispersity index of the unirradiated polymer. Therefore, the difference of R_n and R_g increases as a result of an increase of the unirradiated polymer polydispersity because, apparently, the formation of cycles is delayed. The radiation scission taking place simultaneously with radiation crosslinking results in an increase of the value of R_n due to an increase of the ratio Δ [eq. (3)].

The topology of radiation-induced networks is the principal factor affecting the properties of irradiated polymers. We shall consider the change of molecular characteristics of an irradiated polymer predicted by the theory.

In the region $0 \rightarrow R_g$, the branched structure is forming and the mass-average molecular mass of irradiated polymer $\bar{M}_w$ increases very considerably.[3] In this region, the number-average molecular mass of irradiated polymer increases considerably less. In the region $R_g \rightarrow R_n$, the phases of sol and gel coexist. According to Refs. 3 and 9, the gel is one branched macromolecule of very large molecular mass.

Therefore, it is possible to use the number-average molecular mass of the irradiated polymer $\bar{M}_n^*$ in the region $R_g \rightarrow R_n$. On a basis of Refs. 12 and 13,

$$\bar{M}_n^* = WN_A/(1 + \sum N_i) \qquad (5)$$

where W is the mass of the polymeric sample (W = mass of gel + mass of sol); N_A, the Avogadro number; and $\sum N_i$, the total quantity of i-mers in sol.

(WN_A) is constant for a definite polymeric sample. $\sum N_i$ decreases during irradiation of the polymer if the yield of crosslinking is considerably larger than the yield of scission of the polymer. Therefore, $\bar{M}_n^*$ increases after R_g as a result of irradiation of the polymer. $\bar{M}_n^*$ can be calculated but cannot be determined by means of traditional methods using solvents (e.g., osmometry) because the phases of gel and sol are present.

As an example, we shall calculate the parameter $\bar{M}_n^*$ (or the relative characteristic $\bar{M}_n^*/\bar{M}_n$) for the polymer with an initial random molecular-mass distribution:

$$\bar{M}_n^* \approx WN_A/\sum N_i \qquad (6)$$

The relative characteristic

$$\bar{M}_n^*/\bar{M}_n \approx \bar{M}_n'/(S\bar{M}_n) \qquad (7)$$

where $\bar{M}_n$ is the number-average molecular mass of an unirradiated polymer; $\bar{M}_n'$, the number-average molecular mass of macromolecules in sol; and S, the sol-fraction:

$$S = 0.5 + \gamma_c^{-1} - 0.5(1 + 4\gamma_c^{-1})^{0.5} \qquad (8)$$

$$\bar{M}_n'/\bar{M}_n = \{ [0.5 + \gamma_c^{-1} - 0.5(1 + 4\gamma_c^{-1})^{0.5}]^{-0.5}$$
$$- 0.5\gamma_c[0.5 + \gamma_c^{-1} - 0.5(1 + 4\gamma_c^{-1})^{0.5}] \}^{-1} \qquad (9)$$

where the crosslinking index[3] is

$$\gamma_c = k^{-1}\bar{M}_nRG_c \qquad (10)$$

(R = dose [MGy]; G_c = crosslinking yield [crosslinked units per 100 eV]; $k = 0.96 \times 10^4$.)

$$\bar{M}_n^*/\bar{M}_n \approx \{ [0.5 + \gamma_c^{-1} - 0.5(1 + 4\gamma_c^{-1})^{0.5}]^{0.5}$$
$$- 0.5\gamma_c[0.5 + \gamma_c^{-1} - 0.5(1 + 4\gamma_c^{-1})^{0.5}]^2 \}^{-1} \qquad (11)$$

In Figure 2 it is shown that the value of $\bar{M}_n^*/\bar{M}_n$ increases as a result of irradiation of poly-
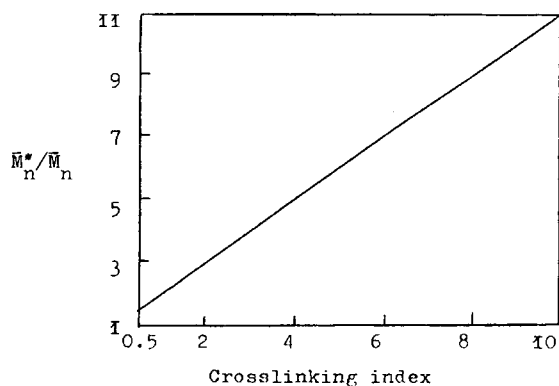
Figure 2 Dependence of $\bar{M}_n^*/\bar{M}_n$ on crosslinking index for polymer with initial random molecular mass distribution.

mer; therewith, in a case of initial random molecular-mass distribution, the dependence of $\bar{M}_n^*/\bar{M}_n$ on the crosslinking index is linear.

In the dose region $R < R_n$, the properties of an irradiated polymer depend mostly on the change of the molecular mass of polymer,[14] especially $\bar{M}'_n$ and $\bar{M}_n^*$. In the dose region $R > R_n$, the properties depend on the change of the molecular mass of interjunction network chains $\bar{M}_c$. The value of $\bar{M}_c$ decreases when a dose increases.

On the basis of previous works,[14,15] the dose dependencies of properties of radiation-crosslinked polymers were determined. The different groups of properties were treated, namely, the volume-mechanical properties (modulus, tensile strength, durability), the surface-mechanical properties (hardness, friction), the thermal properties (heat distortion temperature), and the permeation properties (diffusion of low molecular substances). The results of the theoretical dependencies are given in Table I.

These results show that the dose dependence of applied characteristics has a maximum at dose R_n or a different slope at doses $R < R_n$ and at doses $R > R_n$. These dependencies take place in the case of amorphous polymers. Apparently, these dependencies can take place also in a case of the amorphous-crystalline polymers at the conditions of a recrystallization or a disintegration of crystallites, e.g., as a result of melting, effect of solvents, creep, etc.

In real situations, it is necessary to take into account the influence of peculiarities of the branched form in the region $R < R_n$ and the unequilibrium conditions. The branching of macromolecules influences the properties of polymers differently.[6] Tensile

Table I Properties of Radiation-Crosslinked Polymers

Property	Characteristic	Dose Dependence in Region $0 \rightarrow R_n$	Dose Dependence in Region $R > R_n$
Young's modulus	E_∞ Equilibrium	~ 0	inc. $\sim \bar{M}_c^{-1}$
	E Unequilibrium	const. or inc.	inc. $\sim k\,\bar{M}_c^{-1}$
Tensile strength	σ_b Stress at break	inc. $\sim (k - k_1\bar{M}_n^{-1})$	dec.
	ε_b Elongation at break	inc. $\sim (k - k_1\bar{M}_n^{-1})$	dec. $\sim \bar{M}_c^{1/2}$
Durability (at $\sigma < \sigma_b$)	τ Time until break	inc. $\sim \bar{M}_n^a$	dec.
Hardness	h^{-1} h = penetration depth of indentor	const.	inc. $\sim \bar{M}_c^{-2/3}$
Friction (at rolling)	μ Coefficient of friction	const. or dec.	dec. $\sim \bar{M}_c^{3/2}$
Heat distortion temperature	T_g	inc. $\sim (k - k_1\bar{M}_n^{-1})$	inc. $(k + k_2\bar{M}_c^{-1})$
Permeability	lg D D = coefficient of diffusion	dec. $\sim (k + k_1\bar{M}_n^{-1})$	dec. $\sim (k - k_2\bar{M}_c^{-1})$

$\bar{M}_c$ = molecular mass of interjunctions chains of networks; $\bar{M}_n$ (or equivalent $\bar{M}_n^*$) = number-average molecular mass of irradiated polymer; k, k_1, k_2, a = different empiric coefficients; "inc." = "increasing"; "dec." = "decreasing."

strength and modulus, heat distortion temperature, and hardness are approximately identical for the branched and linear polymers. However, viscoelastic characteristics (e.g., shear-rate viscosity) are less than these of the linear ones. It was concluded[6] that the molecular mass between entanglements is somewhat higher for the branched polymers than for the linear ones. Therewith, the individual cycles function as intramolecular loops, i.e., like specific branches.

Unequilibrium conditions can result in the shift of $\bar{M}_c$ dependence to a lesser value of $\bar{M}_c$ due partly to the influence of entanglements. Apparently, this shift can depend considerably on concrete conditions and one has to be determined for individual properties.

EXPERIMENTAL

Materials

The following polymers were studied: poly(vinyl-chloride) (PVC), plasticized PVC (PVC + 23% dioctylsebacate), SB-block copolymer (SB), SBS-block copolymer (SBS), and low-density polyethylene (LDPE). These unirradiated polymers had the following values of the number-average molecular mass $\bar{M}_n$, determined by the membrane osmometry: $(\bar{M}_n)_{\text{PVC}} = 50,000$, $(\bar{M}_n)_{\text{SB}} = 24,000$ (16,000 for PB-blocks), $(\bar{M}_n)_{\text{SBS}} = 60,000$ (42,000 for PB-blocks), and $(\bar{M}_n)_{\text{LDPE}} = 30,000$. The compression-molded specimens of polymers were formed.

Irradiation

The samples of polymers were irradiated by ^{60}Co γ-rays under vacuum (10^{-3} Torr) at 20–30°C with a dose rate of 1–1.5 Gy/s. The irradiated samples were heated under vacuum at 100°C (PVC) and 120°C (block copolymers and LDPE) during 0.5–1 h.

Analysis

The gel fraction was determined by the method of solvent extraction in the Soxhlet apparatus ($\sim$ 30 h at boiling point of solvent, in the media of inert gas). The following solvents were used: tetrahydrofurane for PVC, benzene for block copolymers, and o-xylene for LDPE. The gel dose R_g was determined[3] by an extrapolation of the linear dependence of $(S + S^{1/2})$ on (R^{-1}) (S is the sol fraction; R is the dose).

The equilibrium modulus E_∞ was determined by an extrapolation of linear part of the relaxation dependence obtained by the method of stress relaxation (for LDPE) or compliance (for block copolymers) at 120°C. The linear part of the relaxation dependence corresponds to the relaxation component with the characteristic time of relaxation $\tau_i \rightarrow \infty$ in a notion[13] of the relaxation process as a sum of relaxation components $\sum E_i e^{-t/\tau_i}$. Equipment of an "Instron" type was used for the relaxation measurements. The values of E_∞ calculated for several doses were used for the determination of the threshold dose R_n by an extrapolation of $(E_\infty)_R$ to a value of $E_\infty = 0$ and for the determination of the radiation-chemical yield of crosslinking G_c.

The equilibrium volume swelling ratio in cyclohexanone[9] V was determined at 25°C by means of dilatometry for the irradiated examples on the basis of PVC; therewith, the equations of Ref. 16 were used and one was used for a determination of the threshold dose R_n by means of an extrapolation of the linear dose dependence of $V^{-5/3}$ up to intersecting with the dose axis. The equipment described in Ref. 16 was used for a measurement of the swelling ratio.

The value of R_n was used for the determination of the molecular mass of interjunctions chains $\bar{M}_c$ at R_n. For this purpose, the linear dependence of $\bar{M}_c^{-1}$ on a dose R determined for the dose region $R > R_n$ was extrapolated to $R = R_n$.

The tensile strength ratio for the irradiated and unirradiated polyethylene was determined at different elongation rates at 90°C. Equipment of the "Instron" type was used for these measurements.

RESULTS AND DISCUSSION

The threshold doses R_g and R_n were determined for irradiated unplasticized and plasticized PVC, block copolymers, and LDPE. In Figure 3, the dependencies $(S + S^{1/2})$ on (R^{-1}) are shown for the studied polymers. Using these dependencies, R_g and the scission-crosslinking ratio Δ were determined. These dependencies are linear for the block-copolymers and the samples on a basis of PVC and nonlinear for LDPE. This nonlinearity is due to the wide molecular mass distribution of LDPE. However, it is possible to separate two approximately linear parts at small and large doses. These parts were used for determination of R_g and Δ accordingly. The values of R_g are shown in Table II. The value Δ is equal to ~ 0.3 for PVC (unplasticized and plasticized), 0.2
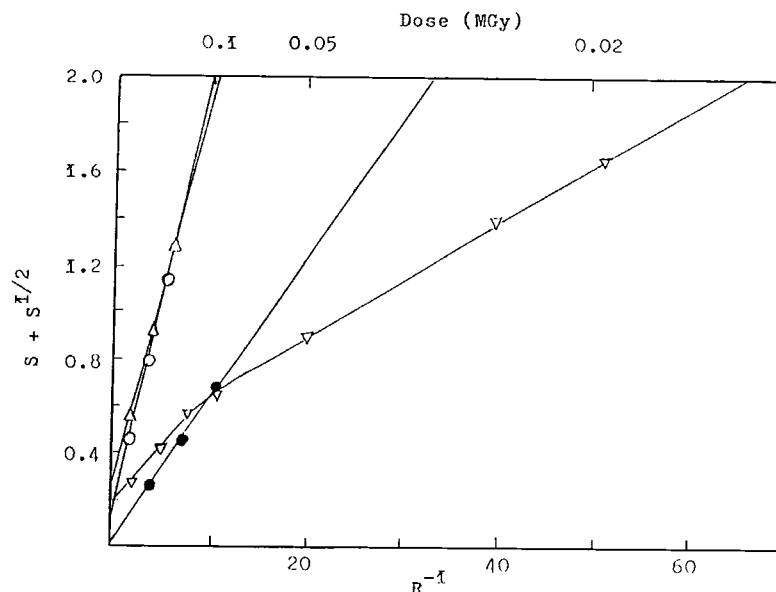
Figure 3 Dependence of $(S + S^{1/2})$ on (R^{-1}) for (∇) LDPE, ($\triangle$) PVC, ($\bigcirc$) SB-, and ($\bullet$) SBS-block copolymers (S is the sol-fraction; R is the dose),

for LDPE, 0.15 for the SB-block copolymer, and ~ 0.05 for the SBS-block copolymer.

For a determination of the network formation threshold dose R_n, the dependencies of the equilibrium modulus E_∞ (in a case of block copolymers and LDPE) and the equilibrium swelling ratio V (in a case of PVC samples) on a dose R were used. The dependencies of E_∞ on R are linear (Fig. 4) in the studied dose region. Therefore, an influence of entanglements on E_∞ apparently does not take place, because in the case of an influence of entanglements, this dependence is nonlinear.[9] In the case of PVC samples, the dependencies $V^{-5/3}$ on R are linear for plasticized and unplasticized PVC; therewith, these dependencies have one point of intersection at R_n (Fig. 5). The different slopes of these straight lines is connected with a different value of the Flory–

Huggins parameter.[9] The determined values of R_n for the studied polymers are shown in Table II. Using the dependencies shown in Figures 3–5, the values of radiation-chemical yield of crosslinking G_c were calculated for the studied polymers. This value for PVC (plasticized and unplasticized) is equal to ~ 1; for LDPE, equal to 4; for the SB-block copolymer, equal to 3.9, and for the SBS-block copolymer, equal to ~ 10 crosslinked chain units per 100 eV absorbed. The different values of G_c for SB-block and SBS-block copolymers is connected with the increased content of cis-consequences in the SBS-block copolymer[17]; therewith, the value of G_c for the SBS-block copolymer is correlated with the data of Ref. 18.

For the studied polymers, $R_n > R_g$ i.e., the threshold doses are separated; therewith, the ratio R_n/R_g

Table II   Characteristics of Irradiated Polymers

Polymer	R_n (MGy)	R_g (MGy)	$\bar{M}_c$ (at R_n), $\times 10^3$
Unplasticized PVC	0.65	0.1	45
Plasticized PVC			
(23% dioctylsebacate)	0.65	~ 0.1	~ 50
SB-block copolymer	0.25	0.1	17
SBS-block copolymer	0.08	0.03	8
LDPE	0.12	0.015	~ 30

R_n = threshold dose of network formation; R_g = incipient gel dose (gel dose); $\bar{M}_c$ = molecular mass of interjunctions network chains at dose R_n.
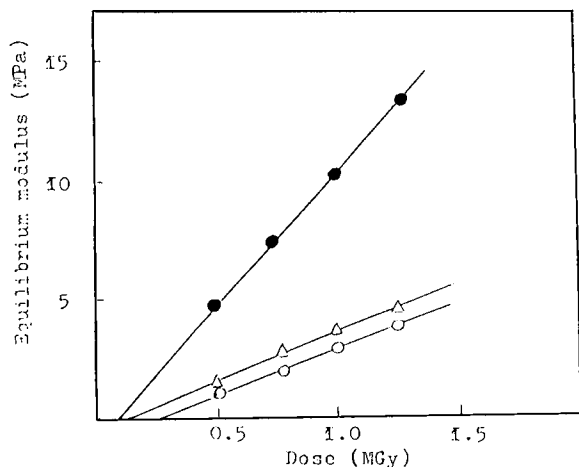
Figure 4 Dose dependence of the equilibrium modulus of irradiated polymers for (△) LDPE, (○) SB-, and (●) SBS-block copolymers at 120°C.
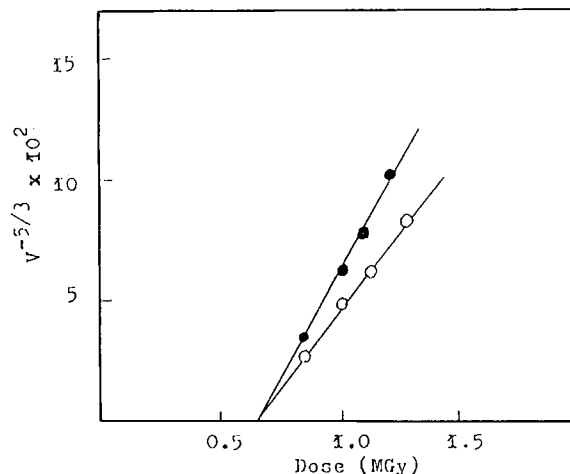

Figure 5 Dose dependence of the volume swelling ratio in cyclohexanone for (○) unplasticized and (●) plasticized PVC at 25°C.

increases in the series SB < PVC < LDPE, mainly because of an increase of the polydispersity of the polymer. Also, in Ref. 3, there is information that in the case of irradiated polyethylene the gel dose and the dose corresponding to an appearance of elasticity (at temperatures above the melting point of crystallites) are separated.

The molecular mass of interjunction chains at the threshold dose R_n was determined. The results are shown in Table II. In fact, the value of $\bar{M}_c$ at R_n is near the value of $\bar{M}_n$ for unirradiated polymers in the case of the SB-block copolymer, LDPE, and samples on a basis of PVC. In the case of the SBS-block copolymer, $\bar{M}_c$ (at R_n) < $\bar{M}_n$, apparently due to a nonhomogeneity of the crosslinks distribution.[17]

Equation (3) deduced for the threshold network formation dose R_n on the basis of Ref. 8 was used for the irradiated SB-block copolymer and PVC. The calculated values of R_n (0.27 MGy for the SB-block copolymer and ~ 0.6 MGy for PVC) are near experimental values, i.e., 0.25 and 0.65 MGy accordingly.

In Ref. 3, an equation was proposed for the connecting of the molecular mass of interjunctions network chains $\bar{M}_c$ and the radiation-chemical yield of crosslinking G_c. Introducing the correction for the radiation scission, it is possible to obtain the equation

$$\bar{M}_c = 0.96 \times 10^4/G_c(1 - 2\Delta)R \qquad (12)$$

where Δ is the scission-crosslinking ratio and R is the dose (MGy). Using eq. (12) and the determined

values of Δ and G_c, the dose dependencies of $\bar{M}_c$ were calculated for the studied polymers (Fig. 6).

It is possible to determine a part of these dependencies corresponding to the continuous network formation. For polymers with $\bar{M}_c$ (at R_n) ≈ $\bar{M}_n$, this part can be determined by means of intersecting the corresponding curve with a straight line parallel to the dose axis. The parallel line corresponds to the number-average molecular mass of the unirradiated
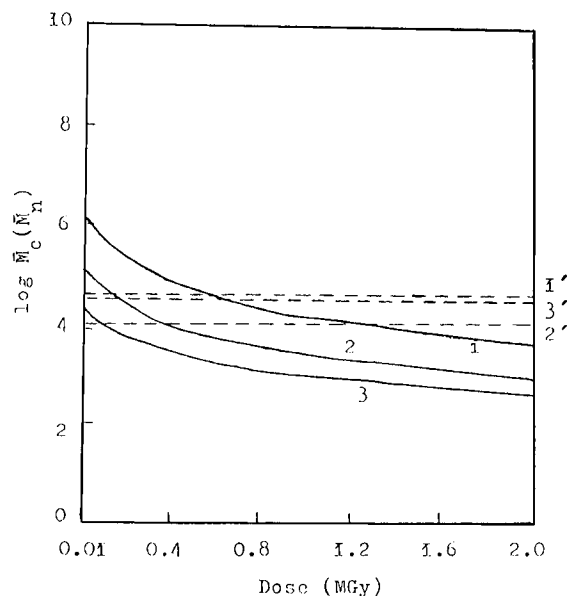

Figure 6 Dose dependence of the molecular mass of interjunction network chains $\bar{M}_c$ for (1) PVC, (2) SB-, and (3) SBS-block copolymers: 1' = $\bar{M}_n$ for PVC; 2' = $\bar{M}_n$ for SB-block copolymer; 3' = $\bar{M}_n$ for SBS-block copolymer.

polymer $\bar{M}_n$. The point of intersecting corresponds to the threshold dose R_n. For the studied polymers, except the SBS-block copolymer, this point coincides with the R_n. In the case of the SBS-block copolymer, the corresponding curve and the straight line do not intersect due to the nonhomogeneous radiation crosslinking SBS-block copolymer.[17]

For the studied polymers, the dose dependencies of some applied characteristics were investigated. The conditions of measurements made it possible to study the dose dependence of the characteristics of the chemical junctions' network, i.e., the physical junctions (crystallites) were absent or disintegrated during the measurements. At a transition from doses $R < R_n$ to doses $R > R_n$, the equilibrium modulus E_∞ of irradiated polymers changes from $E_\infty = 0$ to $E_\infty > 0$ (Fig. 4). Near R_n, the maximum tensile strength takes place for irradiated LDPE (Fig. 7). These results correspond to the dependencies given in Table I. For the study of the influence of nonequilibrium conditions, the tensile strength ratio for irradiated and unirradiated LDPE $(\sigma_b)_R/(\sigma_b)_0$ was determined at different elongation rates (Fig. 7). The marked dose shift of the maximum $(\sigma_b)_R/(\sigma_b)_0$ did not take place, i.e., in this case, the nonequilibrium conditions have little effect on the studied dependence. A value of the maximum at the elongation rate equal to 500 mm/min is larger than at other elongation rates, apparently because of the crystallites conserving at these conditions during stretching.

On a basis of eq. (3), the crosslinking index γ_c, corresponding to the threshold dose R_n, is equal to 2 for the homogeneous network formation. Therefore, in the case of the initial random molecular mass distribution, a maximum value of the ratio $\bar{M}_n^*/\bar{M}_n$ is equal to 3, i.e., one is approximately 2.5 times larger than $\bar{M}_n'/\bar{M}_n$ at the gel dose R_g.[3] The maximum of the applied characteristics is dependent on a maximum value of the parameter $\bar{M}_n^*$ or the ratio $\bar{M}_n^*/\bar{M}_n$. However, it is possible to increase the maximum value of the applied characteristics by means of an increase of the parameter $\bar{M}_n^*$. This increase can take place as a result of the cycle formation delay because of conformational peculiarities of polymers, e.g., in the oriented state, consisting of a departure from the Gaussian coil conformation.

CONCLUSION

In the present work, the topological approach to radiation crosslinking was considered. The research
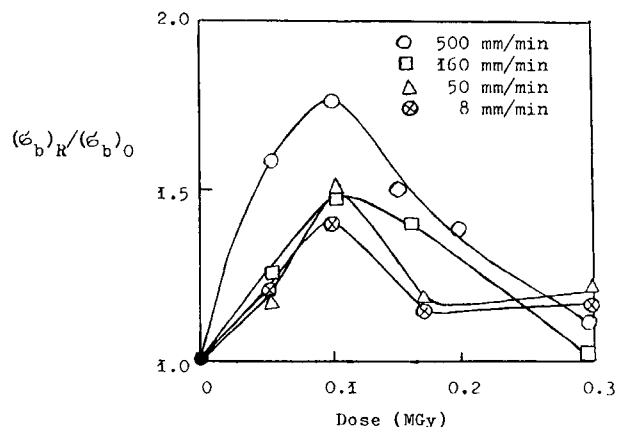

Figure 7 Dose dependence of the tensile strength ratio for irradiated and unirradiated LDPE at 90°C and at different elongation rates.

of a transition from one topological form of macromolecules to another form, especially from the branched form to the network form, is the basis of this approach. This approach uses a notion of threshold doses as the inversion points in the process of a transition from one topological form to another form. Therewith, the second threshold dose, i.e., the network formation dose R_n, is an important characteristic of radiation crosslinking of polymers, depending on the structural mechanism of crosslinking. The topological approach makes it possible to elaborate the principles of prognostication of applied properties of the radiation crosslinked polymers.

Experimental results correlate with the theoretical conclusions. For some of studied polymers, the network formation takes place through intermediate cycles with the molecular mass of interjunction chains commensurable with the number-average molecular mass of unirradiated polymers. These cyclic structures are formed as a result of an intramolecular crosslinking of formerly formed branched structures.

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