Elastic Characteristics of Branched-Network Polymers

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SYNOPSIS

The computed dependencies of elastic characteristics of branched-network polymers were obtained on the basis of the Takayanagi series model. The moduli ratio (γ) for branched-network and branched polymers increases as a result of an increase of the moduli ratio of network and branched phases (E^*_{net}/E^*_{br}) and the network phase fraction (V_{net}). The γ-increase as a function of V_{net} is larger than in the case of the E^*_{net}/E^*_{br} dependence. On the basis of computed dependencies, the experimental results for the radiation crosslinked SBS block copolymer were considered. The experimental results agree with the computed dependencies for the heterogeneous branched-network polymers with $E^*_{net}/E^*_{br} \approx 20$. The influence of entanglements on the elastic characteristics of branched-network polymers is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The equilibrium modulus of polymers depends on their structure.[1] The modulus of heterogeneous polymeric systems is given by mechanical models, in part by the Takayanagi model.[2] In the case of radiation-crosslinked polymers, the heterogeneous structures can be formed in a region of transition from mainly branched to mainly network (cyclic) topological form. On the basis of earlier work,[3] the transition from linear macromolecules to network structure can be shown by the following scheme: linear macromolecules (I) → branched macromolecules (II) → branched macromolecules with individual cycles (III) → branched macromolecules with fragments of three-dimensional network (IV) → three-dimensional network (V). The forms (III) and (IV) can be continuous or discrete according to the form of the matrix branched structure.

In the earlier work,[3] the threshold dose R_n was considered to be a result of formation of the continuous homogeneous form (V) from discrete forms (III) and (IV). In this case, the equilibrium modulus $E_\infty > 0$ at doses $R > R_n$. However, the form (V) can be formed through the continuous forms (III) and (IV). In this case, it is necessary to take into account a probability of a shift of the dose R_n. The continuous form (III) is, in essence, the continuous branched form (II) containing intramolecular loops. These loops function much like specific branches and do not make a contribution to the equilibrium modulus.[2] The continuous form (IV) can contain the phase network domains. Therefore, the Takayanagi approach is applied to this form.

In the present work, the elastic characteristics were calculated for the form (IV) in dependence on the characteristics of the components. The results of calculations were applied to the irradiated SBS block copolymer.

BACKGROUND

The continuous branched-network form (IV) can be considered as the heterogeneous network, because it consists of branched and network phases, corresponding to different topological forms. Therewith, the domains of the network phase are considered as fragments of a homogeneous network, and the branched sections join the domains of the network phase. The series Takayanagi model was used for the above-mentioned complex branched-network

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form (IV). Therewith, the following equation was used:

$$\frac{E_{com}}{E_{br}} = \left[V_{net} \left(\frac{E^*_{br}}{E^*_{net}} - 1 \right) + 1 \right]^{-1} \quad (1)$$

where V_{net} is a volume fraction of the network phase in the heterogeneous structure; E_{com}/E_{br} is a ratio of the macromoduli of the complex branched-network structure, i.e., form (IV), and the branched structure, i.e., form (IV) at $V_{net} \rightarrow 0$ (next, E_{com}/E_{br} is designated as γ); and E^*_{br}/E^*_{net} is a ratio of the moduli of branched and homogeneous network phases, i.e., ones in microvolumes. The calculations were made using the MathCAD program.

EXPERIMENTAL

Materials

The SBS block copolymer used had the following characteristics: The content of PS was equal to 29%, the content of *cis-* and *trans*-isomers and vinyl groups in PB blocks were equal to 40, 35, and 20%, respectively, and the number-average molecular mass was equal to 60,000.

Preparation

The solvent-cast specimens of the SBS block copolymer were formed from benzene solutions. The specimens of the block copolymer were irradiated by ^{60}Co γ-rays under vacuum (10^{-3} Torr) at 20–30°C at a dose rate of 1 Gy/s.

Analysis

1. The content of the gel fraction was determined by the method of solvent extraction (benzene, 80°C, 30 h).
2. The value of the equilibrium modulus of elasticity was calculated by using the equilibrium compliance results obtained at 120°C.

RESULTS AND DISCUSSION

We shall consider eq. (1). A value of the network fraction V_{net} depends on the characteristics of the components:

$$V_{net} = \left(1 + \frac{n_{br}\bar{M}_{br}}{n_{net}\bar{M}_{net}} \right)^{-1} \quad (2)$$

where n_{br} and n_{net} are the numbers of branched and network chains, respectively, and $\bar{M}_{br}$ and $\bar{M}_{net}$ are molecular masses of branched and network chains, respectively. The branched chains are between the network domains.

An increase of V_{net} can take place as a result of the influence of the following factors: (a) an increase of the product ($n_{net}\bar{M}_{net}$) as a result of an increase of n_{net}, and (b) a decrease of the product ($n_{br}\bar{M}_{br}$) as a result of a decrease of n_{br} and $\bar{M}_{br}$.

Another important variable, E^*_{net}/E^*_{br}, is equal to the ratio $\bar{M}_{br}/\bar{M}_{net}$. Therefore, the macrocharacteristics depend on the characteristics of the network phase domains.

In Figure 1, the computed dependencies for γ are shown. As $(E^*_{net}/E^*_{br}) \rightarrow 1$, the value of $\gamma \rightarrow 1$. This indicates that the system converts to a homogeneous one.

A change of the value of γ depends on two factors: (a) an increase of V_{net}, and (b) an increase of $\bar{M}_{br}/\bar{M}_{net}$ or E^*_{net}/E^*_{br}. The contribution of each of these factors depends on a concrete mechanism of the network formation. The data of Figure 1 show that the value of γ increases as a result of an increase of the heterogeneity of a system, i.e., an increase of E^*_{net}/E^*_{br}. It is possible to consider the domains of a network as spheres. Then, in the case of isodiametrical conditions, it is possible to determine the value of V_{net} corresponding to the contact and the growing together (merging) of spheres.

This value of V_{net} is equal to 0.5–0.55. For an agreement between the series model and the results of Figures 1 and 2, it is necessary to assume a wide

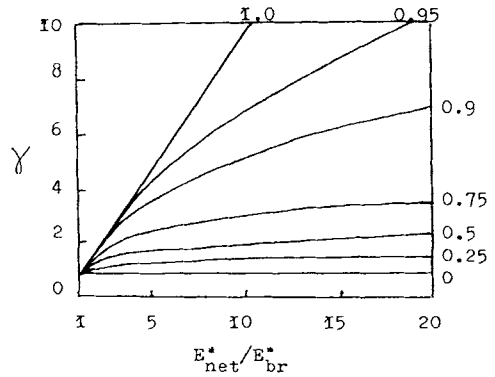

Figure 1 Dependence of γ on E^*_{net}/E^*_{br}. The nos. at curve ends are values of V_{net}.

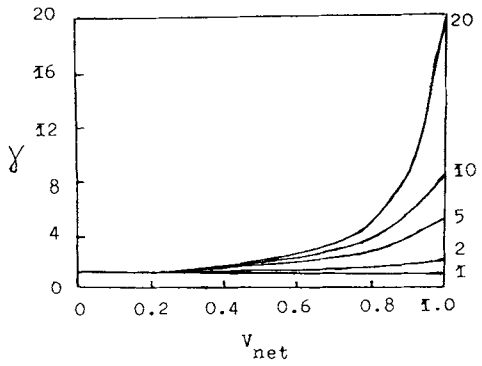

Figure 2 Dependence of γ on volume fraction of the network phase. The nos. at curve ends are values of E^*_{net}/E^*_{br}.

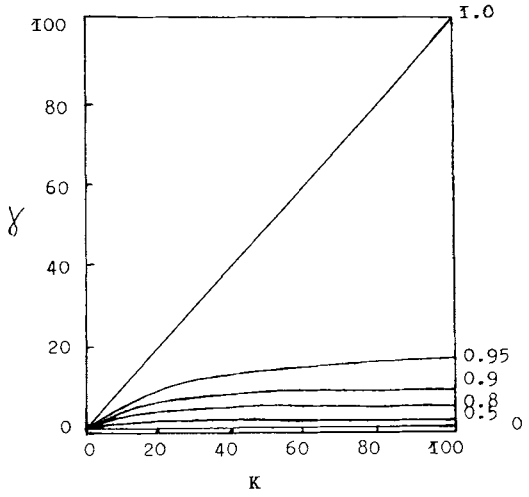

Figure 3 Dependence of γ on coefficient K. The nos. at curve ends are the values of V_{net}.

distribution of domains (spheres) over size. As the formed branched-network structure is considered as the heterogeneous network, then the equation for R_n deduced for the homogeneous network[3] is not apparently applicable.

In Figure 1, the dependence of γ on E^*_{net}/E^*_{br} is shown for the heterogeneous network. As $E_{br} = E^*_{br}$, then a slope of the curves tangent is equal to $\tan \alpha = E_{com}/E^*_{net}$. In the general case, the dependence of γ on E^*_{net}/E^*_{br} is nonlinear. Only at $V_{net} \to 1$ does this dependence become linear with $\tan \alpha = 1$.

If the radiation energy is absorbed by direct and indirect ways, so that $E^*_{net} \sim R$, where R is a dose, it is possible to conclude that the γ value is somewhat dependent on the dose for a wide region of the V_{net} values. Therewith, for this dependence, $\tan \alpha$ decreases as a result of the dose increase.

In Figure 2, the dependence of the γ value on the value V_{net} is shown. In the case of this dependence, $\tan \alpha$ increases as a result of the V_{net} increase. Due to the V_{net} value increase, the γ value and $\tan \alpha$ increase as a result of the dose increase. Therewith, the approximately linear parts of the curves in the region of the V_{net} values are from 0 to ~ 0.5.

We shall now consider a situation in which a value of E^*_{net}/E^*_{br} linearly depends on the network fraction V_{net}, e.g., $E^*_{net}/E^*_{br} = 1 + KV_{net}$ or $V_{net} = [(E^*_{net}/E^*_{br}) - 1]/K$, where K is a coefficient. This dependence can take place in the case of a direct influence of radiation on the network phase. Then, the following equation takes place:

$$\gamma = (1 + KV_{net})/(KV_{net} - KV^2_{net} + 1) \quad (3)$$

In Figures 3 and 4, the results for this equation are given. These dependencies, in essence, are similar to the ones in Figures 1 and 2. Thus, there are total conclusions for cases of the different relationship between V_{net} and (E^*_{net}/E^*_{br}).

At the V_{net}-value ~ 0, the network domains are absent and there is only the branched structure (continuous or discrete, in the general case). The topological form is dependent on a concrete structural mechanism. The discrete form has $E_\infty \sim 0$ because the branched macromolecules are not linked with each other. The continuous form also has $E_\infty \sim 0$ because the molecular mass of this form $\bar{M}_W \to \infty$ and the contour length $\to \infty$. According to other work,[4] $E_\infty \sim$ (1/contour length) and, therefore, $E_\infty \sim 0$.

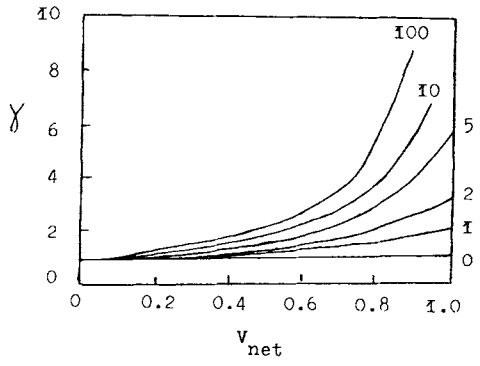

Figure 4 Dependence of γ on volume fraction of the network phase. The nos. at curve ends are values of coefficient K.

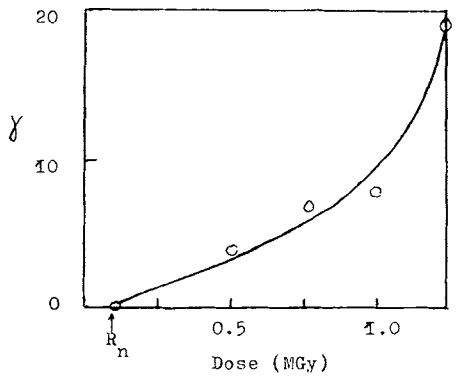

Figure 5 Dose-dependence of γ for the SBS block copolymer.

A value of $E_{br}(E^*_{br})$ in eq. (1) is not equal to zero because it is for the branched macromolecular parts with $\bar{M}_W \nrightarrow \infty$ and is nondiscrete. These parts are between the network fragments and there is a total continuous structure. The condition $V_{net} > 0$ corresponds to the heterogeneous network. The concrete structural mechanism of network formation depends on the peculiarities of a polymer. Research on additional characteristics can help investigations of the network formation. Such a characteristic can be $(\bar{M}_c)_{R_n}$, i.e., a value of the interjunction molecular mass of network chains at the threshold dose R_n. We shall consider experimental results for the SBS block copolymer on the basis of the computed dependencies, because in related work,[5] the heterogeneous structure of a network was assumed for the irradiated SBS block copolymer.

In Figure 5, the experimental dependence of γ on a dose is shown for the SBS block copolymer at 120°C. A value $E_{br} \simeq 1.3$ MPa was used as a result of a calculation for $(\bar{M}_c)_{R_n} \simeq 8000$. This value of $\bar{M}_c$ was calculated at R_n using experimental results.[5] It was assumed that V_{net} is proportional to dose R. Therefore, the dependence of γ on dose R was studied. This dependence is approximately similar to the dependence of γ on V_{net}; therewith, E^*_{net}/E^*_{br} is equal to ~ 20. This is evidence of the heterogeneous network structure in the radiation crosslinked SBS block copolymer. However, there is some difference of slopes of these curves. The probable cause is a nonlinear dependence of the network chain concentration and V_{net} on the absorbed dose. It is due to an increase of the radiation chemical yield of the network chain scission.

It is necessary to consider two problems connected with elastic properties: The first is the problem of entanglements. According to the work of Langley,[6] a probability of the entanglements trapping T_e depends on a gel fraction g. In Figure 6, this computed dependence is shown. For a wide region of the g values, T_e is small, and only above g equal to 0.95 is the T_e value larger than 0.1.

The experimental g values at R_n are from 0.55 to 0.6 (for homogeneous networks) to 0.8 (for heterogeneous networks). Theoretically, the trapped entanglements can have an effect on the modulus of irradiated polymer at doses larger than the threshold dose R_n. The experimental results for a crosslinked polymer with a heterogeneous network (radiation crosslinked SBS block copolymer) do not show agreement between the probability of entanglements T_e and the equilibrium modulus E_∞ (Fig. 6). Better agreement takes place between the experimental results and the computed dependencies on the basis of the series Takayanagi model without use of the entanglement idea.

The second problem is determination of the model type for the so-called defect networks.[2] In equations for these networks, the notions of the elastic active network chains[7] are used—therewith, the concentration of elastic active network chains:

$$n_e = nF \tag{4}$$

where n is a total concentration of chains (active network chains and inactive branched chains), and F, a correction factor.[8] On the basis of these notions, it is possible to deduce the equation

$$\frac{E_{com}}{E^*_{net}} = \frac{n_e}{n}, \text{ i.e., } E_{com} \approx V_{net}E^*_{net} \tag{5}$$

On a basis of the parallel Takayanagi model, it is possible to deduce the equation

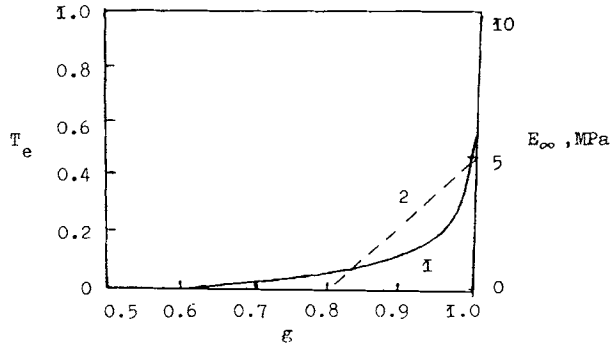

Figure 6 Theoretical dependence of the entanglement probability on the gel fraction (1) and experimental dependence of the equilibrium modulus on the gel fraction (2).

$$E_{com} = V_{net}E^*_{net} + (1 - V_{net})E^*_{br}$$

at

$$E^*_{net} \gg E^*_{br}\ E_{com} \approx V_{net}E^*_{net} \qquad (6)$$

Equations (5) and (6) are identical; therefore, the parallel model is used in the equations for the defect networks.

CONCLUSION

The computed dependencies of the elastic characteristics of the branched-network polymers showed that a value of the moduli ratio of network and branched phases (E^*_{net}/E^*_{br}) can be considered as a condition of the heterogeneity of a system, namely, $E^*_{net}/E^*_{br} > 1$. At this condition, the modulus of the branched-network polymer is dependent considerably on the network phase fraction. Use of computed dependencies for experimental results showed that it is possible to obtain information about characteristics of phases as a result of determination of the complex structure characteristics.

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