Effect of Loop/Bridge Conformation Ratio on Elastic Properties of the Sphere-Forming ABA Triblock Copolymers: Preparation of Samples and Determination of Loop/Bridge Ratio

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Received April 6, 2005; Revised Manuscript Received August 24, 2005

ABSTRACT: To determine the loop/bridge ratio of an ABA triblock copolymer, dynamic viscoelastic measurements were carried out using a polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymer (SIS), a cyclic SI diblock copolymer (cyclic-SI), and a polystyrene-*block*-polyisoprene-*block*-poly(2-vinylpyridine) triblock copolymer (SIP), which were carefully synthesized by the anionic polymerization technique. The three copolymers show similar microphase-separated structures having spherical domains of S and/or P. By blending cyclic-SI and SIS, samples having various loop/bridge conformation ratios were prepared, and the SIP sample was also used as the 100% bridged reference sample. From the dynamic elongational measurements for a series of blended samples and SIP, it was confirmed that the storage modulus (E') is the highest for the SIP, and it linearly decreases with increase of cyclic-SI content. From quantitative analysis of the results, we determined that the bridge fraction, ϕ_{bridge}, in SIS triblock copolymer is 0.93. Although this fraction is significantly higher than the theoretically predicted value and the reported value from dielectric relaxation measurements, the estimated bridge fraction in the present work includes the total contribution from bridged chains and looped chains with interlocked entanglements. Furthermore, it was confirmed that breaking stresses are proportional to the effective bridge fraction in the samples.

Introduction

It is well-known that block copolymers consisting of incompatible components form various microdomain structures. Especially for A−B type diblock copolymers, the composition dependence of morphology[1−3] and molecular weight dependence of microdomain size, etc., have been extensively investigated,[4,5] and their experimental results have been mostly explained by several theories under thermodynamic equilibrium conditions.[6−9]

Morphological feature of A−B−A type symmetrical triblock copolymers have been also investigated, and it is found that their microdomain structures are considered to be almost identical to those of A−B/2 type diblock copolymers.[10,11] Despite the similarity of the domain structure between AB and ABA, the chain conformations of A−B−A triblock copolymers are different from those of A−B diblock copolymers when the B domain of A−B−A triblock copolymer forms continuous phase. Diblock copolymers have only end blocks which always adopt tail conformations, while middle block chains of triblock copolymers choose either a loop conformation whose two ends are anchored on the same domain interface or a bridge conformation whose two ends are pulled apart into the different interfaces. Thus, the structure of the A−B−A triblock copolymer can be specified with the loop/bridge ratio of middle block chains, or bridge fraction, ϕ_{bridge}. This fraction should significantly influence viscoelastisity, mechanical strength, and other physical properties of triblock copolymers that are often used as thermoplastic elastomers.

Theoretical efforts have been made to evaluate ϕ_{bridge};[12−14] however, there are a few experimental reports determining ϕ_{bridge}. An experimental challenge to evaluate ϕ_{bridge} was made by Watanabe et al.[15−17] They prepared dipole inverted polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymers by coupling the living anions on I block ends of two polystyrene-*block*-polyisoprene (SI) diblocks. Comparing slow dielectric relaxations of the dipole inverted I chains in SIS with those of I chains in SI diblock, they determined the loop/bridge fractions for lamellar- and sphere-forming SIS triblock copolymers in a selective solvent for component I. They reported that loop fraction of I chains in SIS increases with decreasing the concentration of ABA due to the stretching and destabilization of bridge conformation on dilution.

In this study, we propose another method to study the loop/bridge problem by rheological measurements using a cyclic AB diblock and a linear ABC triblock copolymer in addition to a linear ABA triblock copolymer. For cyclic AB diblock copolymers, both A and B blocks should possess loop conformation only, since they have no end blocks, while ABC triblock copolymers show a bridge conformation only when three component polymers are incompatible with one another so that they form three different phases. Accordingly, when the molecular weights and the same microphase-separated structures of two copolymers, an ABA and a cyclic AB, are similar to each other, samples having different loop/bridge fractions can be prepared by mixing the cyclic AB and the ABA block polymers. Furthermore, a reference sample with 100% bridge conformation can also be obtained from an ABC triblock copolymer.

On the basis of these ideas, we have synthesized three types of block copolymers, that is, an SIS triblock copolymer, a cyclic-SI diblock copolymer, and a poly-

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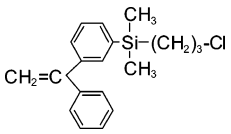
10.1021/ma050712f CCC: $30.25
Published on Web 10/21/2005

styrene-*block*-polyisoprene-*block*-poly(2-vinylpyridine) (SIP) triblock copolymer by anionic polymerization techniques, and they have been characterized carefully. These copolymers are designed to have almost the same molecular weight and polyisoprene content so as to show similar spherical microphase-separated structure where S and/or P domains are periodically packed in I matrices. Especially for the cyclic-SI diblock copolymer, very careful characterization was carried out to determine the purity of the cyclic molecule in the obtained product by using ozonolysis-GPC analysis.[18,19] Subsequently, we have prepared a series of samples having different loop/bridge fractions by mixing the cyclic-SI and the SIS block polymers and measured dynamic Young's modulus for these samples so as to determine the loop/bridge ratio of an SIS triblock copolymer. Furthermore, breaking stress under uniaxial elongation at very high drawing rate for these samples have been also measured and discussed about relationships between mechanical strength and loop/bridge fractions of samples.

Experimental Section

Materials. The synthesis of the initiator, potassium naphthalenide, was described in detail elsewhere.[19] The purification of tetrahydrofuran (THF) used as a solvent, styrene and isoprene monomers, and end-capping agents, 1,1-diphenylethylene (DPE) and 1-[3-(3-chloropropyldimethylsilyl)phenyl]-1-phenylethylene (**I**), were carried out by the same manner as reported previously.[18,19]



Preparation of Telechelic SIS Triblock Copolymer All the operations were carried out in sealed glass apparatuses with break-seals under a pressure of 1×10^{-3} Pa or lower. Synthesis of the telechelic SIS triblock copolymer was as follows: first, isoprene (16 g, 0.24 mol) was anionically polymerized in THF (750 mL) with 1.1 mL of THF solution of potassium naphthalenide (0.22 mol/L) at −78 °C for 24 h to give bifunctional polyisoprenyl potassium. Second, 5% (v/v) of THF solution of styrene (2.0 g, 0.019 mol) was introduced to the living polymer solution and polymerized at −78 °C for 1 h. Third, 1.5 mL of THF solution of DPE (1.3 mol/L) was added to the solution of living polymer for end-capping at the molar ratio of [DPE]/[K] ≈ 8/1 at −78 °C for 3 h, followed by termination with 3.0 mL of THF solution of **I** (0.98 mol/L) at the molar ratio of [**I**]/[K] ≈ 12/1 at room temperature. The polymers obtained were purified by precipitation in an excess amount of methanol three times to remove the residual DPE and **I**.

Preparation of Cyclic-SI Diblock Copolymer Freeze-dried telechelic SIS triblock copolymers (0.5 g) were transferred into vacuum glass apparatuses and then diluted with purified THF (700 mL) for cyclization reactions under extreme diluted condition; that is, polymer concentration for cyclization is ca. 0.07% (w/v). For the cyclization reaction between two end-vinyl groups on an SIS triblock copolymer, 1.0 mL of THF solution of potassium naphthalenide (0.10 mol/L) was introduced into the polymer solution described above at the molar ratio of [K]/[DPE] ≈ 14/1 at room temperature and stirred for 1 days. This cyclization reaction was repeated five times in the same glass apparatus having two 1 L flasks, one is for cyclic reaction under dilute condition and the other is for polymer stock; thus, a total of 2.5 g of SIS triblock copolymer was cyclized in the apparatus. This procedure was carried out two times; that is, a total of 5 g of SIS copolymer was cyclized. After being quenched with dried methanol, the obtained polymer was precipitated into an excess amount of methanol. The cyclic polymer was isolated by GPC fractionation at room temperature using a preparative GPC instrument of Tosoh Ltd. consisting of an SC-8020 system controller, an AS-8071 automatic sample injector, a RI-8020 differential refractive index detector, an FC-8010 fraction collector, and with a pair of columns G4000H_{HR} (bead size is 5 μm, pore size is 10^4 Å) of Tosoh Ltd.; the column size is 300 mm in length, with 21.5 mm inner diameter. THF was used as an eluent; flow rate was 5 mL/min at room temperature. The concentration of the injected polymer solution was ca. 0.2% (w/v).

Preparation of an SIP Triblock Copolymer and an Isoprene Homopolymer (h-I). The SIP triblock copolymer was anionically polymerized in THF with sequential addition of three monomers, styrene, isoprene, and 2-vinylpyridine using cumylpotassium as an initiator at −78 °C. The polymer obtained was purified by precipitation in an excess amount of methanol. Isoprene homopolymer as a reference was also prepared using the same material system as for copolymers.

Molecular Characterization Number-average molecular weight, M_n, was determined by membrane osmometry in toluene at 303 K with a Hewlett-Packard type 502 high-speed membrane osmometer. Apparent molecular weights and molecular weight heterogeneities, M_w/M_n, were determined in THF by the GPC system of Tosoh Ltd. with a RI-8012 differential refractive index detector, a UV-8011 ultraviolet spectroscopic detector, and a series of three G4000H_{HR} columns with 7.8 mm inner diameter each. Standard polystyrenes were used for calibration. ^{1}H NMR spectra were measured with a Varian unity-500 NMR spectrometer to obtain composition of the block copolymer samples and microstructure of polyisoprene. Chemical shifts were referred to chloroform in chloroform-*d*.

Ozonolysis. Ozonized oxygen was generated by a ceramic ozonizer model KA-10 of Koyo Iron Works and Construction Co. Ltd. To cleave the carbon−carbon double bonds in the polyisoprene backbone chain, ozonized oxygen (ca. 2%) was bubbled into dichloromethane/methanol (95/5 vol/vol) solutions of sample copolymers at −78 °C for 30 min with a flow rate of ca. 300 mL/min.

Morphological Observation. Films used for morphological observation were cast for a few days from ca. 5% (w/v) THF solutions of samples. The cast films were dried for 6 h and annealed at 150 °C for a week in a vacuum oven. The films were cut into ultrathin sections (70−100 nm thick) using an ultramicrotome, Leica Ultracut UCT with cryosectioning system at −100 °C. The sections were stained with osmium tetroxide vapor from 5% aqueous solution at room temperature for 8 h. The microphase-separated structures of the sections were observed by a Hitachi transmission electron microscope H-800 operated at an accelerating voltage of 100 kV.

Rheological Measurements. For the rheological measurements, blend samples consisting of cyclic-SI and SIS block copolymers with different compositions were intentionally prepared by solvent-casting method from THF solution of the two polymers. Dynamic elongational measurements are performed with Rheometrics Solid Analyzer RSA-II. Film specimens for measurements are prepared by solvent casting from dilute THF solutions of samples in a Teflon Petri dish for a few days, further dried in a vacuum for a few days, and finally annealed at 150 °C for 12 h in a vacuum oven. The dried films are carefully cut to a rectangular shape of 5 mm wide, 15 mm long, and 0.05 mm thick. Dynamic Young's moduli are measured in a temperature range of −50 to 100 °C with a temperature increasing rate of 5 °C/min. The frequency used was 10 Hz, while strain amplitude was varied in a range of 0.1−1% to obtain the linear response of the wide range of the temperature. Breaking stress of the same film specimens are measured with a Rheometrics Minimat 2000 at room temperature. The drawing rate was 90 cm/min. The breaking stress measurements are performed three or four times for each sample.

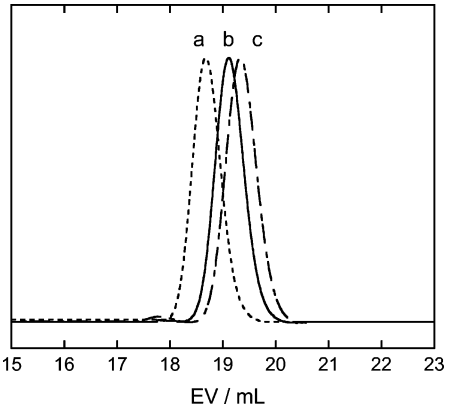


Figure 1. GPC chromatograms of (a) a homopolyisoprene, h-I, (b) an SIS triblock copolymer, and (c) an SIP triblock copolymer.

Table 1. Molecular Characteristics of Polymers

sample code	$10^{-4}M_n$	M_w/M_n[b]	ϕ_I[d]
SIP	13.5[a]	1.03	0.88
SIS	14.7[a]	1.03	0.89
C66	14.4[a]	1.04	0.89
h-I	12.6[c]	1.04	1

[a] Determined by osmometry. [b] Determined by GPC. [c] Determined by light scattering. [d] Volume fraction of polyisoprene estimated from ^{1}H NMR.

Table 2. E' Values for All the Samples at 70 °C

sample code	E' [MPa]	sample code	E' [MPa]
SIP	1.54	C25	1.02
SIS	1.43	C40	0.712
C07	1.21	C66	0.540
C13	1.18		

Results and Discussion

Preparation and Characterization of Polymer Samples. Figure 1 shows GPC chromatograms of triblock copolymers, i.e., SIS, SIP, and that of a homopolymer, h-I. They have all unimodal and symmetric peaks, suggesting reasonably narrow molecular weight distribution. Table 1 lists the molecular characteristics of these polymer samples. They have similar polyisoprene chains of ~130K as designed and have fairly small polydispersity indices ($M_w/M_n \leq 1.04$). From the molar ratio determined by ^{1}H NMR measurements and the densities of the bulk polymers ($d_{polystyrene} = 1.05$ g/cm^3, $d_{polyisoprene} = 0.926$ g/cm^3, $d_{poly(2-vinylpyridine)} = 1.14$ g/cm^3), the volume fractions of polyisoprenes in the SIS and SIP were estimated to be 0.88 and 0.89, respectively. The microstructures of the polyisoprene chains of three samples determined by ^{1}H NMR are practically the same; approximately 4% 1,4 and 96% 1,2 or 3,4 linkages.

The middle curve in Figure 2 shows a multipeak GPC chromatogram for the crude product after coupling reaction between end-vinyl groups on linear SIS molecules in comparison with that of the linear precursor whose peak appears at about 19.2 mL, as shown at the top curve in Figure 2. The polymers eluting in the range of 15−19 mL are high molecular weight polycondensation products formed by intermolecular reactions, while the product eluting at around 19.7 mL is the desired cyclic copolymer produced by intramolecular reaction since the peak position is shifted considerably from that for the original telechelic SIS triblock. The crude product was fractionated by preparative GPC to purify the cyclic

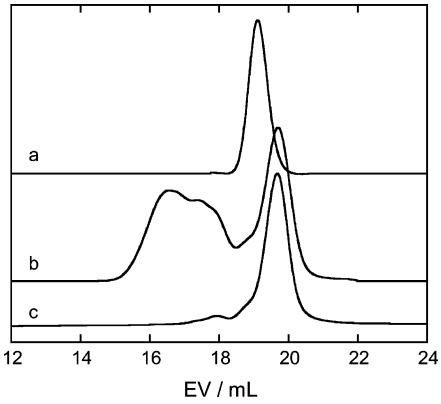


Figure 2. GPC chromatograms of (a) an SIS triblock copolymer, (b) an SIS triblock copolymer after cyclization, and (c) the GPC-fractionated product.

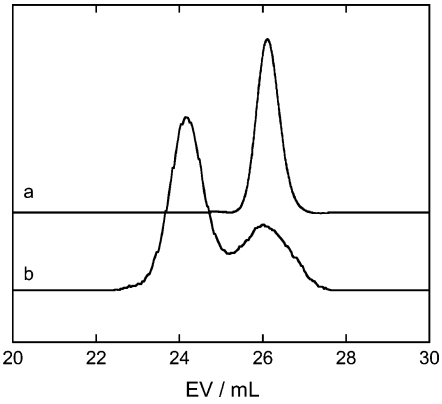


Figure 3. GPC chromatograms after decomposition by ozonolysis of (a) an SIS triblock copolymer and (b) the GPC-fractionated product.

block copolymer; the results are shown at the bottom curve in Figure 2. It is apparent that the chromatogram of the fractionated polymer still includes small amount of polymer contaminates with higher molecular weights. The number-average molecular weight and volume fraction of polyisoprene in the fractionated product, whose code name is C66 as described below, are also summarized in Table 1. The molecular weight of C66 agrees well with that of the parent SIS triblock copolymer, and the compositions of C66 and parent SIS triblock copolymer are almost the same.

The top curve in Figure 3 shows the RI-detected GPC chromatogram of the product from the SIS after ozonolysis, which is unimodal with a narrow molecular weight distribution, and appeared at around 26.0 mL. Its apparent molecular weight estimated by GPC, 9K, is close to the M_n value, 9.0K, of one polystyrene (S) block chain in the SIS calculated from M_n of SIS and composition. The bottom curve in Figure 3 shows the GPC chromatogram of the ozone-decomposed polymer of the fractionated product. The peak is bimodal, which appeared around 24.2 and 26.0 mL, and the corresponding molecular weights are approximately 18K and 9K, respectively. The existence of a peak whose molecular weight is twice that for a polystyrene block in the parent linear triblock copolymer is the direct evidence of forming cyclic structure, as described previously.[18,19] Comparing peak areas for two peaks, the purities of cyclic molecule was estimated to be 0.66; therefore, this sample is coded as C66.

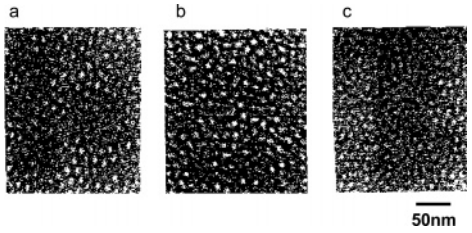


Figure 4. Transmission electron micrographs of (a) an SIP triblock copolymer, (b) an SIS triblock copolymer, and (c) the GPC-fractionated product, i.e., C66.

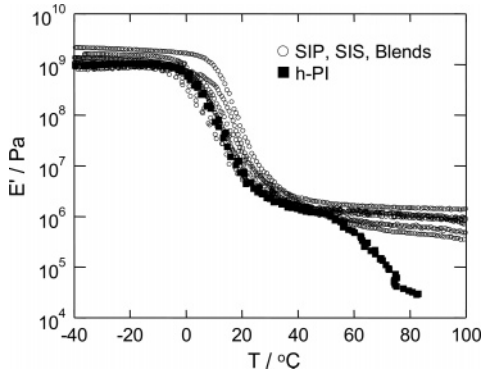


Figure 5. Plots of storage moduli, E', against temperature, for SIP, SIS, C07, C13, C25, C40, C66, and h-I.

Morphological Observation and Rheological Measurements. Figure 4 compares TEM images of SIP, SIS, and C66. It is evident that these three polymers have similar microphase-separated structures, that is, spherical microdomains of S and P embedded in polyisoprene matrices.

Four blend samples with different compositions prepared from C66 and SIS were coded as C07, C13, C25, and C40, whose two-digit number means percentage of cyclic polymer in the blend sample. Figure 5 shows temperature dependence of storage modulus E' measured for all the samples. The data for h−I having similar molecular weight to that of the middle polyisoprene block in copolymers are also shown for comparison. At a temperature higher than 40 °C, there exist rubbery plateau region for all the samples. The plateau region for block copolymers persists up to 100 °C, the highest measuring temperature employed in this work, which is close to glass transition temperatures of S and P, while the data for h-I steeply decrease at $T > 60$ °C due to nonrecoverable deformation and flow of h-I at high temperature. Thus, we can assume that the contribution of entangled I chains, which can relax at long time, to the E' for block copolymers become negligible at higher temperature than 60 °C.

To examine the data more in detail, enlarged plots of E' vs T within the range 60−80 °C for block copolymers and their blends are shown in Figure 6. It is clear that E' data became higher for the samples with lower C66 content and the data for SIP are the highest. All the data decrease with increasing temperature very gradually but continuously, and the data are almost parallel with each other at higher temperature region ($T \geq 70$ °C), implying that the temperature dependences of E' are practically the same. Therefore, the relationship between loop/bridge fractions and elastic property can be discussed at a constant temperature.

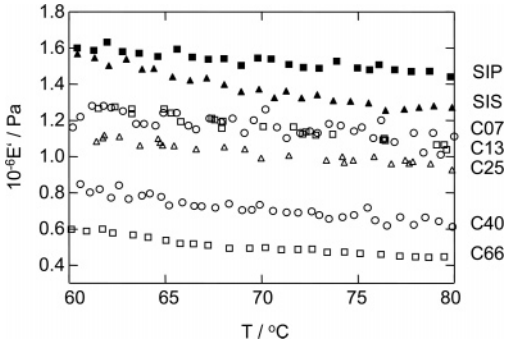


Figure 6. Enlarged plots of storage moduli, E', against temperature, for SIP, SIS, C07, C13, C25, and C66 in the tempareture range 60 °C ≤ T ≤ 80 °C.

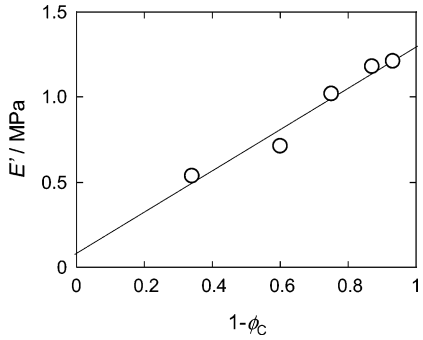


Figure 7. Plots of storage moduli, E', against cyclic polymer fraction at 70 °C.

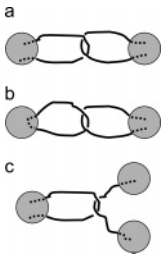


Figure 8. Schematic drawings of chains having interlocked entanglement: (a) looped SIS vs looped SIS, (b) looped cyclic-SI vs looped SIS, and (c) looped SIS vs bridged SIS.

Figure 7 shows the plots of E' at 70 °C against $(1 - \phi_c)$, where ϕ_c denotes cyclic polymer fraction; that is, $(1 - \phi_c)$ means SIS fraction in the blended samples. In these samples there exist some topologically different entanglements among I chains. Though a certain amount of I chains in SIS should have loop conformation, if two looped chains anchored at different S domains are entangled with each other, these chains cannot relax, and they act as two constrained chains under a certain deformation as shown in Figure 8a. Similarly, when an I chain in a cyclic polymer is entangled with that in an SIS having looped conformation, these two I chains also act as two constrained chains under the deformation as depicted in Figure 8b. Furthermore, when a looped chain is entangled with a bridged chain lying between two different microdomains as shown in Figure 8c, these two chains could be regarded as two constrained chains. Hereafter, we call these three types of entanglements as interlocked entanglements. As mentioned above (Figure 5), other types of entanglements can relax at high temperature ($T \geq 70$ °C). It is natural to consider that there is no priority for formation of conformations with certain topology when they are formed during the casting process. It is evident from Figure 7 that E' is

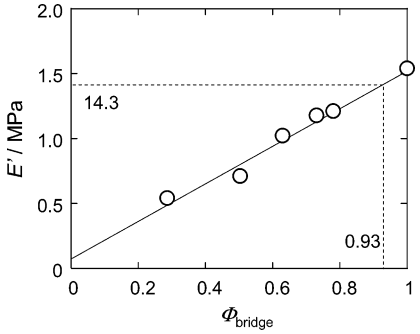


Figure 9. Plots of storage moduli, E', against bridged fraction, ϕ_{bridge}, for C07, C13, C25, C40, C66, and SIP.

linearly increasing with $(1 - \phi_c)$ according to the relationship

$$E' = a(1 - \phi_c) + b$$

Since the fraction of the bridged chain of the blend, ϕ_{bridge}, can be expressed as

$$\phi_{bridge} = (1 - \phi_c)x \tag{2}$$

where x is unknown fraction of the bridged chain in SIS linear molecules. Here we assume that x is independent of ϕ_c since there is no priority for formation of loop/bridge conformation for an I chain in SIS as described above. Combining eqs 1 and 2, we have the linear relationship between E' and ϕ_{bridge} as

$$E' = (a/x)\phi_{bridge} + b \tag{3}$$

From least-squares fitting of the data points in Figure 7, the relationship $E' = 12.2(1 - \phi_c) + 0.793$ was obtained. To convert the data points from ϕ_c into ϕ_{bridge}, the linear regression method via trial and error by changing x values was adopted using the data for SIP ($E' = 15.4$) at $\phi_{bridge} = 1$ in this evaluation; consequently, we obtained the best fit value, 0.84 as x. Using the x value together with a and b, we have the relationship

$$E' = 14.6\phi_{bridge} + 0.793 \tag{4}$$

The plots of E' against ϕ_{bridge} are shown in Figure 9. In this equation, since ϕ_{bridge} is essentially proportional to E', an intercept b should be 0. In practice, however, b may have a small finite value by an influence of lattice deformation, which will be discussed in the next paper. Applying the E' value for SIS ($E' = 14.3$) to eq 4, we obtain 0.93 as ϕ_{bridge} for SIS, which is also shown in Figure 9 using dotted lines. The ϕ_{bridge} value, 0.93, is significantly higher than theoretical values[12−14] and the reported value from dielectric relaxation experiments.[15−17] It should be noted that the latter give simply the fraction of bridge conformation chains. As already mentioned above, some fraction of loop conformation chains actually act as a bridged chains due to the interlocked entanglements under deformation. The difference between the theoretical prediction and our experimental results can be attributed to the possible existence of the many interlocked entanglements.

When these elastomer films are subjected to large uniaxial deformations, they are largely elongated without necking and finally break down. The breakdown of the sample film occurs by pulling out the glassy anchors (S and P chains) of stretched bridged chains (including looped chains with interlocked entanglements) from their spherical domains. If each bridged chain has same strength and most of them are not pulled out before reaching the breaking point, the breaking stress should reflect the number of bridged chains per unit area of the undeformed film. Then the breaking stress should be proportional to the determined bridge fraction, ϕ_{bridge}. Figure 10 shows examples of the stress−strain curve obtained by fast draw measurements. It is clear that the breaking stress decreases with increasing cyclic polymer content.

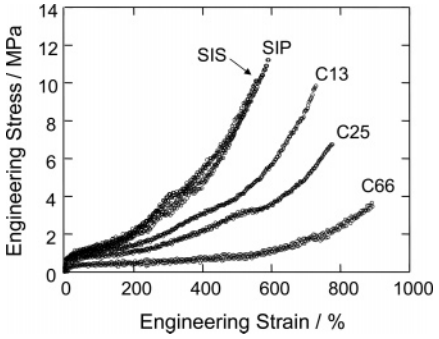


Figure 10. Comparison of engineering stress−engineering strain curves for SIP, SIS, C13, C25, and C66.

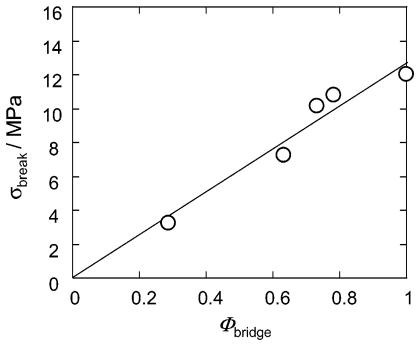


Figure 11. Plots of breaking stress, σ_{break}, against bridged fraction, ϕ_{bridge}.

The breaking stress for each sample was measured for 3 or 4 times, and the average values are plotted against bridge fraction in Figure 11. All the data can be represented by a straight line drawn from the origin as expected. Thus, we conclude that the determined bridge fraction well reflect the total fraction of bridged chains plus looped chains with interlocked entanglements. Detailed studies of simple elongation behavior of these samples combined with small-angle X-ray scattering and infrared dichroism measurements will be reported in the following paper.

Acknowledgment. The authors thank Dr. Arai at the center for Integrated Research in Science and Engineering in Nagoya University for his help in taking transmission electron micrographs.

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MA050712F