NOTES

Elasticity of Sphere-forming Polystyrene-*b*-polyisoprene-*b*-poly(2-vinylpyridine)/Polystyrene-*b*-polyisoprene/ Polyisoprene-*b*-poly(2-vinylpyridine) blends: The role of Dangling Chains

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In networked structure of polymers such as gels and rubbers, there exist bridge, loop and dangling chains which may differently affect the mechanical properties of the system. Sphere-forming triblock copolymers with glassy or crystalline end blocks and rubbery middle block are suitable model systems to study the above problems since sophisticated living anionic polymerization technique enabled us to prepare special middle block chains, which can be used to determine the bridge, loop, and dangling end fractions as mentioned below.

Watanabe *et al.*[1–4] prepared polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) tribrock copolymers with dipole-inverted polyisoprene chains. They determined the bridge fraction of I chains for lamellar-forming SIS and sphere-forming SIS triblock copolymers by dielectric relaxation measurements.

Takano *et al.*[5] synthesized cyclic-SI (C-SI) diblock copolymers and prepared a series of samples having almost the same size of spherical microdomains but different loop/bridge fractions by mixing the C-SI and the original SIS used for the preparation of C-SI. Using a polystyrene-*b*-polyisoprene-*b*-poly(2-vinylpyridine) (SIP) triblock copolymer as a 100% bridged reference, they determined the bridge fraction of the I chains in SIS and SIS/C-SI blends from Young's moduli obtained by dynamic elongational measurements. It was reported that the magnitudes of macroscopic stress and the orientation function of I segments of those samples examined by IR dicroism under simple elongation are proportional to the bridge fraction, while lattice deformation examined by small angle X-ray scattering (SAXS) under simple elongation is independent of the bridge fraction.[6]

In this note, we examine the relationship between the Young's moduli and bridge/dangling chain fractions for the same SIP used in the previous studies,[5,6] in which dangling ends of polyisoprenes are introduced by blending two linear diblock copolymers, polystyrene-*b*-polyisoprene (SI) and polyisoprene-*b*-poly(2-vinylpyridine) (IP) with SIP.

EXPERIMENTAL

Two diblock copolymers, SI and IP are synthesized by anionic polymerization technique as SIP.[5] Number-averaged molecular weight, M_n, of S and I precursors for SI and IP, respectively and their molecular weight distribution index, M_w/M_n, where M_w is weight-averaged molecular weight, are determined by GPC measurements using respective calibration curves. The volume fraction of isoprene in SI and IP, ϕ_I are determined by ^{1}H NMR as reported in the previous work.[5] M_n of SI and IP are calculated from ϕ_I and M_n of the precursors. Molecular characteristics of SI and IP thus determined are tabulated in Table I together with those of SIP.[5]

Table I.   Molecular Characteristics of polymers

Sample code	$10^{-4}M_n$	$M_w/M_n{}^b$	$\phi_I{}^c$
SIP	13.5[a]	1.03	0.88
	15.1[b]		
SI	7.1[b]	1.03	0.89
IP	8.1[b]	1.02	0.88

[a]Determined by Osmometry. [b]Determined by GPC. [c]Volume fraction of Polyisoprene Estimated from ^{1}H NMR.

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The blend samples are prepared by solvent casting from dilute THF solutions of samples for a few days and further dried for 6 h and annealed at 150 °C for 12 h in a vacuum oven. The blending ratio, SIP/(SIP + SI + IP) are 0.94, 0.86, 0.80, and 0.70 in which the ratio SI/IP was always kept as 1. Film specimens for measurements are carefully cut to a rectangular shape of 15 mm long, 5 mm wide, and 0.05 mm thick. It should be noted that the molecular weights of SI and IP are not exactly equal to but slightly higher than the halves of SIP divided at the midpoint. Neglecting the small difference, we simply assume that the bridge fraction ϕ_{bridge} of I chains in the blend samples are equal to the SIP fractions.

Dynamic elongational measurements are performed with Rheometrics Solid Analyzer RSA-II in a temperature range of −40 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 to 1% to obtain the linear response in the wide range of the temperature. It should be noted that all these experimental conditions are practically the same as those employed in the previous work.[5]

RESULTS AND DISCUSSIONS

Figures 1a and 1b shows temperature dependence of storage modulus E' and loss modulus E'' measured for all the samples, respectively. There exist rubbery plateau region of E' for all the samples at the temperature higher than 40 °C, which persists up to the highest measuring temperature employed in this work, 100 °C. Figure 1c shows enlarged linear plots of E' *vs.* T at temperature range of 60 to 80 °C. It should be noted that the data for polyisoprene homopolymer steeply decrease at T > 60 °C due to non-recoverable deformation and flow[5] so that the contribution of entangled I chains, which can relax at long time, to these E' data for block copolymers are negligible in this temperature range.

It is observed in Figure 1c that E' data become lower for the samples with higher diblock copolymer content, though the data for lower diblock copolymer content are somewhat scattered. All the data decrease with increasing temperature very gradually but continuously and the data are almost parallel with each other in this temperature region, implying that the temperature dependences of E' are practically the same. These features are also the same as those reported for blends of SIS and C-SI in the previous work.[5] Therefore, the relationship between bridge/dangling end fractions and elastic property can be discussed at a constant temperature. Here, we employ E' data at 70 °C ($E'_{70°C}$), which is the same temperature as employed in the previous work.[5]
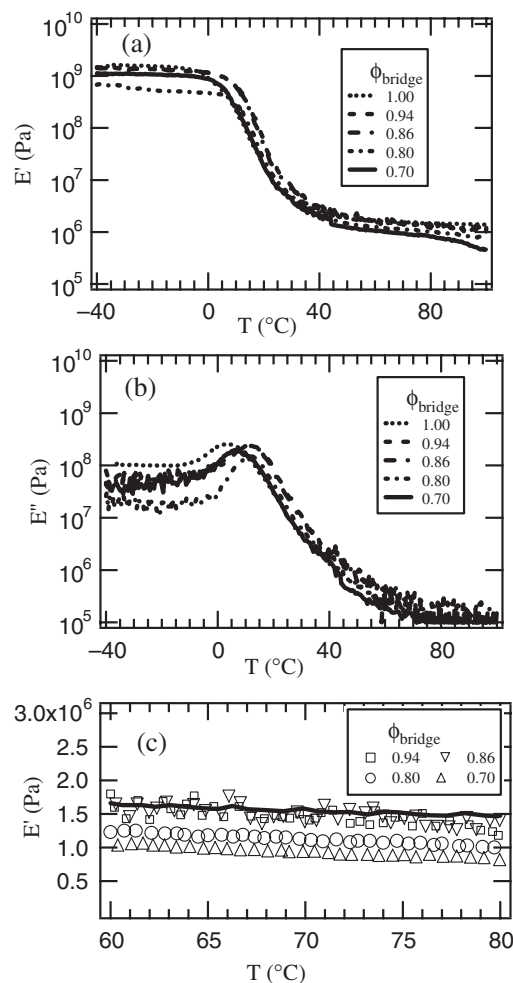

Figure 1. Plots of (a) storage moduli, E' and (b) loss moduli E'' against temperature T for SIP and SIP/SI/IP blend samples. The bridge fractions of the samples are denoted in the figure. Figure (c) shows the enlarged plots of E' in the temperature range of 60 to 80 °C. Solid line in (c) denotes the data for SIP. Other symbols are denoted in each figure.
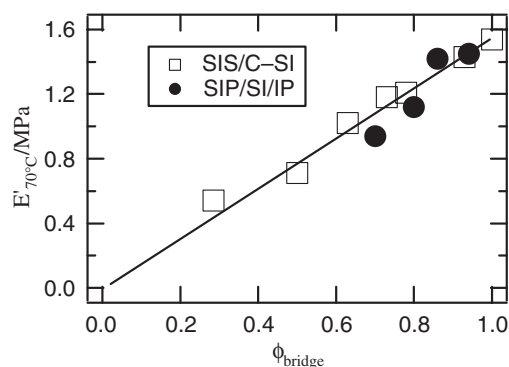

Figure 2. Plots of storage moduli, $E'_{70°C}$ against bridge fraction, ϕ_{bridge}. Symbols are denoted in the figure.

Figure 2 shows plots of $E'_{70°C}$ *vs.* bridge fraction ϕ_{bridge}. The data for SIP, SIS, and SIS/C-SI blends (different loop/bridge ratio) are also shown for com-

parison. It is clear that $E'_{70\,°C}$ data for SIP/SI/IP blends decrease with decrease of ϕ_{bridge}, though the data are somewhat scattered and show a slight tendency to become lower than those of SIS/C-SI blends. However, the deviations of the data for SIP/SI/IP blends from the SIS/C-SI data are within 16%, which can be regarded as experimental errors mainly due to the difficulty in the measurement of thin films. Thus, we conclude that the Young's moduli of sphere-forming triblock copolymers are proportional to the bridge fraction and the difference between dangling ends and loops are very minor.

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