Thermoreversible Physical Gelation of Block Copolymers in a Selective Solvent

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ABSTRACT: Solidlike and liquidlike linear viscoelastic responses were observed at low and high temperatures (T) for polystyrene−polyisoprene−polystyrene (SIS) triblock copolymers dissolved in an I-selective solvent, *n*-tetradecane (C14). These SIS systems behaved as thermoreversible physical gels, with the microphase-separated S domains working as the cross-links at low T. Linear responses of those systems were examined in the vicinity of the sol−gel transition temperature T_{gel}. For the systems fully equilibrated in an isothermal state at T_{gel}, the power-law behavior, $G'(\omega) \sim G''(\omega) \sim \omega^n$, was observed only at high frequencies ω, and a separate slow relaxation mode was observed at low ω. For the system quenched from high T ($>T_{\mathrm{gel}}$) to low T ($<T_{\mathrm{gel}}$), no power-law behavior was found during the transient gelation process. The power-law behavior should have been observed if the system had a self-similar, fractal network structure at T_{gel}. Thus, the observed lack of this behavior indicated that the structural self-similarity vanished over large length scales, possibly due to dynamic compositional fluctuation of the copolymer chains that dominated slow viscoelastic responses at T_{gel} ($\cong T_{\mathrm{ODT}}$). Similar features were observed also for a SI diblock copolymer in C14.

I. Introduction

ABA-type triblock copolymers composed of short, hard A blocks and long, soft B blocks are typical thermoplastic elastomers. These copolymers dissolved in B-selective solvents exhibit rubbery, plastic, and viscous responses at low, intermediate, and high temperatures (T), respectively.[1,2] At low T below the glass transition temperature T_g^A of the A block, the A blocks segregate to form spherical, glassy microdomains. The resulting network structure of the B blocks (cross-linked by these A domains) exhibits the rubbery responses. At intermediate T well above T_g^A but below the order−disorder transition (mixing) temperature T_{ODT}, the A domains are in the liquid state so that they allow the B network structure to flow plastically (by pulling out the connected A block from its domain) under large deformation. At $T > T_{\mathrm{ODT}}$, this structure vanishes, and the system becomes a viscous (or viscoelastic) fluid.

In the linear viscoelastic regime, the above rheological change from the plastic to viscous behavior on the increase of T is observed as a change from the gellike (solidlike) to sollike (liquidlike) behavior. Thus, the ABA triblock copolymer solutions in the B-selective solvents can be classified as a kind of thermoreversible physical gel. It is of particular interest to examine the "gelation" behavior of these solutions within the context of current understanding for gelation of various materials.

For chemical[3−8] and physical gels,[9−13] linear viscoelastic behavior has been extensively studied in the vicinity of the sol−gel transition point. Winter and Chambon[3,4] showed that the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, exhibit the power-law dependence on the angular frequency ω at the critical gelation point

$$G'(\omega) \sim G''(\omega) \sim \omega^n \tag{1}$$

From the Kramers-Krönig relationship, the loss tangent $\tan\delta$ [$=G''(\omega)/G'(\omega)$] at this point is given by

$$\tan\delta = \tan(n\pi/2) = \text{constant} \tag{2}$$

The critical behavior, specified by eqs 1 and 2, emerges when the stress-generating gel network has a self-similarly bifurcated structure (fractal structure) over a wide range of spatial scales.

For the chemically gelling systems, we can fix this self-similar structure by terminating the chemical reaction at a critical conversion. This structure does not change with T (unless the reaction is activated again), resulting in the validity of the time−temperature superposition for the $G'(\omega)$ and $G''(\omega)$ data. This allowed empirical tests of eqs 1 and 2 over an effectively wide range of ω, establishing the critical behavior of many chemical gels.[3−8] For these gels, the power-law index n (cf. eqs 1 and 2) agreed with the prediction of the percolation theory.[14−16]

For physical gels formed by rather weak interactions, e.g., the segregation interaction in block copolymers, the gel network structure often changes with T. Then the time−temperature superposition fails, in particular in the vicinity of the sol−gel transition temperature T_{gel}. In addition, the cross-linkage in some physical gels is easily disrupted under relatively small stress/strain. Thus, it is not easy to observe the critical behavior over a wide ω range for the physical gels. Indeed, for homopolymer-based physical gels,[9−13] the critical behavior specified by eqs 1 and 2 was observed in the ω range covering 4 decades at most. Furthermore, the power-law index n is not the same for these gels.

For the physical gels of our interest, the ABA-type triblock copolymers in B-selective solvents, structural and rheological features have been extensively studied,[1,2,17−19] but the sol−gel transition behavior in the linear viscoelastic regime is not well understood yet, partly because of experimental difficulties explained above. Only a few reports are found for this behavior. For example, Yu et al.[20] studied the sol−gel transition of syndiotactic poly(methyl methacrylate)−polybutadiene−*s*-poly(methyl methacrylate) (MBM) triblock co-

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Table 1. Characteristics of SIS and SI Block Copolymers

code	$10^{-3}M_w$	M_w/M_n	$10^{-3}M_w^{PS}$	M_w^{PI}
SIS-1	50.2	1.07	*7.2[a]	35.8
SIS-2	60.2	1.07	*8.6[a]	43.0
SI[b]	51.6	1.07	8.6	43.0

[a] M_w^{PS} for each PS block for the case of SIS. [b] A precursor SI for SIS-2.

polymers in *o*-xylene and reported power-law behavior (eqs 1 and 2) with $n \cong 0.7$. Soenen et al.[21] found this behavior for a polystyrene−poly(ethylene−butylene)−polystyrene (SEBS) triblock copolymer dissolved in a hydrocarbon oil.

In the above studies by Yu et al.[20] and Soenen et al.,[21] the power-law behavior was observed during the transient gelation process after a thermal quench of the copolymer solution from $T > T_{ODT}$. Thus, this behavior was found only at *high* ω (covering one decade or a little more) where $G'(\omega)$ and $G''(\omega)$ can be accurately measured during the transient process. It is not clear whether this behavior is observed also at low ω. Specifically, we note a possibility that the self-similarity in the gel network structure vanishes and the power-law fails at low ω because of thermodynamic interactions in the block copolymer systems.

Under the above background, we attempted to investigate linear viscoelastic behavior of polystyrene−polyisoprene−polystyrene (SIS) triblock copolymers in an I-selective solvent, *n*-tetradecane (C14), in the vicinity of the sol−gel transition temperature T_{gel}. Considering the importance of the low-ω responses, we conducted measurements for the SIS systems that were isothermally equilibrated at various T around T_{gel}, in addition to the transient experiments after quenching. The low-ω responses were successfully measured in the isothermal state, and deviations from the power-law behavior were observed.

We also investigated the behavior of a SI diblock copolymer in C14. Spherical micelles with S cores and I coronas were formed at low T. These micelles formed a lattice structure at low T to exhibit the solidlike (gellike) linear responses, despite the lack of bridging chains between the micelles.[22] The behavior of the SI/C14 system was compared with that of the SIS/C14 systems to examine the importance of thermodynamic interaction in the "gelation" behavior of the copolymers.

II. Experimental Section

Two polystyrene−polyisoprene−polystyrene (SIS) triblock copolymers and a SI diblock copolymer were synthesized and fully characterized in our previous work.[2,23] Table 1 shows the characteristics of the copolymer samples. The solvent, *n*-tetradecane (C14), was purchased from Wako Chemical Co. Ltd. and used without any purification. The SIS/C14 and SI/C14 solutions were prepared by first dissolving prescribed amounts of the copolymer and C14 in a large excess of benzene and then allowing benzene to thoroughly evaporate.

The linear viscoelastic measurements were performed with laboratory rheometers, ARES and RMS605 (Rheometrics). A cone−plate fixture with a diameter $d = 2.5$ cm and a cone angle $\theta = 0.1$ rad was used for ARES. The cone-plate fixture with $d = 4.0$ cm and $\theta = 0.1$ rad, equipped with a laboratory-made solvent trap that successfully prohibited the solvent (C14) vaporization at high T, was used for RMS605. In both rheometers, the sample temperature was controlled with an accuracy better than 0.1 °C (as revealed from a calibration utilizing a thermocouple). The angular frequencies examined were $\omega = 0.01-100$ rad s^{-1}, and the applied strain amplitude was kept small ($\gamma = 0.005-0.03$) to detect the linear responses. Specifically, very small γ (<0.01) was required to detect those responses at $T \cong T_{gel}$.

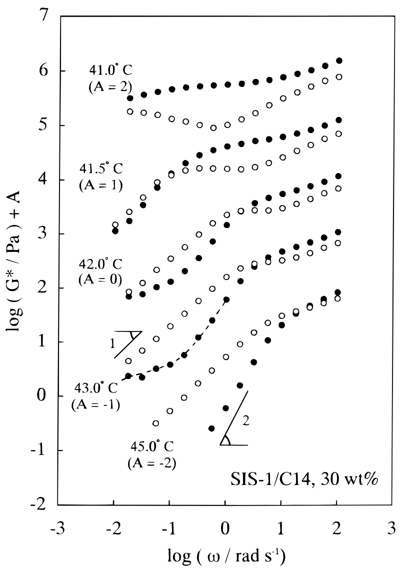

Figure 1. Storage and loss moduli, $G'(\omega)$ and $G''(\omega)$ (filled and unfilled symbols), of a 30 wt % SIS-1/C14 solution at various temperatures. The plots at each temperature are shifted vertically by the factor A as indicated.

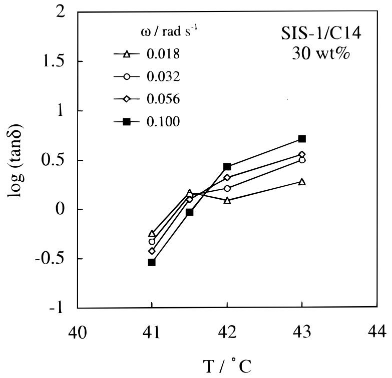

Figure 2. Temperature dependence of tan δ of a 30 wt % SIS-1/C14 solution at various frequencies (ω).

III. Results

Isothermal Behavior of SIS Triblock Copolymer Systems. For a 30 wt % SIS-1/C14 solution, Figure 1 shows the storage and loss moduli, $G'(\omega)$ (filled symbols) and $G''(\omega)$ (unfilled symbols). The $G^*(\omega)$ data at respective T's are shifted vertically by factors of A to avoid heavy overlapping of the data points. The measurements were conducted for the solution isothermally equilibrated at least for 1 h at respective T's. The data, which were very sensitive to T, were accurately and reproducibly obtained in those well-equilibrated states. Figure 2 shows the T dependence of tan δ at low ω.

In Figure 1, the rubberlike and liquidlike behavior is observed at 41.0 and 45.0 °C, respectively. The sol−gel transition of the SIS-1/C14 solution takes place in this narrow range of T, specifically at T_{gel} between 41.0 and 42.0 °C.

One might consider that the critical gelation behavior is observed at this T_{gel}. In fact, Figure 2 indicates that the tan δ value is insensitive to ω (tan $\delta \cong 1.5$) and eq 2 is superficially valid at $T_{gel} \cong 41.7$ °C. However, at 41.5 °C in a close vicinity of this T_{gel}, both $G'(\omega)$ and $G''(\omega)$ are roughly proportional to ω at $\omega < 0.1$ rad s^{-1}

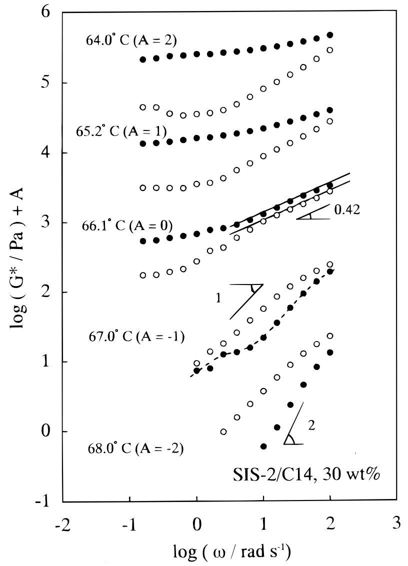

Figure 3. Storage and loss moduli, $G'(\omega)$ and $G''(\omega)$ (filled and unfilled symbols), of a 30 wt % SIS-2/C14 solution at various temperatures. The plots at each temperature are shifted vertically by the factor A as indicated.

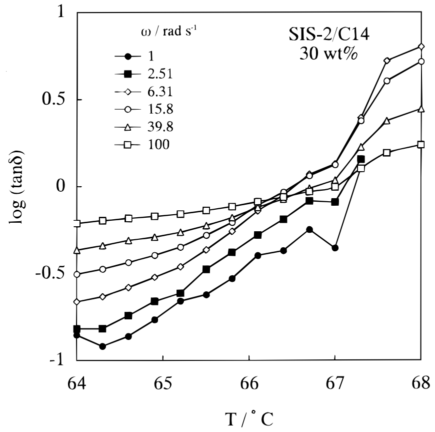

Figure 4. Temperature dependence of tan δ of a 30 wt % SIS-2/C14 solution at various frequencies (ω).

(Figure 1), and the corresponding power-law index, $n \cong 1$, is inconsistent with this tan δ value (cf. eq 2). This result means that the real power-law behavior, specified by both eqs 1 and 2, is not observed for the SIS-1/C14 solution. In other words, the self-similarly bifurcated gel network exhibiting the power-law behavior is not formed in this solution at T_{gel}.

For a 30 wt % SIS-2/C14 solution, Figure 3 shows the ω dependence of $G'(\omega)$ and $G''(\omega)$ (filled and unfilled symbols) at the representative T's in the vicinity of T_{gel}. In Figure 4, the tan δ data are plotted against T. These data were obtained for the solution isothermally equilibrated at respective T's at least for 1 h. The S/I composition is the same for the SIS-2 and SIS-1 samples but the molecular weight M_{SIS} is larger (by a factor of 1.2) for the former; cf. Table 1. Thus, the T_{gel} ($\cong T_{ODT}$) is higher (by $\cong$25 °C) for the SIS-2/C14 solution than for the SIS-1/C14 solution having the same c; cf. Figures 1−4. A similar difference in T_{ODT} was noted also for the SIS-1 and SIS-2 solutions at a higher c, 50 wt %.[2,23]

For the SIS-2 solution, the power-law behavior (eq 1) is observed at high ω at 66.1 °C; cf. solid lines in Figure 3. (For the SIS-2 solution having larger M_{SIS} than the SIS-1 solution, no power-law-like behavior is seen at the low ω examined.) The power-law index of the SIS-2 solution, $n = 0.42$, is consistent with the tan δ value at high ω, and eq 2 is valid. However, $G'(\omega)$ becomes considerably larger than $G''(\omega)$ and exhibits a plateau on a decrease of ω. This behavior is similar to that of the chemically gelling systems with the cross-linking density a little larger than the critical density. At 67.0 °C, $G''(\omega)$ is approximately proportional to ω and $G'(\omega)$ is smaller than $G''(\omega)$, indicating a liquidlike feature at this T. Thus, the gelation temperature T_{gel} is between 66.1 and 67.0 °C.

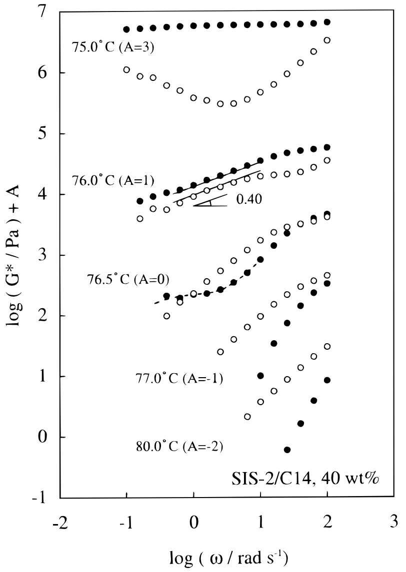

Figure 5. Storage and loss moduli, $G'(\omega)$ and $G''(\omega)$ (filled and unfilled symbols), of a 40 wt % SIS-2/C14 solution at various temperatures. The plots at each temperature are shifted vertically by the factor A as indicated.

From the above results, one might expect that the power-law behavior (eqs 1 and 2) is observed at T between 66.1 and 67.0 °C. However, Figure 4 demonstrates that a cross of the tan δ vs T curves at $T = 66.3 \pm 0.1$ °C is observed only for the data at high ω ($\geq$6.31 rad s^{-1}). For the data at lower ω ($\leq$2.51 rad s^{-1}), we find no indication of the crossing of those curves. Thus, the ω-insensitive tan δ value ($\cong$0.77) is observed, and eq 2 is valid only at high ω. Namely, the SIS-2/C14 solution does not exhibit the *real* power-law behavior (that holds down to low ω) at any T. (The isothermal measurements enabled us to obtain the data at low ω and to find this feature.) Thus, the self-similarly bifurcated gel network was not formed in the two SIS/C14 systems (with $c = 30$ wt %) at their respective T_{gel}'s.

The sol−gel transition behavior of SIS/C14 systems of various c (>30 wt %) was qualitatively similar to that seen for $c = 30$ wt %. As an example, Figure 5 shows the G^* data of a 40 wt % SIS-2/C14 solution at several T's. The T_{gel} is close to T_{ODT} and thus higher for larger c: For SIS-2, $T_{gel} = 66.1-67.0$ °C at $c = 30$ wt % (Figures 3 and 4) and $T_{gel} = 76.0-76.5$ °C at $c = 40$ wt % (Figure 5). (On a further increase in c to 50 wt %, T_{gel} increased to 80−90 °C.[2]) Despite these differences of T_{gel}, the behavior of the 40 wt % SIS-2/C14 solution at T's around T_{gel} (Figure 5) is qualitatively similar to that seen for the 30 wt % solution (Figure 3).

For the $G'(\omega)$ curves of the SIS-1 and SIS-2 systems (of $c = 30$ and 40 wt %) at T just above T_{gel}, we observe a slow relaxation mode separated from fast modes (see the dashed curves in Figures 1, 3, and 5). A similar slow

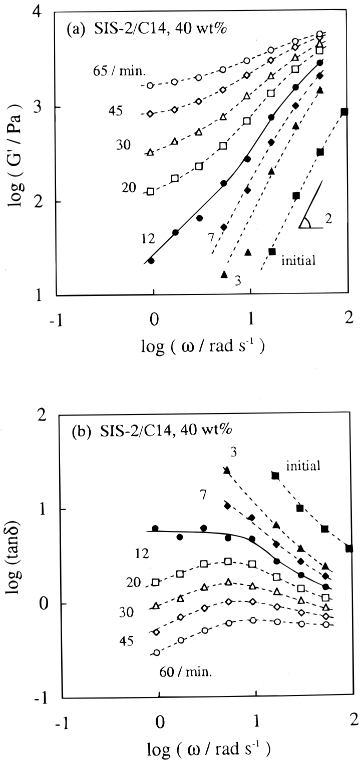

Figure 6. Evolutions of (a) $G'(\omega)$ and (b) tan δ for a 40 wt % SIS-2/C14 solution during the transient gelation process after a temperature-jump from 80.0 to 75.0 °C. The numbers represent the time of the start of dynamic measurements after this jump.

mode was found also at a higher c (= 50 wt %).[2,23] This slow mode is never observed for chemically gelling homopolymer systems. The relationship between the slow mode and the lack of real power-law behavior is discussed later.

Transient Behavior of SIS Triblock Copolymer Systems. The 40 wt % SIS-2/C14 solution has T_{gel} between 76.0 and 76.5 °C (cf. Figure 5). We quenched this solution from 80.0 °C (where the terminal behavior, $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$, is observed in Figure 5) to 75.0 °C ($<T_{\mathrm{gel}}$) and examined the time evolution of $G'(\omega)$ and tan δ values during the transient gelation process. The results are shown in Figure 6. The data referred to as "initial" are the data obtained in the isothermal state at 80.0 °C.

In the above transient test, the solution temperature became constant (=75.0 °C) within 2 min after the temperature control in the rheometer chamber was switched from 80.0 to 75.0 °C. Each set of data began to be measured at a prescribed time t_{m} (numbers in Figure 6) after this T-switch. It took less than 2 min to obtain each set of data at $\omega \geq 1$ rad s^{-1}, meaning that those data reflect the nearly isochronal structure during the gelation that occurred in time scales of ~10 min (The data at lower ω (<1 rad s^{-1}) were affected by transient changes in the gel structure during the measurements and were not accurately determined.)

At $t_{\mathrm{m}} = 12$ min, tan δ becomes almost independent of ω at low ω (≤ 5.34 rad s^{-1}); see Figure 6b. However, $G'(\omega)$ at 12 min is roughly proportional to ω at these ω and the corresponding, apparent power-law index ($n \cong 1$) is inconsistent with the ω-insensitive tan δ value ($\cong 6$); cf. eq 2. Thus, in contrast to the previous results,[20,21] the real power-law behavior was not observed for our SIS/C14 solution during the transient gelation process. (For our solution, the power-law, if valid, was to be observed at ω/rad s^{-1} = 0.251−6.31, as judged from the isothermal $G^*(\omega)$ data at T = 76.0 and 76.5 °C (just below and above T_{gel}) shown in Figure 5.)

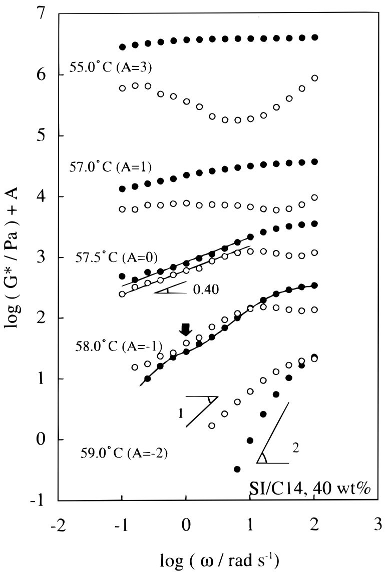

Figure 7. Storage and loss moduli, $G'(\omega)$ and $G''(\omega)$ (filled and unfilled symbols), of a 40 wt % SI/C14 solution at various temperatures. The plots at each temperature are shifted vertically by the factor A as indicated.

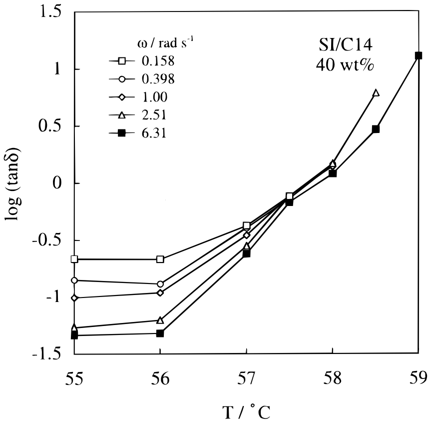

Figure 8. Temperature dependence of tan δ of a 40 wt % SI/C14 solution at various frequencies (ω).

SI Diblock Copolymer System. For a 40 wt % SI/C14 solution, Figure 7 shows the $G'(\omega)$ (filled symbols) and $G''(\omega)$ (unfilled symbols) data in well equilibrated isothermal states at T as indicated. In Figure 8, the corresponding tan δ data at low ω (≤ 6.31 rad s^{-1}) are plotted against T.

In Figure 7, the power-law behavior is observed at $T_{\mathrm{gel}} = 57.5$ °C in a range of $\omega < 6.31$ rad s^{-1}. The power-law index, $n = 0.40$, is consistent with the ω-insensitive tan δ value at this T_{gel} (tan $\delta \cong 0.72$; Figure 8). However, at 58.0 °C, just above T_{gel}, a slow relaxation mode separated from fast modes, which is similar to the slow mode found for the SIS/C14 systems, is observed as the inflection of the $G'(\omega)$ curve (shown with the thick arrow). This separate relaxation mode could have existed also at T_{gel} in a low ω range not covered in our experiments, meaning that we cannot rule out the possibility of the failure of the power-law at low ω even at T_{gel}. This possibility is further discussed later in relation to thermodynamic interactions in block copolymer systems.

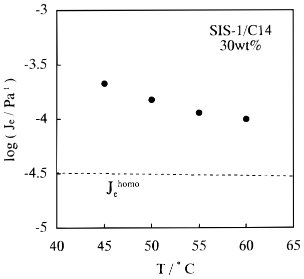

Figure 9. Temperature dependence of the steady-state compliance J_e of a 30 wt % SIS-1/C14 solution at $T > T_{gel}$.

IV. Discussion

Triblock Copolymer System. In the isothermal state at T_{gel}, the power-law behavior of the SIS/C14 solutions, if any, is observed only in a narrow range of ω (at high ω), and a separate relaxation mode is found at low ω; see Figures 1−5. Thus, the power-law behavior is not found for our SIS systems at low ω, meaning that the self-similarity in the gel structure vanishes in large length scales.

Homopolymer-based chemical gels never exhibit the slow, separate mode explained above. From this difference between these gels and SIS solutions, we speculate that an interaction specific to block copolymers (absent for homopolymers) disrupts the self-similarity in the large-scale gel structure and leads to the failure of the power-law for SIS at low ω.

Before discussing the molecular origin of the slow mode in the block copolymer systems, we examine whether this mode corresponds to the motion of individual copolymer chains or not. For this purpose, we can examine changes in the steady-state recoverable compliance J_e ($=[G'/(G'')^2]_{\omega\to 0}$) with T ($> T_{gel}$). If the SIS solutions are homogeneous in both static and dynamic senses, J_e should be insensitive to T in our experimental window ($J_e \sim T^{-1}$ with T in the scale of absolute temperature) and close to the J_e^{homo} value of a corresponding solution of homopolymers.

For the 30 wt % SIS-1/C14 solution in the sol state at $T > T_{gel}$, Figure 9 shows a plot of J_e against T. In this solution, the SIS-1 chains have a reduced molecular weight $M_r = c_{SIS}M_{SIS} \cong 1.3 \times 10^4$ with c_{SIS} ($\cong$0.25 g cm^{-3}) being the mass concentration of SIS. This M_r is close to a characteristic molecular weight M_c ($=1.0 \times 10^4$)[24] for the onset of entanglement for polyisoprene (hI), the major component in SIS. Thus, the SIS chains in the solution are barely entangled. These chains should behave similarly to the corresponding hI chains with $M_{hI} = M_{SIS} = 5.0 \times 10^4$ and $c = 0.25$ g cm^{-3} *if* the SIS solution is homogeneous in both static and dynamic senses.[2,23] The dotted line in Figure 9 shows J_e^{homo} of this hI

$$J_e^{homo} = 2M/5cRT \tag{3}$$

(Experiments[24] indicate that the J_e data of nonentangled and/or lightly entangled homopolymers (with $M_r = cM < 3M_c$) are close to J_e^{homo} given by eq 3 (Rouse model). Good coincidence with this J_e^{homo} value was found also for the J_e data of nonentangled block copolymers in the *homogeneous* state.[2,23])

Clearly, the J_e data of the SIS solution change with T and are considerably larger than J_e^{homo} in the range of T examined. This result suggests that some sort of dynamically heterogeneous structure, that changes with T ($> T_{gel}$), exists in the system and governs the terminal relaxation at $T > T_{gel}$. In other words, the slow mode disturbing the appearance of the power-law behavior at low T is attributed to this structure and not to motion of individual SIS chains.

The above dynamically heterogeneous structure would be the composition fluctuation pattern that has been established for block copolymers at T in the vicinity of T_{ODT}.[25,26] The distortion of this pattern due to the applied strain increases the (dynamic) free energy of systems to raise the mechanical stress, and the relaxation of this distortion occurs via cooperative motion of many copolymer chains and is much slower than the motion of individual chains.

Under the presence of this dynamic fluctuation pattern, the gel network structure of the SIS solution loses its fractal nature at scales larger than the characteristic length scale of the fluctuation. This breakdown of the fractal nature, intimately related to the thermodynamic feature of block copolymers, quite possibly leads to the failure of the power-law seen for our SIS solutions.

Comments on Previous Work. Yu et al.[20] and Soenen et al.[21] observed the power-law behavior for MBM/*o*-xylene and SEBS/hydrocarbon−oil systems during the gelation (microphase separation). In contrast to their results, the power-law behavior is observed in *neither* the isothermal *nor* the transient states for our SIS/C14 systems (cf. Figures 1−6). The observed differences may be attributed to three possible factors. The first factor is the limitation of the ω range examined in the previous studies: The power-law might have vanished at low ω not covered in those studies.

The second factor, suggested by a referee for this paper, is related to the segregated (precipitated) M and/or S domains in the MBM, SEBS, and SIS systems. The previous experiments were conducted at c between 2 and 10 wt % for the MBM systems[20] and at $c = 6$−50 wt % for the SEBS systems.[21] Our experiments for the SIS systems were carried out at $c = 30$ and 40 wt %. Thus, the SIS systems had the volume fraction of the S domains larger than the fractions of the M and/or S domains in most of the MBM and SEBS systems. Those spherical S domains, rather densely packed in the SIS/C14 (as well as SI/C14) systems, might cause the lack of the real power-law behavior.

The third, most important factor is the T dependence of the Flory−Huggins χ parameter that changes from system to system. If this dependence is very strong, the compositional fluctuation would become prominent only in a narrow range of T, resulting in no clear appearance of the slow mode due to this fluctuation at T_{gel}. The power-law behavior may be observed for this case.

Concerning the third factor, we again note that the copolymer is more concentrated in the SIS systems than in most of the previously examined MBM and SEBS systems. Thus, the triblock copolymer network formed at $T \leq T_{gel}$ could have been less stretched (less swollen with the solvent) in the SIS systems. The observed difference between the SIS systems and MBM/SEBS systems, the lack of the real power-law behavior in the former, may be also related to a difference in χ due to this difference in the network stretching.

Diblock Copolymer Systems. As explained for Figures 7 and 8, the SI micellar system at T_{gel} exhibits the power-law behavior at high ω (>0.1 rad s^{-1}). There is no bridging chain between the SI micelles in this solution. Thus, *at high ω*, the power-law behavior can emerge even if the copolymer systems include no networks composed of such bridges. In this sense, thermodynamic interactions in the block copolymer systems potentially have an ability to raise the power-law behavior at high ω.

The slow mode, which disturbs the appearance of this behavior *at low* ω, can be related to the compositional fluctuation commonly existing in the diblock and triblock copolymer systems. For the SI diblock copolymers, this slow mode might be also related to Brownian motion of their micelles, as in the case of SI micelles randomly dispersed in homopolyisoprene matrices.[27] Further studies are desired for the latter mechanism of slow relaxation in the SI/C14 solution.

V. Conclusion

The composition fluctuation, which is unique to block copolymers in the vicinity of T_{ODT}, greatly affects the sol−gel transition behavior of the copolymers. For SIS/C14 systems in the isothermally equilibrated state, the power-law behavior (eqs 1 and 2) emerges only in a narrow ω range at high ω. The separate, slow relaxation mode, possibly due to the composition fluctuation, disturbs the appearance of the power-law at low ω. In transient gelation processes, no power-law behavior is observed for the SIS systems. These results strongly suggest that the self-similarity in the gel network structure at T_{gel} vanishes at large length scales due to the fluctuation effect.

The SI micellar system at T_{gel} exhibits the power-law behavior at high ω, despite the lack of bridging chains (no network structure). This result means that the thermodynamic interactions of the copolymer chains can raise the power-law behavior at high ω. However, at low ω, the power-law behavior at T_{gel} vanishes because of the composition fluctuation (and of the Brownian motion of the micelles).

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