Thermorheological Properties of Hydrogenated Pseudorandom Styrene−Butadiene Copolymers

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ABSTRACT: Rheological properties of amorphous hydrogenated styrene−butadiene copolymers (HSBC) were investigated. The structure corresponds to styrene−ethylene−1-butene terpolymers. Entanglement molecular weights (M_e) of 2380−3270 g/mol were obtained at 50 °C for HSBCs containing 49.5−68.9 wt % of styrene. These values were closer to polyethylene rather than polystyrene. The vertical shift factor, b_T, showed quite different temperature dependence from the classical expression of $b_T = \rho T/\rho_0 T_0$, where ρ and ρ_0 are the densities at temperature T and a reference temperature T_0, respectively. This had also been observed in poly(ethylene-*co*-1-butene) and could be attributed to the temperature coefficient of unperturbed polymer chain dimension, $\kappa = \mathrm{d} \ln \langle R^2\rangle_0/\mathrm{d}T$, by using the packing model. The temperature dependence of b_T indicated the temperature dependence of M_e for HSBCs. The M_e at 140 °C were estimated as 3100−4200 g/mol for HSBCs containing 49.5−68.9 wt % of styrene, which was about 30% higher than at 50 °C. Plateau moduli obeyed the following equation: $G_N{}^0{}_{cp}{}^{1/3}/\rho_{cp} = \Sigma\varphi_j G_N{}^0{}_j{}^{1/3}/\rho_j$, where φ_j is the volume fraction of comonomer j, and $G_N{}^0{}_{cp}$, $G_N{}^0{}_j$ is the plateau modulus and ρ_{cp}, ρ_j is the density of the copolymer and homopolymer j, respectively. This relation could also be applied to poly(ethylene-*co*-1-butene). The dependence of plateau moduli on backbone chain length suggested that styrene comonomer incorporation into ethylene-based polymers increases the trans conformation, while α-olefin incorporation increases the gauche conformation.

1. Introduction

Recent improvement of catalyst synthesis and polymerization techniques allows synthesizing new types of copolymers, especially ethylene-derived copolymers. Because these copolymers may exhibit new properties, their effective development is of great technical and economic importance. Since there are numerous adjustable parameters in developing copolymers, e.g., a variation of comonomer and their contents, molecular weight, and molecular weight distribution, it will be a great help for an effective development to predict properties of copolymers before a development process. Since chain entanglement plays a key role for controlling the processing and final properties, it is desirable to predict entanglement properties of the copolymers from the constituent homopolymers. Although many studies have compared entanglement properties of copolymers with those of corresponding homopolymers, a comprehensive relationship is still missing. Since comonomer incorporation would give some effect on polymer chain conformation, it would be helpful to consider the relationship between polymer chain parameters, such as the unperturbed mean-square end-to-end distance $\langle R^2\rangle_0$, and entanglement properties, such as the plateau modulus $G_N{}^0$ and the entanglement molecular weight M_e.

Several theoretical works have tried to predict $G_N{}^0$ and M_e by correlating them to chain properties, like $\langle R^2\rangle_0$ and the characteristic ratio C_∞.[1−5] The “packing model”, developed by Fetters and co-workers[3,4] on the basis of earlier works,[6−11] is one of the most powerful methods for the prediction of entanglement properties from data of chain structure of the polymer and vice versa. The basic idea of this model is that the larger the dimensions of a chain, the greater is the volume it sweeps out, and therefore the greater is the number of other chains with which it might entangle. From the relationship between the volume the chain occupies (given by M/ρ where M is the molecular weight and ρ is the density of the polymer) and the volume spanned by the chain, they proposed the following relationship

$$G_N{}^0 \propto Tp^{-3} \tag{1}$$

$$p = \frac{M}{\langle R^2\rangle_0 \rho N_A} \tag{2}$$

where p is the packing length and N_A is Avogadro’s number. Since $\langle R^2\rangle_0$ can be expressed as $\langle R^2\rangle_0 = N_K b_K{}^2$, using b_K as the Kuhn length and N_K as the number of Kuhn steps, eq 2 can also be expressed as follows

$$p = \frac{M}{b_K{}^2 N_K \rho N_A} = \frac{(\pi/4)d^2}{b_K} \tag{3}$$

where d is the effective chain diameter. Hence, the larger p is, the thicker the chain is. The authors applied this model to various kinds of polymers and confirmed its applicability.[3,4]

Fetters and coauthors[12] observed the following relationship between comonomer content and $\langle R^2\rangle_0$ for poly(ethylene-*co*-1-butene):

$$\langle R^2\rangle_0/M \propto \mathrm{e}^{-A\alpha_B} \tag{4}$$

where A is an empirical constant and α_B is the number of ethyl branches per 100 backbone carbons, which means the mole fraction of 1-butene in the copolymer,

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n_B, can be described as $n_B = \alpha_B/50$. By using the packing model together with eq 4, the following relationship between the plateau modulus of the copolymers and those of the corresponding homopolymers can be found (see Appendix)

$$\log(G_{N\ cp}^{0}/\rho_{cp}^{3}) = \sum n_j \log(G_{N\ j}^{0}/\rho_j^{3}) \tag{5}$$

where $G_N{}^0{}_{cp}$ and ρ_{cp} are the plateau modulus and the density of the copolymer, n_j is the mole fraction of a comonomer with $\sum n_j = 1$, and $G_N{}^0{}_j$ and ρ_j are the plateau modulus and the density for the corresponding homopolymer j. Equations like (5) are called mixing rules because they allow one to predict the properties of any copolymer of desired composition from the properties of the corresponding homopolymers. In a sense, we can say eq 5 is the limit for a more general mixing rule:

$$\left[\frac{G_N{}^0}{\rho^3}\right]_{cp}^{1/a_n} = \sum_j n_j \left[\frac{G_N{}^0}{\rho^3}\right]_j^{1/a_n} \tag{6}$$

where a_n is a parameter defining the degree of nonlinearity. In the limit of $a_n \rightarrow \infty$, eq 6 can be considered as identical to eq 5.

Sun and coauthors[13] reported that square of radius of gyration $R_g{}^2$ of various α-olefin copolymers in trichlorobenzene at 135 °C, which is a good solvent, vary linearly with comonomer weight fraction. Assuming a similar relationship can be applied to $\langle R^2\rangle_0$, namely

$$[\langle R^2\rangle_0/M]_{cp} = \sum w_j [\langle R^2\rangle_0/M]_j \tag{7}$$

where w_j is the weight fraction of comonomer j, we can derive following general mixing rule by applying packing model to eq 7.

$$\left[\frac{G_N{}^0}{\rho^3}\right]_{cp}^{1/a_w} = \sum_j w_j \left[\frac{G_N{}^0}{\rho^3}\right]_j^{1/a_w} \tag{8}$$

Here a_w is again a parameter defining the degree of nonlinearity and considered as 3 in this case. Since in the case of polyolefin copolymers difference of densities between constituent homopolymers are not so large, a mixing rule with volume fraction φ_j as the concentration measure might also be plausible.

$$\left[\frac{G_N{}^0}{\rho^3}\right]_{cp}^{1/a_\varphi} = \sum_j \varphi_j \left[\frac{G_N{}^0}{\rho^3}\right]_j^{1/a_\varphi} \tag{9}$$

The volume fraction φ_j is calculated as follows:

$$\varphi_j = \frac{\dfrac{w_j}{\rho_j}}{\displaystyle\sum_i \frac{w_i}{\rho_i}} \tag{10}$$

A similar mixing rule was proposed by Wu and Beckerbauer.[14] They examined copolymers and terpolymers consisting of methyl methacrylate, styrene, and *N*-phenylmaleimide and proposed the following relationship for plateau modulus

$$\log G_{N\ cp}^{0} = \sum \varphi_j \log G_{N\ j}^{0} \tag{11}$$

where φ_j is the volume fraction of comonomer j. Although eqs 5 and 11 look very similar, there will be significant differences for copolymers composed of monomers of very different molecular weight, since the difference between mole and volume fractions become quite large for those copolymers. Therefore, the question regarding the validity of those equations is important.

Moreover, Chen and co-workers[15] studied creep behavior of ethylene–styrene copolymer in the glass transition region and reported very small entanglement molecular weight (M_e). The values were 1600, 1870, and 2040 g/mol for the copolymers containing 62, 69, and 72 wt % of styrene, respectively. The values were closer to the M_e of polyethylene (1390 g/mol)[2] than polystyrene (18 700 g/mol).[2] They also mentioned that the plateau moduli obeyed the volume-mixing rule like eq 11 when the copolymers were considered as copolymers consisting of ethylene–styrene dimer and ethylene.[16] Copolymers consisting of styrene and olefins are interesting since the corresponding homopolymers are widely used, and their chemical natures are very different, although only few rheological studies have been done for this polymer[15–19] due to the difficulty of polymerization.

In this study, we investigate melt rheology of copolymers similar to ethylene–styrene copolymer, prepared by hydrogenation of pseudo-random styrene–butadiene copolymers. The polymer structure is essentially that of a styrene–ethylene–1-butene terpolymer. There are two areas of focus in this study.

First, we examine the themorheological effects of styrene comonomer incorporation on chain characteristics and rheological properties of copolymers compared with α-olefin incorporation into polyethylene. Because of the difference in conformational properties, it is expected that chain characteristics, and hence rheological properties, will be changed with the styrene incorporation. With the aid of the packing model, we can observe the change of chain characteristics by examining the dependence of plateau modulus on comonomer contents. We can also examine the temperature dependence of $G_N{}^0$, namely the temperature dependence of b_T, and make inferences about rotational isomeric state.

Second, we examine the relationships of plateau modulus between a copolymer and homopolymers that is constructed of component comonomers. In the case of this study, we would like to find a relation that adequately explains the plateau modulus of the hydrogenated styrene–butadiene copolymer (HSBC) by using plateau moduli of polystyrene, polyethylene, and poly(1-butene). We prepared several kinds of HSBCs with different comonomer contents. As we avoided the difficulty of obtaining plateau moduli caused by crystallinity, the number and the comonomer contents variety of copolymers were not enough for establishing the rule by itself. We therefore examine possible mixing rules described above together with plateau moduli of poly(ethylene-*co*-1-butene) from literature data[3,20] to determine whether the same mixing rule as for polyolefin copolymers can be applied to the styrene-incorporated copolymer. Because of the adoption of anionic polymerization for preparation, we could compare entanglement properties of HSBCs with those of polystyrene and poly(ethylene-*co*-1-butene), which were also prepared by anionic polymerization, without considering the effects of tacticity on the properties.

Table 1. Characteristics of Polymers

polymer code	composition (wt %)			T_g (°C)	mol wt[a]	
	styrene	ethylene	1-butene		M_w (kg/mol)	M_w/M_n
SEB50	49.5	39.1	11.4	−13.7	315.0	1.33
SEB57	57.4	35.0	7.6	−1.0	169.0	1.37
SEB59w	58.7	32.5	8.8	−0.8	247.8	1.89
SEB69	68.9	27.6	3.5	19.1	169.1	1.27
PS330	100.0	0.0	0.0	105.5	330.0	1.10

[a] Polystyrene equivalent molecular weight.

2. Experimental Section

Polymer Preparation. Hydrogenated styrene−butadiene copolymers (HSBC) and polystyrene (PS) were studied. Table 1 lists all the polymers used. The PS330 was provided by BASF.

The HSBCs were prepared by hydrogenation of styrene−butadiene copolymers. The styrene−butadiene copolymers were synthesized by anionic polymerization using *n*-butyllithium as an initiator in a cyclohexane solvent. Commercially available monomers and solvent were purified in the usual way. Since butadiene monomer is more favorable to react to lithium chain end than styrene,[21] we took special care for polymerization process in order to uniformly maintain the incorporation ratio of styrene to butadiene during the reaction.

SEB50, SEB57, and SEB69 were prepared by semibatch polymerization. Diluted monomers were continuously fed to the reactive solution in a stirred reactor vessel in order to keep the ratio of styrene monomer to butadiene monomer in the solution constant during the polymerization process. In addition, about 0.7 mol of *N,N,N′,N′*-tetramethylethylendiamine (TMEDA) for 1 mol of lithium initiator was added to the solution at the beginning in order to make the reactivity of styrene close to that of butadiene.[21] The reactions were carried out at 70−90 °C for about 1 h. To confirm the uniformity of the comonomer incorporation during the copolymerization, we took several samples from the reactor during the reaction and measured unreacted monomer concentration with gas chromatography for SEB57. We confirmed that the composition of the copolymer during reaction was within 2% deviation from the values listed in Table 1.

SEB59w were prepared by the continuous polymerization technique. The initiator, TMEDA, and monomers with solvent were continuously fed to the bottom of a stirred reactor, and the polymer solution was continuously removed from the top of reactor. About 0.9 mol of TMEDA for 1 mol of lithium was added. Reaction was carried out at about 90 °C, and the average residence time was 45 min.

To confirm uniform comonomer incorporation during the copolymerization, we performed ozonolysis−GPC measurement[22] for SEB59w. Double bonds of butadiene units in the copolymer were decomposed by ozonolysis, and then residual styrene sequences were measured with GPC. Figure 1 shows the GPC curve. The three distinct peaks correspond to styrene monomer (S_1), dimer (S_2), and trimer (S_3). The area of these three peaks amounts to more than 90% of total area of the GPC chart, and no significantly large styrene sequence can be seen. So we assume that styrene was almost randomly incorporated into the copolymer.

After each polymerization, heptanol was added for terminating the reaction. Then hydrogenation of butadiene unit was carried out using bis(cyclopentadienyl)titanium compound as a catalyst and triethyl aluminum as a cocatalyst in a cyclohexane solvent. Hydrogenation of styrene unit could not be observed for this system by UV absorption or ^{1}H NMR for this catalyst. The pressure of hydrogen was about 0.6 MPa, and the temperature was 70−90 °C.

Molecular Characterization. The microstructure of the copolymers was determined by measuring ultraviolet (UV) absorption spectra and infrared (IR) absorption spectra for prehydrogenated styrene−butadiene copolymers. The proportion of styrene to the copolymers was determined by UV absorption spectra (absorption bands at 269 nm). Measurements were made with diluted styrene−butadiene copolymer solution in chloroform. The calibration curve was made from various styrene−butadiene copolymers for which styrene contents were already known. The proportions of 1,2 (vinyl), 1,4-cis, and 1,4-trans additions in butadiene incorporation were determined by IR spectroscopy. Absorption bands at 911, 724, and 967 cm^{-1}, respectively, and extinction coefficients determined by Hampton[23] were used. Measurements were made with styrene−butadiene copolymer solution in carbon disulfide. The 1,2 and 1,4 additions correspond to 1-butene and ethylene units, respectively, after hydrogenation. The degree of hydrogenation was obtained by comparing IR absorption before and after hydrogenation, and it was higher than 97%.

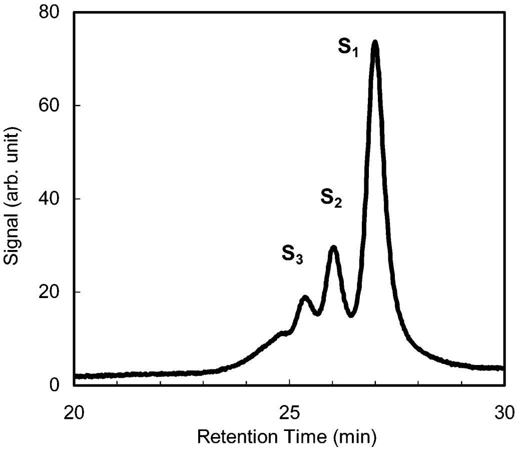

Figure 1. Ozonolysis GPC curve for SEB59w.

The molecular weights M_w and M_n and polydispersity M_w/M_n were determined by GPC using THF as solvent at 40 °C. The GPC was calibrated with polystyrene standards.

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC). Measurements were made at a heating rate of 10 K/min, and the temperature at the midpoint of heat capacity jump was taken as a T_g. Crystallization was not observed in the DSC measurement.

Melt density of HSBC at a certain temperature was estimated by interpolation of melt densities of polystyrene and hydrogenated polybutadiene by weight. The method is valid for the ethylene−styrene copolymer.[24] The melt density of polystyrene at a temperature above T_g was obtained from an earlier publication.[25] The melt density at a temperature below T_g was obtained by linear extrapolation from above T_g. Typical values used for this study were 1.057, 1.002, and 0.985 g/cm^3 for 50, 140, and 170 °C, respectively. The melt density of hydrogenated polybutadiene was estimated as 0.837 and 0.784 g/cm^3 for 50 and 140 °C.[26]

Melt Rheology. For the rheological measurements, the HSBC and polystyrene pellets were dried under vacuum at 60 °C for several days. The samples were compression-molded at 200 or 170 °C in a vacuum to form disks 25 mm in diameter with a thickness of about 1.5 mm. The dynamic shear moduli G' and G'' were obtained with a Rheometrics ARES rheometer in 25 mm parallel plate geometry under a nitrogen atmosphere. The applied strains were within the limits of linear viscoelasticity, i.e., within 5%. Isothermal frequency sweeps were recorded in the frequency range from 10^2 to 10^{-1} rad/s. The temperature was changed between 30 and 210 °C for HSBCs and between 130 and 220 °C for PS330.

3. Results and Discussion

Master Curves and Shift Factors. Figure 2 shows the $\delta-|G^*|$ plots for SEB57 and PS330. For SEB57, two plateaus are visible in the plots. As $|G^*|$ values get smaller, the first plateau of δ seems to exist around 72°−80° for $|G^*| \sim 2 \times 10^4$ Pa, and then the δ values go closer to 90°, the second plateau. This is attributed to the presence of a small portion of high molecular weight

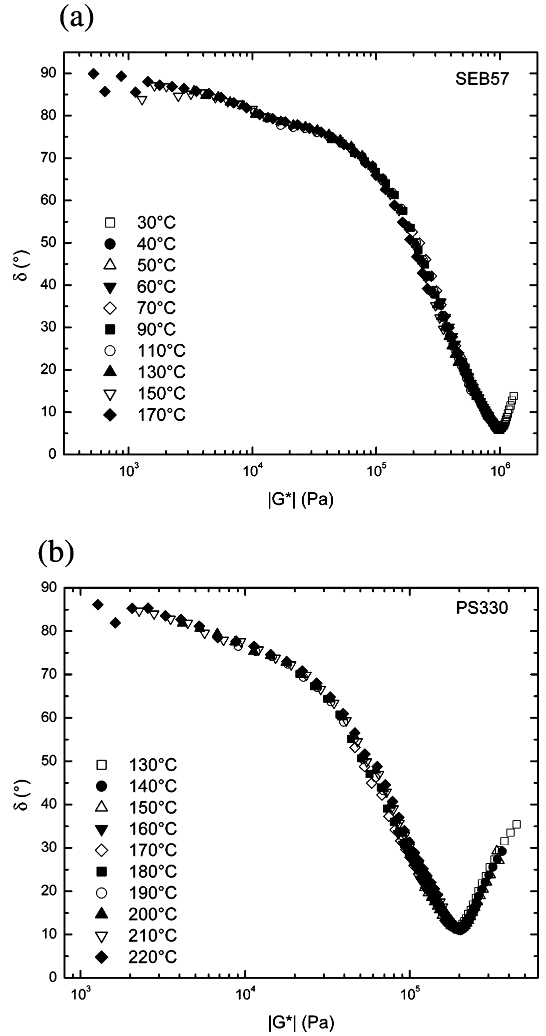

Figure 2. $\delta - |G^*|$ plots for (a) SEB57 and (b) PS330.

component. This is also supported by the GPC chart where a little bump is present at a molecular weight of about 2 times higher than the main peak. The weight fraction of the high molecular content was estimated as less than 8% from the GPC chart. This could be due to the coupling reaction at the two lithium ends during the polymerization process. Since the polymerization took place over a long period at a low concentration of monomers, especially at the last stage of synthesis, coupling reactions seemed to have occurred. We presume that these bumps have no effect on obtaining plateau modulus. Because of the fact that the isotherms fall on one common line without any shifting, the time−temperature superposition principle appears to work for the polystyrene and copolymers. Figure 3 shows the master curves of shear storage modulus G', loss modulus G'', and loss tangent tan δ for SEB57 and PS330. The reference temperatures were 50 °C for SEB57 and 170 °C for PS330. The shifts were performed for both horizontal and vertical directions by the least-squares method using the LSTEMP software.[27] Horizontal and vertical shifts were also independently carried out to confirm the validity of the shift factors: first, tan δ isotherm curves were shifted only horizontally to obtain a_T values, and then horizontally shifted G' and G'' isotherms were vertically shifted to obtain b_T values. As the shift factors obtained by these two methods were essentially the same, their reliability was confirmed.

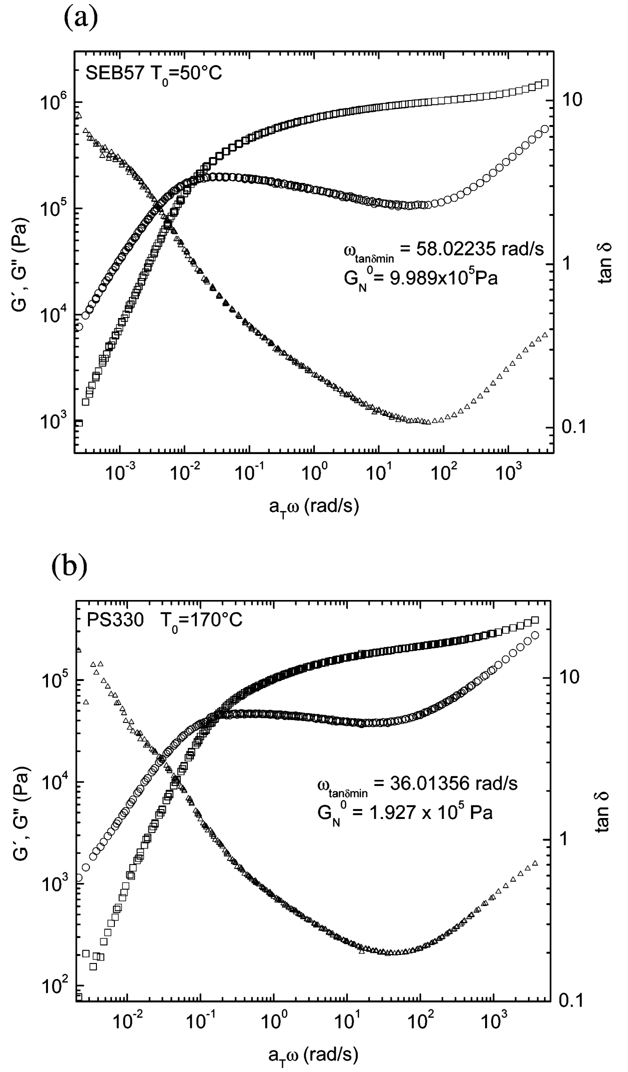

Figure 3. Master curves for (a) SEB57 and (b) PS330. The reference temperature was 50 °C for SEB57 and 170 °C for PS330.

The shift factor a_T obtained in this study can be expressed by the WLF equation[28]

$$\log a_T = -c_1(T - T_0)/(c_2 + T - T_0) \quad (12)$$

$$f_0 = B/2.303c_1 \quad (13)$$

$$\alpha_f = B/2.303c_1c_2 \quad (14)$$

where f_0 is the fractional free volume at an arbitrary reference temperature T_0 and α_f is the thermal expansion coefficient of the fractional free volume. Table 2 shows the parameters characterizing temperature dependence of a_T at the reference temperatures 70−84 °C above the glass transition temperatures. Carella and coworkers[29] reported $c_1 = 6.35$ and $c_2 = 146$ K as the parameters for hydrogenated polybutadiene, which were independent of 1-butene content, at the reference temperature of $T_g + 77$ °C. In the present case, both f_0/B and α_f/B seem to be dependent on comonomer content. Although there are some differences in $T_0 - T_g$ for each polymer in Table 2, we can compare α_f values since the product c_1c_2 is independent of temperature.[28] The value for hydrogenated polybutadiene is $\alpha_f/B = 4.68 \times 10^{-4}$ K^{-1}, which is very close to SEB50. According to Ferry,[28]

Table 2. Parameters Characterizing Temperature Dependence of a_T

					WLF parameters			
polymer code	styrene (mol %)	T_g (°C)	T_0 (°C)	$T_0 - T_g$ (°C)	c_1	c_2 (K)	f_0/B	α_f/B (10^{-4} K^{-1})
HPB[a]	0			77	6.35	146	0.068	4.684
SEB50	21.8	−13.7	70.0	83.7	6.02	155.9	0.072	4.628
SEB57	27.4	−1.0	70.0	71.0	6.15	135.1	0.071	5.225
SEB59w	28.6	−0.8	70.0	70.8	5.72	121.2	0.076	6.268
SEB69	37.8	19.1	90.0	70.9	5.95	132.5	0.073	5.508
PS330	100.0	105.5	180.0	74.5	4.94	120.7	0.088	7.279

[a] Hydrogenated polybutadiene. The data were taken from ref 22.

B can be considered as unity. This suggests the free volume expansion of HSBCs is smaller than that of polystyrene and close to that of hydrogenated polybutadiene. On the other hand, reported thermal expansion coefficients obtained by the PVT measurement are $\alpha = (5.4-5.7) \times 10^{-4}$ K^{-1} (100−230 °C)[25] for polystyrene and $\alpha = (7-8) \times 10^{-4}$ K^{-1} (50−170 °C)[26,30−32] for hydrogenated polybutadiene. The tendency of α obtained with the two methods is contrary: one method provided higher α for polystyrene than hydrogenated polybutadiene while the other gave the reverse result. When considering this fact, it seems inappropriate to consider B as a material independent parameter: the value for polystyrene is higher than for hydrogenated polybutadiene, and the values for HSBCs may lie in between.

The vertical shift factor b_T is defined by the temperature dependence of the plateau modulus $G_N{}^0$ as follows:

$$b_T \equiv \frac{G_N{}^0(T)}{G_N{}^0(T_0)} \tag{15}$$

The plateau modulus of $G_N{}^0$ measured at temperature T is connected with the entanglement molecular weight, M_e, in the following way:

$$G_N{}^0 = K\frac{\rho RT}{M_e} \tag{16}$$

where R is the gas constant and K is a constant, 1[28] or 4/5.[33] Applying eq 16 to eq 15, we obtain

$$b_T = \frac{\rho(T)T}{\rho(T_0)T_0}\left(\frac{M_e(T)}{M_e(T_0)}\right)^{-1} \tag{17}$$

Normally, M_e is considered as almost independent of temperature, and the following expression is used:

$$b_T = \frac{\rho(T)T}{\rho(T_0)T_0} \tag{18}$$

The temperature dependence of b_T for PS330 and SEB50 is shown in Figure 4. The slope for SEB50 is negative, which is contrary to the positive slope for PS330. The temperature dependence was close to eq 18 for PS330, but rather strange for SEB50. If eq 18 could be applied for SEB50, the thermal expansion coefficient would be $\alpha = -\mathrm{d}\ln\rho/\mathrm{d}T\,|_{T_0} = (3-4) \times 10^{-3}$ K^{-1}, which is too large compared to the thermal expansion coefficient of polystyrene and hydrogenated polybutadiene.

The slope of b_T vs T plot for HSBCs at the reference temperature of 130 °C, $\mathrm{d}b_T/\mathrm{d}T\,|_{T_0}$, obtained by assuming a linear relation between b_T and T, are plotted against ethylene comonomer content in Figure 5. Values for hydrogenated polybutadiene[29] and polyethylene[2,20] obtained from temperature dependence of plateau moduli are also plotted in Figure 5. The tendency of both kinds of copolymers is quite similar. If eq 18 is valid, which means M_e is almost independent of temperature, $\mathrm{d}b_T/\mathrm{d}T\,|_{T_0}$, is expressed by the following equation:

$$\left.\frac{\mathrm{d}b_T}{\mathrm{d}T}\right|_{T_0} = \left.\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\rho T}{\rho_0 T_0}\right)\right|_{T_0} = \left.\left(\frac{\rho}{\rho_0 T_0}\frac{\mathrm{d}T}{\mathrm{d}T}\right)\right|_{T_0} + \left.\left(\frac{T}{\rho_0 T_0}\frac{\mathrm{d}\rho}{\mathrm{d}T}\right)\right|_{T_0} = \frac{1}{T_0} - \alpha_0 \tag{19}$$

where α_0 is α at $T = T_0$. In this case $1/T_0 = 1/(273 + 130) = 2.48 \times 10^{-3}$ K^{-1}. Since α is normally on the order of 10^{-4}, $\mathrm{d}b_T/\mathrm{d}T\,|_{T_0}$ should be positive, but both copolymers showed negative $\mathrm{d}b_T/\mathrm{d}T\,|_{T_0}$ at high ethylene content side. This fact indicates a marked temperature dependence of M_e for ethylene containing copolymers: M_e becomes smaller at lower temperature.

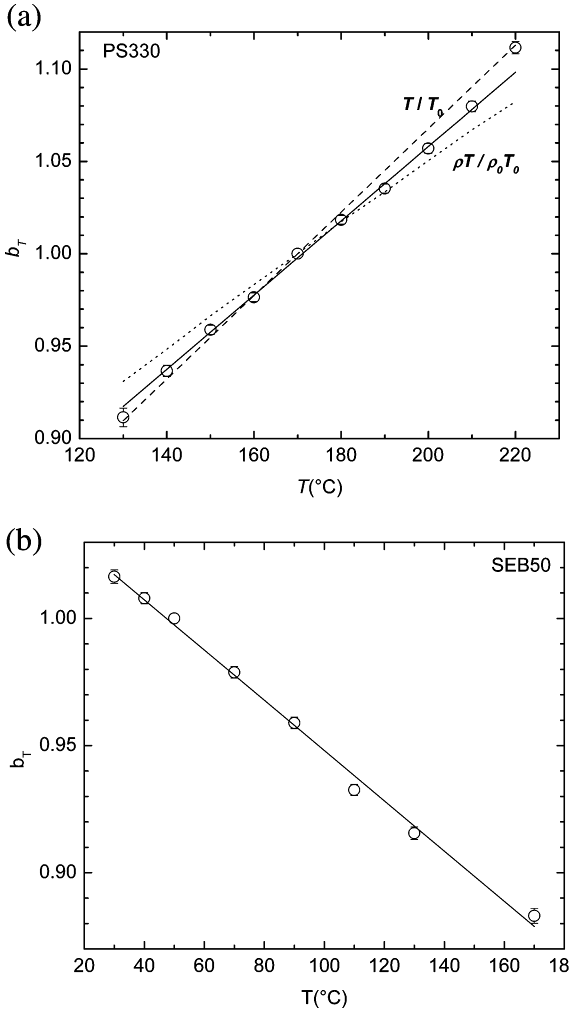

Figure 4. Temperature dependence of vertical shift factor b_T for (a) PS330 and (b) SEB50. The dotted line in (a) is $\rho T/\rho_0 T_0$, and the dashed line is T/T_0.

Table 3. Plateau Moduli and Entanglement Molecular Weight of HSBCs and Polystyrene

polymer code	T_0 (°C)	density at T_0 (g/cm^3)	(a) $G'(\omega_{\tan\delta_{\min}})$ $G_N{}^0$ (MPa)	(a) $G'(\omega_{\tan\delta_{\min}})$ M_e (g/mol)	(b) $\lvert G^*\rvert_{\delta_{\min}}$ $G_N{}^0$ (MPa)	(b) $\lvert G^*\rvert_{\delta_{\min}}$ M_e (g/mol)
SEB50	50	0.946^a	1.068	2379	1.088	2334
SEB57	50	0.963^a	0.999	2590	1.015	2549
SEB59w	50	0.966^a	0.837	3101	0.830	3127
SEB69	50	0.989^a	0.812	3270	0.818	3246
PS330	170	0.985^b	0.193	18825	0.202	17962

^{a} Estimated values as described in the Experimental Section. ^{b} Reference 19.

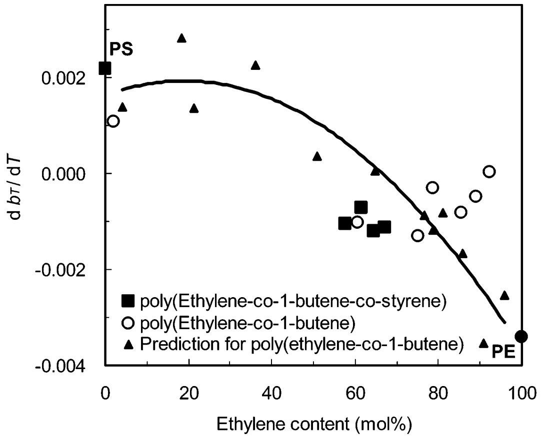

Figure 5. Slopes of plots of b_T ($T_0 \sim 130$ °C) vs temperature against ethylene content for hydrogenated styrene−butadiene copolymer (open squares) hydrogenated polybutadiene (open circles, calculated from data by Carella and co-workers[22]) and polyethylene (closed circle, calculated from data by Fetters and co-workers[13]). Closed triangles are estimates for poly(ethylene-*co*-1-butene) by the Packing model using κ ($= \mathrm{d}\ln\langle R^2\rangle_0/\mathrm{d}T$) measured by Fetters and co-workers[6] and α ($= -\mathrm{d}\ln\rho/\mathrm{d}T$) estimated from interpolation of the values obtained by Graessley and co-workers[24] at 121 °C. The solid line is a polynomial fit (second order) of the estimation and serves only as a guide for the eye.

Correspondingly, the vertical shift factor can alternatively be expressed by using eqs 1 and 2 as follows:

$$b_T \equiv \frac{G_N{}^0(T)}{G_N{}^0(T_0)} = \frac{Tp(T)^{-3}}{T_0p(T_0)^{-3}} = \frac{\rho(T)T}{\rho(T_0)T_0}\left[\frac{\rho(T)[\langle R^2\rangle_0(T)]^{3/2}}{\rho(T_0)[\langle R^2\rangle_0(T_0)]^{3/2}}\right]^2 \qquad (20)$$

Thus, eq 18 is valid for polymers to which $(\langle R^2\rangle_0(T))^{3/2} \propto \rho(T)^{-1}$ can be applied. Both $(\langle R^2\rangle_0(T))^{3/2}$ and $\rho(T)^{-1}$ have volume dimension: $(\langle R^2\rangle_0)^{3/2}$ is considered as the volume a polymer chain pervades, and $1/\rho$ is considered as the specific volume. Thus, eq 20 as a whole suggests the deviation of the temperature dependence of b_T from the classical expression of b_T (eq 18) is due to the difference of thermal expansion coefficient between the specific volume and the volume a single chain pervades.

Using eq 20, temperature dependence of b_T can be expressed alternatively

$$\left.\frac{\mathrm{d}b_T}{\mathrm{d}T}\right|_{T_0} = \left.\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{T\rho(T)^3[\langle R^2\rangle_0(T)]^3}{T_0\rho(T_0)^3[\langle R^2\rangle_0(T_0)]^3}\right)\right|_{T_0} = \frac{1}{T_0} - 3\alpha_0 + 3\kappa_0 \qquad (21)$$

where κ is the temperature coefficient of unperturbed polymer chain dimension described as $\kappa = \mathrm{d}\ln\langle R^2\rangle_0/\mathrm{d}T$ and κ_0 is κ at $T = T_0$. For poly(ethylene-*co*-1-butene), κ was obtained by Fetters and co-workers,[12] and α can be estimated from the data obtained by Graessley and co-workers[31] at 121 °C. The calculated data are plotted as closed triangles in Figure 5, and solid line is the second-order polynomial fit for guiding the eye. The predicted values could sufficiently explain the tendency of the temperature dependence of b_T for poly(ethylene-*co*-1-butene). Since κ is very sensitive to 1-butene content in contrast to the value of α and has strong negative values at high ethylene content side, the main cause of the observed negative temperature dependence of b_T could be attributed to κ. Since the energy state of gauche conformation in polyethylene is higher than that of trans conformation, the trans conformation is more favorable at low temperature, resulting in the negative κ and the negative temperature dependence of b_T. As comonomers like 1-butene and styrene are being incorporated, the energy difference between trans and gauche is assumed to decrease, and the degree of negative temperature dependence of b_T diminishes.

Plateau Moduli. The plateau moduli of HSBCs and polystyrene were obtained from the storage modulus (G') at the frequency where tan δ is at a minimum. The plateau moduli were also obtained from $|G^*|$ where δ is at a minimum in the $\delta-|G^*|$ plot. The values are listed in Table 3. The entanglement molecular weight, M_e, calculated with eq 16 ($K = 1$) are also listed in the table. The $G_N{}^0$ values obtained by the two methods conform well together. This is quite natural in a sense because both methods are essentially the same. Considering the high weight fraction of styrene incorporated into the copolymers, $G_N{}^0$ and M_e were much closer to those of polyethylene ($G_N{}^0 = 2.1$ MPa and $M_e = 1390$ g/mol at 190 °C[2]) than those of polystyrene, as observed for ethylene−styrene copolymer.[15]

To compare the plateau moduli at the same temperature, we converted the $G_N{}^0$ of polymers to 140 °C by applying b_T to eq 15. The b_T at 140 °C were obtained by interpolation of b_T vs T plots. The reduced $G_N{}^0$ and M_e values are listed in Table 4. The M_e values were about 30% larger than the values at 50 °C.

Although one of the objectives was to derive an equation predicting a plateau modulus of a copolymer from plateau moduli of homopolymers, the number of our data was unfortunately not enough for this purpose. We therefore examined our data together with the reported plateau moduli of hydrogenated polybutadiene (the structure corresponded to poly(ethylene-*co*-1-butene) at 140 °C obtained by Fetters and co-workers.[3,20]

As mentioned in the Introduction, the analysis of comonomer content dependence of $\langle R^2\rangle_0$ for poly(ethylene-*co*-1-butene) by Fetters and co-workers (eq 4) led to an expression of plateau modulus as described in eq 5. More generally, the form of eq 6 might be used. Additionally, we examine other similar forms of a mixing rule as described in eqs 8 and 9.

Plateau moduli of hydrogenated polybutadiene and HSBC at the reference temperature of 140 °C are

Table 4. Plateau Moduli Reduced to 140 °C

polymer code	styrene content (wt %)	(vol %)	(mol %)	T_0 (°C)	$G_N^0(T_0)$ (MPa)	b_T(140 °C)	G_N^0(140 °C) (MPa)	ρ(140 °C) (g/cm^3)	M_e(140 °C) (g/mol)
SEB50	49.5	43.7	22.9	50	1.068	0.904	0.966	0.892[a]	3095
SEB57	57.4	51.6	28.5	50	0.999	0.897	0.896	0.909[a]	3399
SEB59w	58.7	53.0	30.0	50	0.837	0.937	0.784	0.912[a]	3896
SEB69	68.9	63.7	38.7	50	0.812	0.917	0.745	0.934[a]	4203
PS330	100	100	100	170	0.193	0.938	0.181	1.002[b]	18578

[a] Estimated values as described in the Experimental Section. [b] Reference 19.

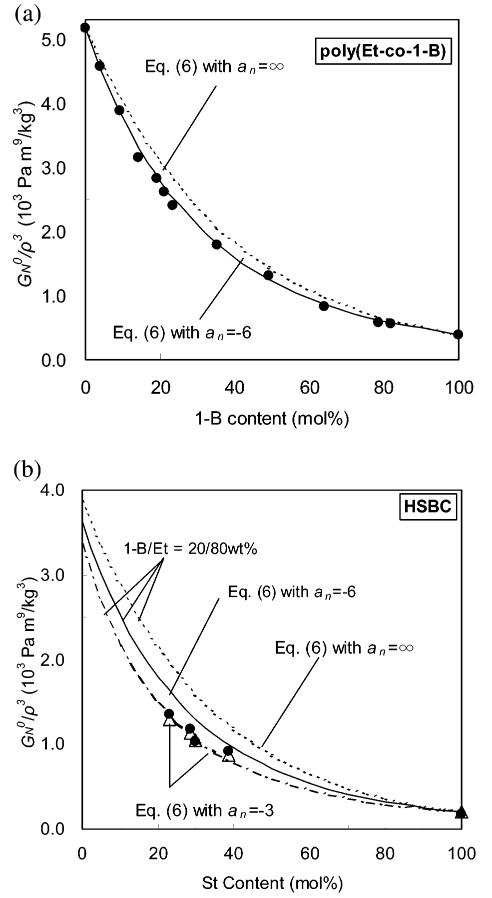

Figure 6. Plateau moduli of (a) poly(ethylene-*co*-1-butene) and (b) HSBC at 140 °C plotted against mole fraction of 1-butene or styrene.

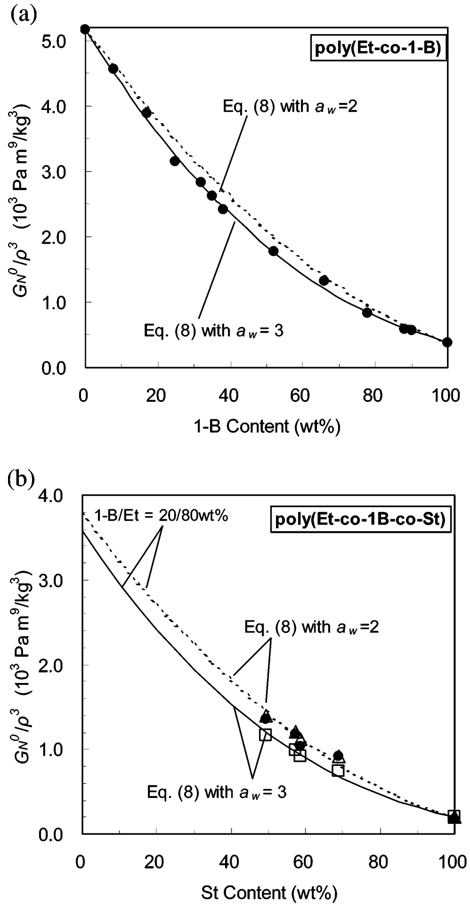

Figure 7. Plateau moduli of (a) poly(ethylene-*co*-1-butene) and (b) HSBC at 140 °C plotted against weight fraction of 1-butene and styrene.

plotted against mole, weight, and volume fraction as shown in Figures 6, 7, and 8, respectively. Curves calculated using eqs 6, 8, and 9, respectively, are also shown in the figures. Plateau moduli of polyethylene, poly(1-butene), and polystyrene were chosen as 2.5, 0.2, and 0.2 MPa[3,20] for the calculation. The lines for HSBCs drawn in the figure were calculated for HSBCs containing 1-butene and ethylene comonomer unit in the ratio of 1/4 by weight, which is the typical 1-butene/ethylene ratio for our HSBCs and the left end of the lines represent hydrogenated polybutadiene containing 20 wt % of 1-butene.

In the case of the mixing rule based on mole fractions as the concentration measure (Figure 6), a different a_n gave a good fit for hydrogenated polybutadiene ($a_n = -6$) and HSBCs ($a_n = -3$). Similarly, in the case of the mixing rule based on weight fraction as the concentration measure, $a_w = 3$ for hydrogenated polybutadiene and $a_w = 2$ for HSBC gave a good fit as shown in Figure 7. Only in the case of mixing rule based on volume fraction as the concentration measure, the same value of $a_\varphi = 3$ gave a good fit for both hydrogenated polybutadiene and HSBCs as shown in Figure 8. So we conclude eq 9 with $a_\varphi = 3$, namely

$$\left[\frac{G_N{}^0}{\rho^3}\right]_{cp}^{1/3} = \sum_j \varphi_j \left[\frac{G_N{}^0}{\rho^3}\right]_j^{1/3} \tag{22}$$

is the most appropriate description.

The transformation of the plateau moduli data to coil dimension data can now be checked using the packing model. Using eq 9 together with eqs 1 and 2, we arrive at the mixing rule for $\langle R^2\rangle_0/M$.

$$\left[\frac{\langle R^2\rangle_0}{M}\right]_{cp}^{3/a_\varphi} = \sum_j \varphi_j \left[\frac{\langle R^2\rangle_0}{M}\right]_j^{3/a_\varphi} \tag{23}$$

When $a_\varphi = 3$ is applied to this equation, $\langle R^2\rangle_0/M$ is linearly dependent on the volume fraction. $\langle R^2\rangle_0/M$ for

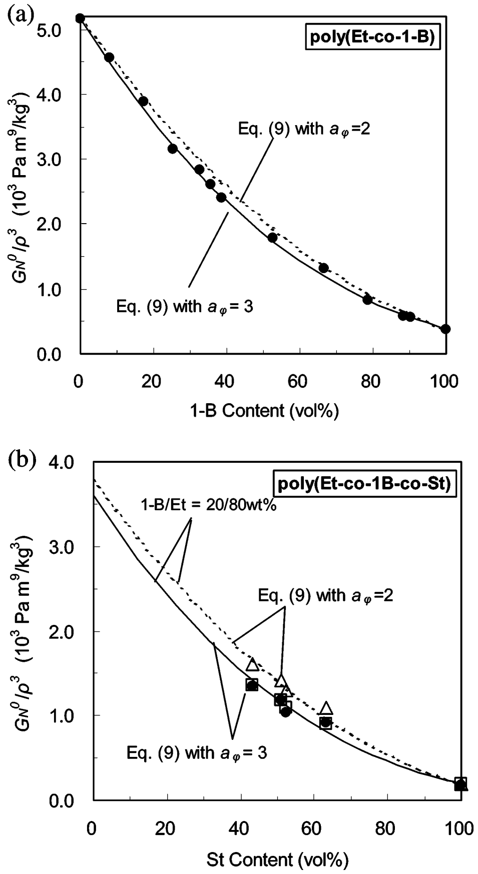

Figure 8. Plateau moduli of (a) poly(ethylene-*co*-1-butene) and (b) HSBC at 140 °C plotted against volume fraction of 1-butene or styrene.

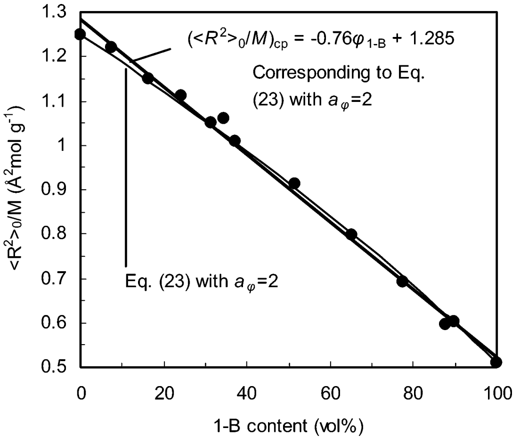

Figure 9. Composition dependence of unperturbed end-to-end distance for poly(ethylene-*co*-1-butene) obtained by Fetters and co-workers[3,14] expressed in volume fraction. The lines were linear fitting and calculated from eq 23 with $a_\varphi = 2$.

hydrogenated polybutadiene obtained by Fetters and co-workers[3,20] are plotted against volume fraction of 1-butene comonomer in Figure 9. At a first glance, $\langle R^2\rangle_0/M$ seems to depend linearly on weight and volume fraction of 1-butene, but a more detailed inspection reveals a slight curvature: $a_\varphi = 2$ instead of 3 appears to be a good description for expressing $\langle R^2\rangle_0/M$. The deviation is small but systematic. The discrepancy indicates either imperfectness of the packing model or imperfectness of the mixing rule or systematic error in measured data.

As mentioned by Fetters and co-workers, the exponent in eq 1 may slightly deviate from 3.[3] With our best fit, the exponent for their poly(ethylene-*co*-1-butene) data was 3.14 ± 0.15. It might be a part of the reason for the observed discrepancy in our mixing rules for G_N^0 and $\langle R^2\rangle_0$. Another possibility of the reason is the imperfectness of our mixing rule. Since the volume of side groups must play an important role in conformation of a chain, it makes sense that the end-to-end distance of a copolymer has something to do with the volume fraction of comonomers. However, the right description might not be as simple as described in eqs 9 and 23. Although some amendment may be required and many more data sets are necessary, the equations provide the best mixing rule we found so far.

For estimating chain conformational change by incorporation of styrene comonomer, we further examined one of the simplest, although unrealistic, assumptions about $\langle R^2\rangle_0$ of vinyl polymers: $\langle R^2\rangle_0$ is only dependent on backbone length.[20] In other words, a vinyl polymer has the same $\langle R^2\rangle_0$ as the linear polyethylene that contains the same number of backbone bonds as the vinyl polymer contains. Under this assumption, the relation of $\langle R^2\rangle_0$ for copolymers and polyethylene can be expressed as follows:

$$\left(\frac{\langle R^2\rangle_0}{M}\right)_{\mathrm{cp}} = \frac{14}{m_{\mathrm{b,cp}}}\left(\frac{\langle R^2\rangle_0}{M}\right)_{\mathrm{PE}} \tag{24}$$

where m_b is the average molecular weight per backbone bond. Of course, this assumption is less realistic because it is more natural to believe that the conformation of polyethylene will be changed with the incorporation of short chain branching, but this analysis is useful for estimating conformational change with incorporation of branching by comparing measured $\langle R^2\rangle_0$ values with assumed values with eq 24. The Packing model allows us to do this analysis with plateau moduli. Using eqs 1, 2, and 24, G_N^0 at constant temperature can be written as

$$\frac{{G_N^0}_{\mathrm{cp}}}{{\rho_{\mathrm{cp}}}^3} = \left(\frac{14}{m_{\mathrm{b,cp}}}\right)^3 \frac{{G_N^0}_{\mathrm{PE}}}{{\rho_{\mathrm{PE}}}^3} \tag{25}$$

Fetters and co-workers examined plateau moduli for various poly(α-olefin) copolymers with this method.[20] They found $\langle R^2\rangle_0$ and G_N^0 for polyolefin copolymers were smaller than predicted by eqs 24 and 25 for m_b of 14−28 and temperature of 373−463 K. They attributed it to increase of gauche conformation due to the existence of branches. We also applied this analysis to our case. Figure 10 shows the result. The plots for HSBCs were close to the connected line between polyethylene and polystyrene. Moreover, those plots were above the line predicted by eq 25, which means the polymer chain is spreading more than eq 25 predicts and suggests enhancement of trans conformation by styrene comonomer. The bulky side chain is thought to be the cause of the increasing population of trans conformation. It is interesting to compare this with 1-butene, which seemed to enhance gauche conformation.

4. Conclusions

Entanglement molecular weights (M_e) for hydrogenated styrene−butadiene copolymers (HSBCs) at 50 °C were obtained as 2380−3270 g/mol for HSBCs containing 49.5−68.9 wt % of styrene, which is closer to polyethylene rather than polystyrene. The vertical shift

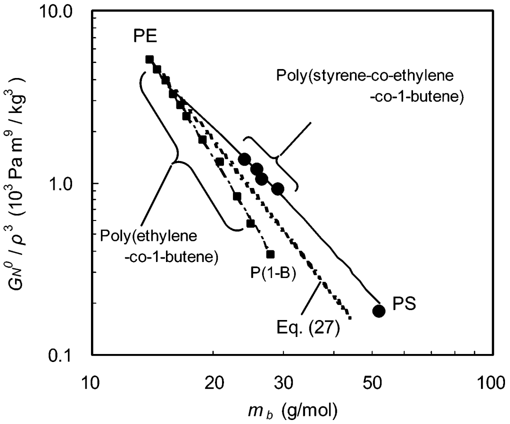

Figure 10. G_N^0/ρ^3 vs m_b plot at 140 °C. Closed circles are measured in this study. Open diamonds are polyethylene and poly(1-butene), and closed squares are poly(ethylene-*co*-1-butene) measured by Fetters and co-workers.[20] The dotted line is the predicted value by eq 25, and the solid lines were calculated from eq 9 with $a_\varphi = 3$ (see Appendix).

parameter, b_T, showed a strong negative temperature dependence, which cannot be described by the classical description of b_T. From the point of view of the packing model, this behavior can be understood as the difference of thermal expansion between the specific volume, $1/\rho$, and the volume that a polymer chain sweeps out, proportional to $(\langle R^2\rangle_0)^{3/2}$. Copolymers containing ethylene comonomers are assumed to be favorable for taking trans conformation at a low temperature, as a result of which $\kappa = \mathrm{d}\ln\langle R^2\rangle_0/\mathrm{d}T$ can be negative for ethylene-rich copolymers. Judging from the temperature dependence of b_T, there was the temperature dependence of M_e: M_e at 140 °C were estimated as 3100−4200 g/mol for HSBCs containing 49.5−68.9 wt % of styrene, which were 30% higher than M_e at 50 °C.

Plateau moduli of copolymers could be expressed as $G_{N\,cp}^{0\;1/3}/\rho_{cp} = \sum \varphi_j G_{N\,j}^{0\;1/3}/\rho_j$, where φ_j is the volume fraction of comonomer j, $G_{N\,cp}^0$ and $G_{N\,j}^0$ are the plateau moduli of the copolymer and the homopolymer of j, respectively, and ρ_{cp} and ρ_j are the density of the copolymer and the homopolymer of j, respectively. Although this relation could also be applied to poly(ethylene-*co*-1-butene), the measured unperturbed end-to-end distance deviated slightly but systematically from the mixing rule of end-to-end distance deduced from the mixing rule of plateau modulus by using the packing model. There might be a more appropriate way of expressing comonomer contents that is more consistent with the packing model.

The dependence of plateau moduli on backbone chain length suggested styrene comonomer incorporation into ethylene-based polymers increases the trans conformation, while α-olefin incorporation increases the gauche conformation.

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Appendix

A. Derivation of a Mixing Rule with the Packing Model from $\langle R^2\rangle_0$ Data Obtained by Fetters and Co-workers. We will show the derivation of mixing rule described as eq 5 from eq 4 with the packing length model. Combining eqs 1, 2, and 4, and considering the mole fraction of 1-butene in the poly(ethylene-*co*-1-butene) is expressed as $n_B = \alpha/50$, we can express G_N^0 as follows under the condition of constant temperature

$$\log\left[\frac{G_N^{\,0}}{\rho^3}\right]_{cp} = \log K - 150An_B \tag{A1}$$

where K is a constant. The plateau moduli of homopolymers can be expressed as follows, considering the fact that $n_B = 0$ corresponds to polyethylene and $n_B = 1$ corresponds to poly(1-butene).

$$\log\left[\frac{G_N^{\,0}}{\rho^3}\right]_{PE} = \log K \tag{A2}$$

$$\log\left[\frac{G_N^{\,0}}{\rho^3}\right]_{P1-B} = \log K - 150A \tag{A3}$$

Combining eqs A1, A2, and A3, we can obtain the following equation:

$$\log\left[\frac{G_N^{\,0}}{\rho^3}\right]_{cp} = (1 - n_B)\log\left[\frac{G_N^{\,0}}{\rho^3}\right]_{PE} + n_B\log\left[\frac{G_N^{\,0}}{\rho^3}\right]_{P1-B} \tag{A4}$$

B. Transformation of the Volume Mixing Rule of Plateau Modulus (Eq 9) into G_N^0 vs m_b Plot. In this section we will demonstrate how the curves in Figure 10 can be calculated.

The volume fraction of a copolymer was defined as eq 10. In the case of vinyl polymers, the weight fraction of the copolymer is described as

$$w_i = \frac{n_i m_{bi}}{\sum_j n_j m_{bj}} \tag{A5}$$

Combining eq 9 with eqs 10 and A5, we can obtain

$$\left[\frac{G_N^{\,0}}{\rho^3}\right]_{cp}^{1/a_\varphi} = \sum_j \frac{\dfrac{n_j m_{bj}}{\rho_j}}{\sum_i \dfrac{n_i m_{bi}}{\rho_i}}\left[\frac{G_N^{\,0}}{\rho^3}\right]_j^{1/a_\varphi} \tag{A6}$$

which was applied to hydrogenated polybutadiene and HSBCs in Figure 10.

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