$$\mathbf{T} = \begin{bmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{bmatrix}$$

where

$$\cos\theta = R_Z/R$$

$$\cos\phi = R_X/R\sin\theta$$

$$R = (R_X{}^2 + R_Y{}^2 + R_Z{}^2)^{1/2}$$

The original fractional coordinate, say of the jth atom, is transformed to the new Cartesian coordinate as

$$\mathbf{X}_j{}^{\mathrm{s}} = \mathbf{TU}\mathbf{x}_j$$

For an arbitrarily chosen reference atom the above transformation is applied to $\mathbf{x}_0 = (x_0,y_0,z_0)^{\mathrm{T}}$, $\mathbf{x}_a = (x_0 + 1, y_0, z_0)^{\mathrm{T}}$, and $\mathbf{x}_b = (x_0, y_0 + 1, z_0)^{\mathrm{T}}$, giving $\mathbf{X}_0{}^{\mathrm{s}}$, $\mathbf{X}_a{}^{\mathrm{s}}$, and $\mathbf{X}_b{}^{\mathrm{s}}$ from which the subcell dimensions are deduced as

$$a_{\mathrm{s}} = a,\ b_{\mathrm{s}} = b,\ c_{\mathrm{s}} = R$$

$$\cos\alpha_{\mathrm{s}} = (Z_b{}^{\mathrm{s}} - Z_0{}^{\mathrm{s}})/b_{\mathrm{s}}$$

$$\cos\beta_{\mathrm{s}} = (Z_a{}^{\mathrm{s}} - Z_0{}^{\mathrm{s}})/a_{\mathrm{s}}$$

$$\cos\gamma_{\mathrm{s}} = \{(X_a{}^{\mathrm{s}} - X_0{}^{\mathrm{s}})(X_b{}^{\mathrm{s}} - X_0{}^{\mathrm{s}}) + (Y_a{}^{\mathrm{s}} - Y_0{}^{\mathrm{s}})(Y_b{}^{\mathrm{s}} - Y_0{}^{\mathrm{s}}) + (Z_a{}^{\mathrm{s}} - Z_0{}^{\mathrm{s}})(Z_b{}^{\mathrm{s}} - Z_0{}^{\mathrm{s}})\}/a_{\mathrm{s}}b_{\mathrm{s}}$$

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Viscoelastic Properties of Homogeneous Triblock Copolymers of Styrene–α-Methylstyrene and Their Polyblends with Homopolymers

David R. Hansen and Mitchel Shen*

Department of Chemical Engineering, University of California, Berkeley, California 94720.
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ABSTRACT: Seven triblock copolymers of styrene–α-methylstyrene were prepared via anionic polymerization. Two types of block structures, ASA and SAS, were made. By the use of the Time Temperature Superposition Principle, stress relaxation isotherms of these block copolymers were readily shifted into smooth viscoelastic master curves. The shift factor data of all the block copolymers follow the classical WLF equation. Loss tangent data obtained by dynamic mechanical measurements show only one glass transition in each of these block copolymers, thus indicating the homogeneous nature of these materials. From the master curves, maximum relaxation times (τ_{m}) were determined by the Procedure X method of Tobolsky and Murakami. These maximum relaxation times were found to vary as a function of copolymer composition and block structure. Comparison with τ_{m}'s computed from molecular theory was satisfactory. Viscoelastic data of polyblends of the block copolymers with their respective homopolymers indicate that they are all homogeneous, except for the blend of an ASA triblock copolymer with poly(α-methylstyrene) which shows some signs of heterogeneity.

It is now well known that most block copolymers show microphase separation as a consequence of their positive free energy of mixing between the polymeric blocks. Because of this heterophase nature, many unique properties have been found to be dramatically different from those of the homogeneous homopolymers. For example, the viscoelastic behavior of heterophase block copolymers has been found to be thermorheologically complex.[1,2] However, a limited number of block copolymers are known to show no microphase separation, for example, the styrene–α-methylstyrene system.[3–6] It is therefore of interest to examine the properties of such homogeneous block copolymers in order to compare with those of the heterogenous ones.

An additional motivation to study these materials was provided by the recent interest in the molecular theoretical investigations of the viscoelastic properties of block copoly-

Table I
Characteristics and Viscoelastic Parameters of Polymer Samples

Sample No.	Composition, wt % αMS: Monomer charge	NMR	Ir	$\bar{M}_w \times 10^{-5}$	H.I. ($\bar{M}_w/\bar{M}_n$)	T_i, °C (100 sec)	T_i', °C (110 Hz)	T_{ref}, °C (WLF)	Log τ_m, sec (at T_i + 29)	Log ξ at T_i, (dyn sec)/cm	n
A (S-5A-S)	3	5		1.53	1.29	103	131	101	2.76	3.60	1.57
B (S-17A-S)	10	17		1.23	1.28	107	136	105	2.85	3.37	1.55
C (S-34A-S)	25	34		1.29	1.23	113	140	112	3.27	3.66	1.23
D (S-42A-S)	40	42		1.48	1.37	122	152	119	3.15	3.08	1.20
E (S-65A-S)	60	65		0.93	1.99	129	163	125	4.02	3.78	1.08
F (A-73S-A)	30	27	33	1.64	1.58	117	146	116	4.52	4.81	0.77
G (A-55S-A)	76	45	55	1.20	1.24		164				
H (PαMS)	100	100	100	1.63	1.54		190				0.75[c]
I (PS)	0	0	0	1.51	1.52		127		2.26[a]		1.60[b]

[a] Average valve from ref 31–34. [b] Reference 32. [c] Reference 30.

mers.[6-12] The model utilized in these theoretical works is the Rouse–Bueche–Zimm bead-and-spring model. Since the validity of these models is restricted to only homogeneous systems, experimental data on such systems are thereby required to verify the theoretical predictions. In this work, we shall report on the viscoelastic properties of block copolymers of styrene and α-methylstyrene as well as their blends with respective homopolymers. Data will be compared with the theoretical calculations based on the theory given in a previous paper.[9]

Experimental Section

Seven triblock copolymers of styrene and α-methylstyrene were anionically polymerized (see Table I). The polymerization was performed under high vacuum and at low temperatures, following the procedures outlined by Baer[3] and by Fetters.[13] Tetrahydrofuran was used as the solvent and sodium naphthalene as the initiator. Since sodium naphthalene is a difunctional initiator, both poly(styrene-*b*-α-methylstyrene-*b*-styrene), or SAS, and poly(α-methylstyrene-*b*-styrene-*b*-α-methylstyrene), or ASA, can be readily synthesized by interchanging orders of addition of the monomers in the reaction.

Copolymer compositions were determined by both infrared and nuclear magnetic resonance spectroscopy. The ir determination was made by using the absorption bands at 8.11 and 11.08 μ, which are respectively characteristic of poly(α-methylstyrene) and polystyrene.[3] A calibration curve was made by plotting Abs.(8.11)/Abs.(11.08) ratios against known compositions of mixtures of homopolymers of styrene and α-methylstyrene in 10% benzene solutions. Data for ASA samples are given in Table I. For SAS samples, peak intensities at 8.11 μ were extraordinarily low in comparison with the standard solutions. In the absence of a plausible explanation for this observation, these data were not used in computing for copolymer composition. All measurements were carried out on a Perkin-Elmer 337 Infrared Spectrophotometer.

A Varian T-60 Spectrometer was employed for NMR analysis. In the NMR spectrum for polystyrene and poly(α-methylstyrene) there are three broad characteristic peaks[14,15] in the regions of 7.75 to 5.75 ppm, 2.7 to 0.4 ppm, and 0.8 to −0.8 ppm, where tetramethylsilane is 0 ppm (see Figure 1). Since the peak in the region of 0.8 to −0.8 is associated solely with poly(α-methylstyrene), the ratio of the areas under the peaks in the regions of 2.7 to −0.8 ppm and 7.75 to 5.75 ppm will indicate the percentage of α-methylstyrene. A calibration curve, therefore, was made from known mixtures of the two homopolymers by plotting the composition against $\text{area}_{2.7 \text{ to } -.8}/\text{area}_{7.75 \text{ to } 5.75}$. All solutions were 4% in CCl_4 and 1,4-dioxane was used as the reference standard since TMS overlaps one of the α-methylstyrene peaks. Results were reproducible to ±7%.

The molecular weight of the copolymers was determined by a Waters Model 200 gel permeation chromatograph, courtesy of Dr. A. C. Ouano of IBM-San Jose.[16] A polystyrene calibration curve was used to calculate the molecular weight from the elution volume data. The molecular weight of the copolymers was then corrected for the difference in monomer molecular weight of αMS. The results of the GPC are given in Table I.

This approach of using a polystyrene calibration curve will only be valid if hydrodynamic volumes of polystyrene, PαMS, and their copolymers are nearly the same. One such measure of the hydrodynamic volume is the intrinsic viscosity. According to the theories of Debye,[17] Kirkwood,[18] and Flory,[19-21] the intrinsic viscosity is proportional to the effective hydrodynamic volume of the molecule in solution. The intrinsic viscosities determined by the Mark–Houwink constants in toluene at 25°C for polystyrene[22] and poly(α-methylstyrene)[23] are very similar, $8.48 \times 10^{-5} M^{0.748}$ and $1.08 \times 10^{-4} M^{0.71}$, respectively. No Mark–Houwink correlations have been published for the copolymers, but Goldwasser and Williams[24] reported that within experimental error the unperturbed dimensions of a random copolymer of styrene and α-methylstyrene with 24 wt % styrene is indistinguishable from either of the homopolymers. Thus the molecular weights of our block copolymers determined by GPC should be very realistic.

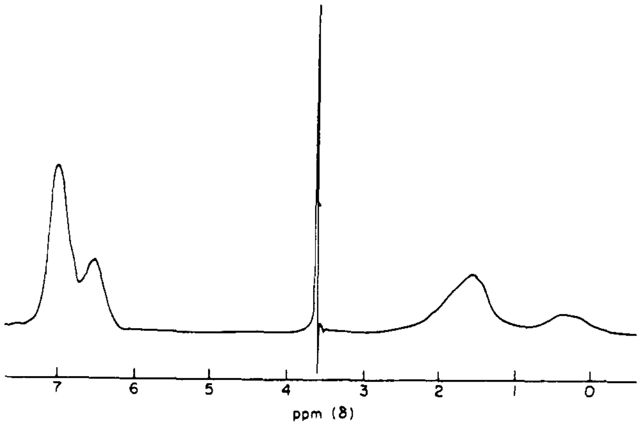

Figure 1. The NMR spectrum for sample F (4% in CCl_4). 1,4-Dioxane was used as a reference.

Samples were prepared for mechanical testing by hydraulically pressing the samples at ~30°C above their T_g's. The samples were subsequently annealed in vacuo at ~15°C above their T_g's for 24 hr, thus releaving stresses. Samples were cut into strips and sanded to obtain uniform dimensions. The typical sample dimensions for stress relaxation were $9 \times 1 \times 0.4$ cm^3, while for dynamical mechanical measurements they were $2 \times 0.5 \times 0.07$ cm^3. All dimensions were measured with a micrometer to ±0.0005 cm.

Stress relaxation experiments were performed on an Instron *Universal Testing Machine*. The temperature was controlled to ±0.2°C with a Missmer Model PITC Temperature Conditioner. Flexural mode experiments were used for moduli above 10^9 dyn/cm^2. Below this value, the tensile mode was used. Dynamical mechanical data was obtained on a Rheovibron DDV IIB Viscoelastometer at the frequency of 110 Hz.

Homopolymers of styrene (PS) used in blending with the block copolymers were obtained from the Dow Chemical Co. (S-103 and S-108) and from Polysciences, Inc. The homopolymer of α-methylstyrene (PαMS) was polymerized by the same anionic technique already described. Four blends of each copolymer of samples C and F were made. Three of the four blends were 20% blends of three different molecular weights of PS as shown in Table II. The fourth blend consisted of a mixture of the copolymer and 25% PαMS. After thorough drying, samples were compression molded at ~30°C above T_g's. They then were annealed in the previously mentioned manner for testing on the Rheovibron.

Table II
Characteristics of the Polyblends

Sample	Block copolymer	Homopolymer	Wt % homopolymer	$\bar{M}_w$ homopolymer	T_i, °C (110 Hz)
C-1	C (S-34A-S)	PS (S-103)	21	1.2×10^5	134
C-2	C (S-34A-S)	PS (S-108)	20	2.54×10^5	134
C-3	C (S-34A-S)	PS (Polysci)	20	0.3×10^5	122
C-4	C (S-34A-S)	PαMS	24	1.6×10^5	151
F-1	F (A-73S-A)	PS (S-103)	21	1.2×10^5	139
F-2	F (A-73S-A)	PS (S-108)	21	2.54×10^5	139
F-3	F (A-73S-A)	PS (Polysci)	21	0.3×10^5	130
F-4	F (A-73S-A)	PαMS	25	1.6×10^5	159

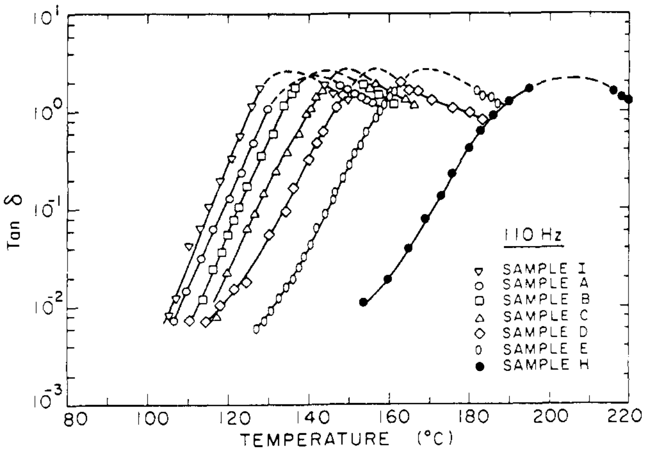

Figure 2. Loss tangent vs. temperature data for S-A-S copolymers at 110 Hz.

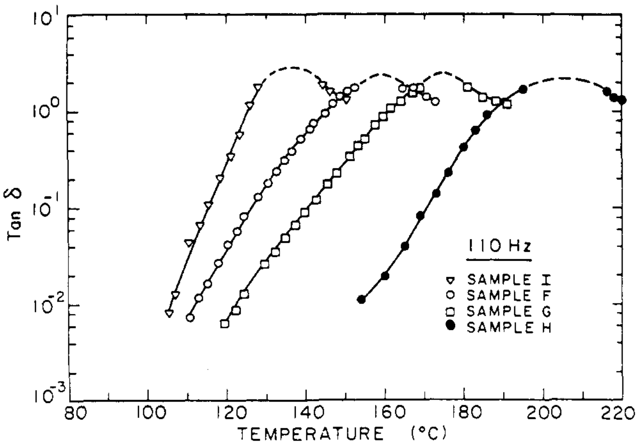

Figure 3. Loss tangent vs. temperature data for A-S-A copolymers at 110 Hz.

Results and Discussion

1. Viscoelastic Properties of the Block Copolymers. Figure 2 shows the loss tangent data for five SAS block copolymers (samples A–E) as well as for the homopolymers of styrene and α-methylstyrene, determined on the Rheovibron at a frequency of 110 Hz. Maxima of the loss curves for PS and PαMS are located at 136 and 204°C, which are indicative of the onset of their respective primary glass transition processes at this testing frequency. By comparison, we note that the literature values[25,26] of the T_g's for these two polymers have been reported to be 100 and 167°C. Figure 2 also shows that loss curves for all of the block copolymers exhibit only single peaks, their temperature positions being intermediate between those of the homopolymers and approximately proportional to the αMS content. Even though continued experimentation on the Rheovibron became impossible at temperatures considerably above the T_g's, the trend is clear that the breadth of the loss peaks increases with increasing αMS content. On the other hand, the data for ASA block copolymers in Figure 3 show that the breadth of their loss curves is greater than the corresponding SAS, although the general feature of a single intermediate peak is the same. The fact that all of the block copolymers exhibit only single loss peaks is indicative of the absence of microphase separation in these systems. By contrast, the loss curve for a blend of PS and PαMS (not shown here) clearly exhibited two maxima, respectively attributable to the glass transition of each of the homopolymers. The finding that block copolymers of styrene and α-methylstyrene are homogeneous, but their polyblends are heterogeneous, is in agreement with the observations of Baer[3] and Robeson et al.[5] The homogeneity of these block copolymers has also been predicted by the statistical mechanical analysis of Krause.[4]

Stress relaxation isotherms for samples C–F are shown in Figure 4. Those for samples A and B have already been published previously,[6] and will not be repeated here. The amount of sample G prepared was insufficient for stress relaxation experiments. Time Temperature Superposition Principle[27,28] was employed in shifting these isotherms into smooth viscoelastic master curves (Figure 5). Shift factor data utilized in effecting the superposition are given in Figure 6. The curve in the figure was computed from the Williams–Landel–Ferry (WLF) equation,[28] using the constants $C_1^g = 13.7$ and $C_2^g = 50.0$ characteristic of PS.[28] Values of these constants are very close to those for PαMS,[28] which are $C_1^g = 13.7$ and $C_2^g = 49.3$. Reference temperatures (T_{ref}) shown in Table I were chosen in order to obtain the best fit of the copolymer data to the WLF equation. The good agreement of the shift factor data with the WLF equation is another verification of the thermorheological

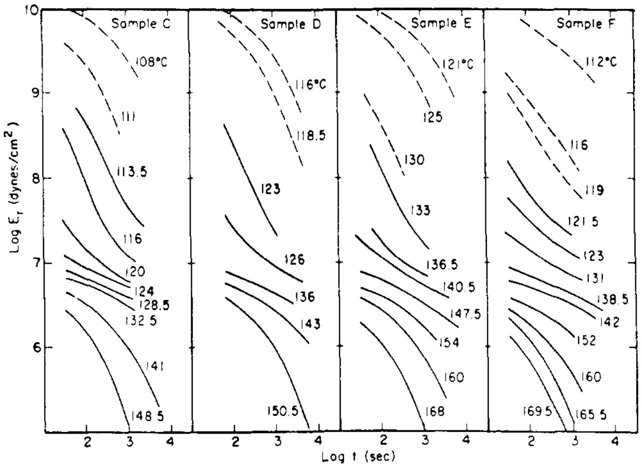

Figure 4. Stress relaxation isotherms of samples C through F: (- - -) flexural data (—) tensile data.

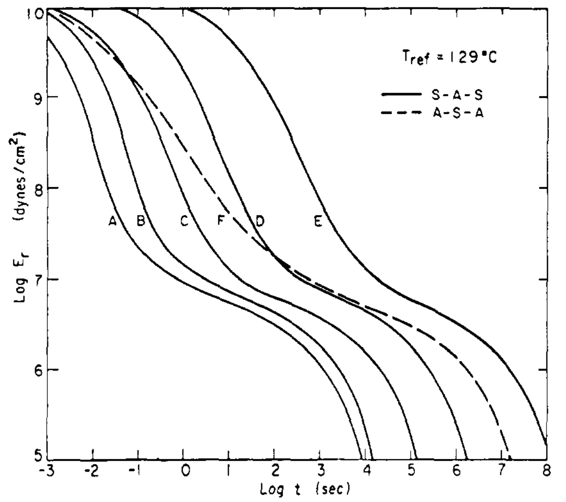

Figure 5. The viscoelastic master curves of samples A through F.

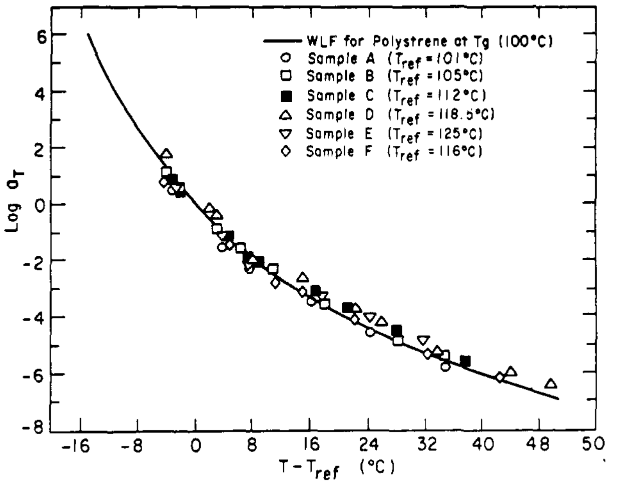

Figure 6. Shift factor data for samples A through F. The solid curve is the calculated WLF with $C_1 = 13.7$ and $C_2 = 50.0$.

simplicity of these samples. Since it has been demonstrated that heterogeneous block copolymers are always thermorheologically complex,[1,2] the preceding observation is therefore another evidence of the homogeneous nature of the ASA and SAS systems studied.

By choosing 100 sec as the reference time, the isothermal stress relaxation data can be crossplotted to yield isochronal modulus–temperature curves. The temperature at which the modulus reaches 10^9 dyn/cm^2 can be taken as the inflection temperature[27] (T_i). As shown in Table I, values of T_i for the block copolymers are close to the WLF T_{ref}'s.

We note in Figure 5 that viscoelastic master curves (reference temperature 129°C) of all of the SAS block copolymers are very similar, except that those containing increasing amounts of αMS are shifted to longer time scales. Such shifts are to be expected since the glass transition temperatures are higher for these samples. By contrast, the master curve for the ASA sample is distinctly different from all of the SAS curves in that the transition region is greatly broadened. Such broadening has already been observed in the loss tangent curves (Figures 2 and 3) determined dynamic mechanically. As shown in Table I, maximum transition region slopes (n) of all the SAS master curves are close to that of pure PS, while the ASA slope is close to the PαMS slope. Thus it happens that the breadths of the transitions of the block copolymers are primarily determined by the nature of the end blocks.

2. Comparison with Theory. In the previous paper,[9] we have computed the retardation spectra for homogeneous block copolymers on the basis of a modified Rouse–Bueche–Zimm bead-and-spring model. Both the distribution of retardation times and the maximum retardation times were calculated for a number of block copolymer types, including triblock copolymers. Since the retardation times differ from the relaxation times by a factor of 2, results from the theory should readily be comparable with the experimental data in this paper.

For an SAS block copolymer, the equation of motion can be written as[9]

$$\dot{\mathbf{x}} = -\sigma_S \mathbf{D}^{-1}\mathbf{Z}\mathbf{x} \tag{1}$$

In eq 1, $\mathbf{x}$ and $\dot{\mathbf{x}}$ are column vectors of bead positions and velocities, respectively, $\mathbf{Z}$ is the nearest neighbor Zimm matrix, and $\sigma_S = 3kT/b_S{}^2f_S$, where k is Boltzmann constant, T is the absolute temperature, $b_S{}^2$ is the mean-square end-to-end distance of a styrene submolecule, and f_S is the friction coefficient of a polystyrene submolecule. For the SAS block copolymer, $\mathbf{D}^{-1}$ is the inverse of the following matrix[37]

$$\mathbf{D} = \begin{bmatrix} 1 & & & & & & & & & \\ & 1 & & & & & & & & \\ & & 1 & & & & & & & \\ & & & \ddots & & & & & & \\ & & & & \delta_A & & & & & \\ & & & & & \delta_A & & & & \\ & & & & & & \ddots & & & \\ & & & & & & & 1 & & \\ & & & & & & & & 1 & \\ & & & & & & & & & 1 \end{bmatrix} \tag{2}$$

where

$$\delta_A = b_A{}^2 f_A / b_S{}^2 f_S = a_A{}^2 m_A{}^2 \zeta_A / a_S{}^2 m_S{}^2 \zeta_S \tag{3}$$

In eq 3, m is the number of monomer units per submolecule, a is the characteristic length, ζ is the monomeric friction coefficient, and $b^2 = ma^2$. Subscripts A and S refer to α-methylstyrene and styrene, respectively. It should be pointed out that in our previous publication[9] we assumed that the spring constants and the submolecule sizes were the same. However, this assumption may not be valid for PS and PαMS. In their recent work Osaki and Schrag[29] have found that the number of monomer units is 11 for PS(m_S) and 16 for PαMS(m_A). The size of the submolecule is arbitrary, however, for there is little difference in computed τ_m (~0.07 log units) depending on whether the submolecule sizes are assumed equal or different in the ratio found by Osaki and Schrag. The reason is that the maximum relaxation time is a function of the number of beads in the chain, the value of δ_A, and the percentages of A and B beads. If m_A/m_S is changed, these three parameters are modified in such a way that they compensate for one another to leave τ_m relatively constant. To be consistent with Osaki and Schrag, however, and for simplicity of calculation we will assume $m_A/m_S = 1.4$. In addition it has been reported that the characteristic length for PS(a_S)[28] is 7.4 × 10^{-8} cm, while for PαMS[30] $a_A = 8.0 \times 10^{-8}$ cm. The monomeric friction coefficients[28,30] in eq 3 are $\zeta_S = 1.15 \times 10^2$ and $\zeta_A = 2.08 \times 10^4$ (dyn sec)/cm at their respective glass transition temperatures (100 and 167°C). The glass transition temperature is chosen as the reference state for comparing the monomeric friction coefficients because it is preferable to compare the ζ's at equivalent states of molec-

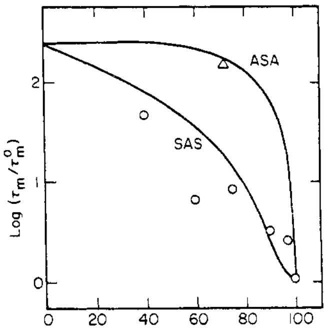

Figure 7. Comparison of theoretical prediction of τ_M/τ_M^0 (—) and experimental data (O, SAS; Δ, ASA).

ular motion as would be the case in a homogeneous copolymer. Using these values in eq 3, we find that $\delta_A = 423$.

A matrix with 140 beads was used to compute the maximum relaxation time for 100% S beads. In calculating τ_m for the copolymers the molecular weight must remain fixed for a meaningful comparison. For simplicity we will assume that the monomer molecular weight of styrene is equal to that of αMS. Thus

$$N_S + N_A\,(m_A/m_S) = 140 \qquad (4)$$

where N_A and N_S are the number of PS and PαMS beads. Therefore the total number of beads in the chain ($N_A + N_S$) will decrease as the weight percent of αMS (eq 5) increases.

$$\text{wt \% } \alpha\text{MS} = N_A m_A/(N_S m_S + N_A m_A) \qquad (5)$$

The computed maximum relaxation times of the block copolymers are normalized by that of the styrene homopolymer as follows:

$$\tau_m(\text{normalized}) = \frac{1}{2\sigma_S\lambda_{\min}} \Big/ \frac{1}{2\sigma_S{\lambda_{\min}}^0} = \frac{{\lambda_{\min}}^0}{\lambda_{\min}} \qquad (6)$$

where $\lambda_{\min}$ is the minimum eigenvalue[9] of the matrix $\mathbf{AD}^{-1}\mathbf{A}^T$, $\mathbf{Z} = \mathbf{A}^T\mathbf{A}$, and superscript ^{0} denotes pure PS. The computed values for both SAS and ASA block copolymers are given in Figure 7 (solid line).

The experimental maximum relaxation times of the block copolymers were determined from the viscoelastic master curves (Figure 4) by using Procedure X of Tobolsky and Murakami.[31] Because the maximum relaxation times are strong functions of temperature and molecular weight, these effects must be compensated for in order to make a valid comparison. We shall use T_i + 29°C as the reference temperature and 1.2×10^5 as the reference molecular weight. The relationship $d \ln \tau_m/d \ln M_w = 3.4$ was used to extrapolate the maximum relaxation times to the reference molecular weight. These experimental values of τ_m are given in Table I.[38] The maximum relaxation times were then normalized by τ_m for pure polystyrene. Since literature values[31–34] for τ_m of pure polystyrene differ somewhat from each other, an average value of $\log \tau_m^0 = 2.36$ sec was used.

Figure 7 compares the normalized experimental and computed maximum relaxation times for the SAS and ASA block copolymers. Although there is appreciable scatter in the experimental data, the agreement with the theory is generally satisfactory. In particular we note that the value of τ_m for the only ASA value in the figure is substantially higher than that of the SAS of comparable composition, as predicted by the theory.

It should be pointed out that in the above calculations many parameters contain some possible uncertainties. One uncertainty is in the values of the characteristic length, a. These were taken from measurements in dilute Θ solutions, assuming that conformations were unperturbed by long-range effects.[20] Whether such conditions still hold true in bulk copolymers is unknown at this time, although recent neutron inelastic scattering experiments seem to confirm the essentially random nature of polymers in bulk systems.[35]

Second, the computed relaxation times were modelled for polymers without entanglements. For our bulk polymers with molecular weights exceeding 10^5, the entanglement effect is certainly not negligible. We justify this simplification by following the argument of Ferry,[28] who suggested that the net effect of entanglements as far as the longest relaxation times are concerned is to increase all of the frictional coefficients of the submolecules by a factor $Q = (M/M_c)^{2.4}$, where M is the molecular weight and M_c is the critical entanglement molecular weight.[39] Thus the relative differences of the frictional coefficients are still the same as we have modelled the system and our analysis should still be valid.

Third, one may question if the effective monomeric friction coefficient calculated from homopolymer data is valid for block copolymers. It may be envisioned that in the homogeneous block copolymer, styrene segments may be moving against a mixture of styrene and α-methylstyrene segments. The friction coefficient in this instance may not be the same as segments moving against their own kinds. This situation may not be as serious in dilute solutions, where the segments are moving against mutual solvent molecules. In the case of bulk polymers this problem is at present not easily resolvable.

To further scrutinize this problem, we can compute the effective monomeric friction coefficients for our homogeneous block copolymers from their master curves. These master curves are first converted to relaxation spectra by the method of second approximation.[28] These spectra are shown in Figure 8. The effective monomeric friction coefficient can then be calculated by the following equation:

$$\log \zeta = 2 \log H + \log \tau + \log (6/kT) + 2 \log (2\pi M^0/a\rho N_0) \qquad (7)$$

where H is the value of the relaxation spectrum at relaxation time τ which conforms to the theoretical slope of $-\frac{1}{2}$, M^0 is the monomer molecular weight, ρ is density, and N_0 is the Avogadro number. For values of a and M^0, we shall use the following simple mixing rules:

$$a = \phi_S a_S + (1 - \phi_S)a_A \qquad (8)$$

$$M^0 = \phi_S M_S^0 + (1 - \phi_S)M_A^0 \qquad (9)$$

where subscripts A and S refer to α-methylstyrene and styrene respectively, and ϕ_S is the weight fraction of styrene. In eq 7 ρ was taken to be 1.0. Results are given in Table I, where reference temperatures were chosen to be T_i's. It is of interest to note that the coefficients of all of the SAS block copolymers are all nearly the same and intermediate between styrene and αMS at their T_g's, while the coefficient of the ASA copolymer is much higher. Thus the effective friction coefficients of the block copolymers are apparently influenced by the end blocks.

An additional difficulty in the determination of monomeric friction coefficient from relaxation spectra is its sensitivity to the reference temperature, which we have taken to be the glass transition temperature. If we had used 165°C instead of 167°C as the value of T_g for PαMS, the value of ζ_A would have changed by a factor of 2.8. The same

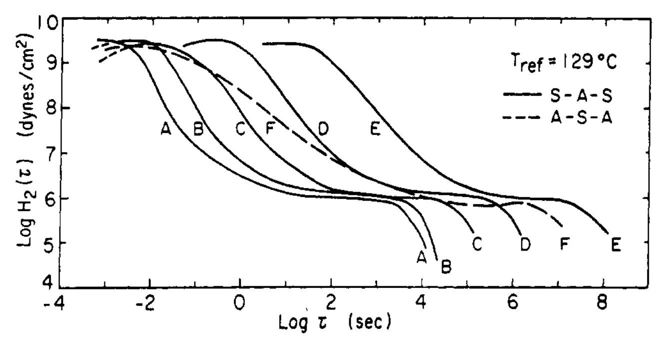

Figure 8. Relaxation spectra of samples A through F.

is also true in the determination of maximum relaxation times.

A more serious uncertainty is the degradation that has occurred as a consequence of compression molding and subsequent testing of the samples at high temperatures. A comparison of the GPC data of the polymers before and after testing indicated a decrease in molecular weight in all of the block copolymers by an average of one-third. Molecular weights after testing were used in all of the calculations. The presence of diblock fragments may only have minor effects in SAS block copolymers, since our theory predicts that the maximum relaxation times of the SAS triblock copolymers are all but indistinguishable from those of the AS diblock copolymers except at very high styrene content.[9] The effect on the ASA systems may be more serious according to theory. However, in view of the relatively good agreement between the experimental and computed values of τ_M for the ASA block copolymer, the effects of degradation appear to be not as significant as one might suspect.

Another kind of degraded fragments may be the presence of homopolymers in the block copolymer. The effect of the homopolymers on the viscoelastic properties is described in the subsequent section on polyblends.

3. Viscoelastic Properties of Polyblends. One sample of SAS block copolymer (Sample C containing approximately 66% styrene) and one ASA (Sample F containing 73% styrene) were blended with four homopolymers, i.e., S-103 and S-108 polystyrene from Dow Chemical Co., one low molecular weight polystyrene from Polysciences, and one sample of poly(α-methylstyrene) anionically polymerized in this laboratory. Characteristics of these blends are summarized in Table II. The SAS polyblends loss tangent curves are shown in Figure 9. For the sake of comparison, the data for pure sample C are also included. We note that the shapes of these curves are all very similar. There is only one single loss peak for each of the polyblends, and the widths of these loss peaks are comparable to the block copolymer. Polyblends C-1 and C-2 both contain about 20% moderately high molecular weight. Because the T_g's of the two polystyrene homopolymers are nearly the same, the loss curves of the two blends are superposed on each other. The temperature positions of the loss peak maxima for both curves (T_{max} at 110 Hz) are lower (143°C) than that of the pure sample C (149°C), since the T_{max}'s of these PS are lower than the T_{max} of the block copolymer. Polyblend C-3 containing the low molecular weight PS is shifted to an even lower temperature (133°C). On the other hand, Polyblend C-4 containing 24% PαMS is located at the higher temperature scale because of the higher T_{max} of the homopolymer.

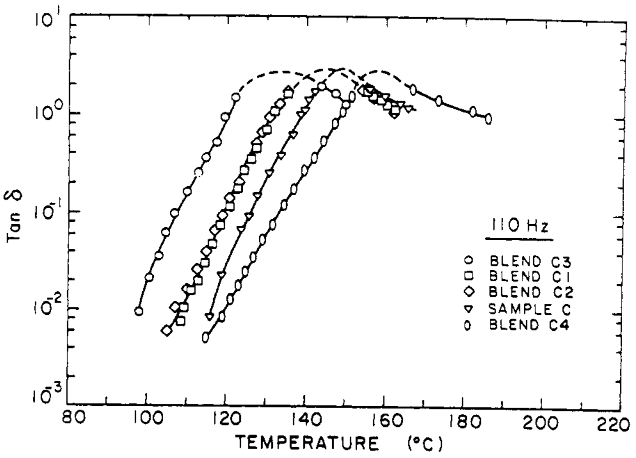

Figure 9. Loss tangent vs. temperature data of blends C1 through C4 at 110 Hz.

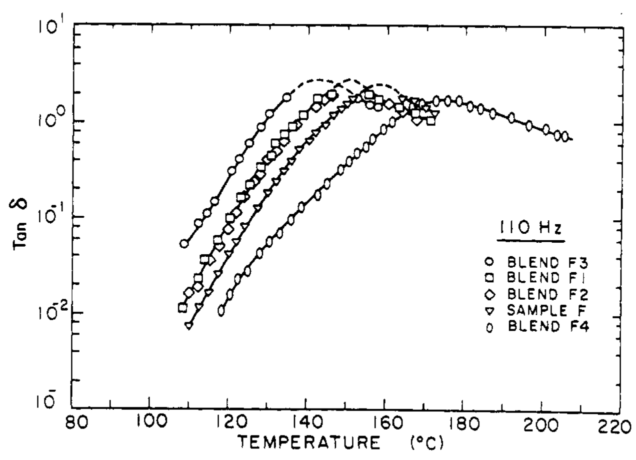

Figure 10. Loss tangent vs. temperature data of blends F1 through F4 at 110 Hz.

Loss tangent curves for ASA polyblends are given in Figure 10. Here the general observations made for the SAS polyblends appear to hold for those samples blended with PS. However, the polyblend F-4 containing 25% PαMS exhibits a very much broader loss curve. Although there is only one clear loss peak, there is also some indication of the presence of an additional weak loss peak near 120°C. Of all the block copolymers and polyblends studied in this paper, polyblend F-4 is the only one that shows a hint of heterophase structure.

In their recent work, Robeson et al.[5] reported on the viscoelastic data of diblock copolymers (AS) containing equal amounts of styrene and α-methylstyrene. Their data indicated that polyblends of the high molecular weight diblock copolymer (4×10^5) with PαMS are homogeneous, but those with PS show clear signs of heterogeneity (two loss peaks). On the other hand, the lower molecular weight SA diblock copolymer ($1.0–1.5 \times 10^5$) is compatible with PS. No similar data were given for polyblends with PαMS. The trend of lower molecular weight blends being more compatible is consistent with the theory of Krause.[4] If this trend is valid for the αMS blends, there appears to be an inconsistency between the data of Robeson et al. and ours for blend F-4. Part of this discrepancy may be attributable to the differences in block structures (diblock vs. triblock's), especially in view of the observed differences in properties between ASA and SAS triblock copolymers in this work. The resolution of this problem, however, must await further work in this area.

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(37) For ease of computation, possible effects of the junctions between blocks are neglected.

(38) The τ_m reported in ref 6 were too high by a factor of 2.303.

(39) It is now generally agreed that the relaxation times in the terminal zone are more closely clustered than that predicted by the Rouse Theory.[36] The Q factor is not strictly correct, but is used for the sake of convenience. A more rigorous calculation for block copolymers with chain entanglements will be given in a future publication.

Melting Point Depression and Kinetic Effects of Cooling on Crystallization in Poly(vinylidene fluoride)–Poly(methyl methacrylate) Mixtures

T. Nishi[1] and T. T. Wang*

Bell Laboratories, Murray Hill, New Jersey 07974. *Received August 20, 1975*

ABSTRACT: Thermal analysis of solution cast mixtures of poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA) has been carried out with various programmed temperature profiles. Results from experiments conducted in a quasi-equilibrium state show that PVF_2 crystallizes in the mixture upon cooling. Furthermore, depressions were observed in the melting and the crystallization temperatures. The melting point depression phenomenon is found to be explicable in terms of thermodynamic mixing of a crystalline polymer with an amorphous polymer. To this end, an analytical expression appropriate to the crystalline–amorphous polymer pair is derived from Scott's equation for thermodynamic mixing of two polymers. From this expression the interaction parameter for the polymer pair is found to be −0.295 at 160°C, indicating that the system is compatible in the molten state. The depression of crystallization temperature which depends strongly on both the composition and the cooling rate is attributed to the ability of the PVF_2 segments to migrate and to the change of composition in the melt during crystallization. For mixtures with a PVF_2 content by weight of less than 0.5, it is possible to suppress the crystal transformation at room temperature with a moderate cooling rate. Finally, it is pointed out that because of the strong kinetic effects of cooling on the thermodynamic state of the mixture, caution should be exercised in the calorimetric study of compatibility of the polymer pair.

In previous studies[2] concerned with compatibility of polymer–polymer systems it has been found helpful to interpret the miscibility of the mixtures in terms of their phase diagrams. It has also been shown that the thermal history of the mixture has a pronounced effect on the mixing behavior of the polymer pair when the experimental temperature approaches or falls below the glass transition temperature of the mixture.[3,4] These studies have been confined so far to the amorphous polymer pair or, in the case of a crystalline–amorphous polymer pair, the mixing of amorphous fraction of the crystalline polymer and the amorphous polymer. An examination of the compatibility between a crystalline polymer and an amorphous polymer therefore becomes a natural extension of our general study.

Recently, it was reported in the literature that poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA) form a compatible mixture when blended in the melt.[5–9] It was also reported that PVF_2 crystallizes in the