Entanglement Spacing Variability in Blends of Narrow Molecular Weight Distribution Polystyrenes

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ABSTRACT: The viscoelastic response of some thermoplastics can be altered by their previous shear history, or by recovery from solution under controlled conditions, without changes in molecular weight distribution. Large variations in the viscosity and the entanglement molecular weight of solution-treated narrow molecular weight distribution polystyrenes have been observed previously.[1] In this study, blends of polystyrene narrow fractions were recovered from chloroform solutions and dried. Residual solvent was present only in trace quantities and there was no change in molecular weight distribution of any blend. Large variations in the mean entanglement molecular weight and in the zero shear viscosity were observed. Smaller variations in the entanglement molecular weight coincided with larger variations in zero shear viscosity than for narrow molecular weight distribution polystyrenes. Samples having the same weight-average molecular weight did not have the same zero shear viscosity. The steady-state compliance was dependent only on sample polydispersity and did not vary with sample history. Trends expected from the reptation scaling law were observed, but the data did not fit a unique curve. The behavior of these samples could be rationalized using a modification of the theory of Kavassalis and Noolandi.[19-21] It is concluded that the prior treatment of the polymers altered the entanglement spacing. This may be the result of a change in the spatial dimensions of the polymer molecules in the bulk.

Introduction

Previously, we reported[1] the results of experiments with narrow molecular weight distribution polystyrenes, in which the polymer molecular weight was varied (by choice of sample) and in which the mean entanglement spacings of the samples were also varied by control of the sample history. These experiments provided a unique test of some current reptation model theories. Here we report the results of similar experiments using blends of these narrow polystyrene fractions.

If diffusion of polymer segments is possible for a sufficient period of time, under favorable conditions, the attainment of an "equilibrium" entanglement state will ultimately result.[2] The entanglement spacings of narrow polymer fractions that have been allowed to equilibrate depend only on the type of species, providing the polymer molecular weight is sufficiently large.[3-5] Most of the measurements on narrow fractions have apparently been carried out in this regime, and these data are commonly used to test the predictions of current theories concerning entanglements and their relationship to observed polymer dynamics.

Phenomenological studies[6-18] of melt elasticity and viscosity have implied that average entanglement spacings are also dependent upon the prior treatment of the polymer. Altering variables such as the processing time and temperature of extrusion, the intensity of shearing, or the temperature and time allowed for annealing can produce large variations in melt elasticity and/or viscosity. Commercial processors of thermoplastics have used this result to their advantage when they "shear refine" their materials.

Similar variations in melt elasticity and viscosity are observed when polymers are abruptly precipitated out of dilute or concentrated solutions.[2,13-16] More recently, the measured average entanglement spacings of narrow molecular weight distribution polystyrenes that had been precipitated out of solutions of various concentrations were found to change as a result of their solution treatment.[1]

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The zero shear viscosities of these samples were observed to vary as well, for samples of identical molecular weight distribution, but the viscosities of the solution-treated samples could not be reconciled with the observed changes in the entanglement spacing by use of simple reptation scaling relationships. The results could be rationalized by introducing a version of the coordination number model developed by Kavassalis and Noolandi.[19-21]

Surprisingly, the steady-state compliances of the narrow fractions studied were not concurrently altered with the average entanglement spacing.

The present set of experiments is an attempt to assess the effects of polydispersity on polymer property changes that result from various solution treatments. The test samples are composed of blends of narrow fractions so that comparisons can be made between samples having the same weight-average molecular weight but different molecular weight distributions. The modified reptation scaling relationship, which successfully rationalized the behavior of solution-modified polystyrene narrow fractions, is tested with these data as well. As before,[1] this work provides a unique test of modern reptation-based theories in that sample molecular weight, polydispersity, and mean entanglement spacing can all be treated as independent variables.

Experimental Section

Commercial narrow distribution anionic polystyrenes ($M_w/M_n < 1.2$) were used to make binary and ternary blends of variable molecular weight distribution. The appropriate weights of the components of each blend were dissolved in chloroform such that the concentration of the blend in solution varied from 5 to 50 g/L. After dissolution of all observable polymer solids had occurred, the solutions were allowed to sit for a minimum of 1 week with occasional agitation to ensure good mixing.

The polymers were recovered from solution by abrupt precipitation with ethanol during stirring. The ethanol/chloroform volume fraction was 2:1. The stirrer speed was approximately constant for solutions of similar concentration. Agitation was continued until the precipitated polymer coagulated, leaving a clear solvent mixture. The polymer was then recovered by suction filtration and dried in a vacuum oven at 40 °C for a minimum of 6 weeks. During the 6-week period, the recovered samples

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Table I
Molecular Weight Distributions of Binary and Ternary Polystyrene Blends[a]

Binary Blends							
sample[b]	W_L	W_S	$10^{-3}M_n$	$10^{-3}M_w$	$10^{-3}M_z$	M_w/M_n	M_z/M_w
600208	0.74	0.26	402	498	558	1.24	1.12
900208	0.42	0.58	307	498	732	1.62	1.47
600090	0.80	0.20	281	498	582	1.77	1.17
900090	0.50	0.50	165	498	827	3.02	1.66

Ternary Blend								
sample[c]	W_L	W_M	$10^{-3}W_S$	$10^{-3}M_n$	$10^{-3}M_w$	M_z	M_w/M_n	M_z/M_w
602009	0.55	0.30	0.15	248	406	523	1.63	1.29

[a] W_L is the weight fraction of the larger molecular weight component; W_M is the weight fraction of the medium molecular weight component; W_S is the weight fraction of the smaller molecular weight component. [b] The first and last three numbers in the sample code refer to the molecular weight (in thousands) of the fractions used to make the blend. [c] Every consecutive two digits refers to the molecular weights (in ten thousands) of the blend components.

were pulverized in a mechanical grinder, at liquid nitrogen temperature, to facilitate residual solvent removal and to produce samples that were physically convenient for further work.

The residual solvent content in all of the samples was measured by gas chromatography at 130 °C. Solutions of 1.5% (w/w) polystyrene in 1,2,4-trichlorobenzene were injected into columns (10% Carbowax 20M TPA on Chromosorb W 80–100 mesh) fitted with a glass wool plug to prevent fouling due to polymer. Column eluent was detected by flame ionization.

Size exclusion chromatography (SEC), at room temperature, was used to measure molecular weight distributions before and after solution and mechanical treatment. The SEC solvent was tetrahydrofuran. A UV detector recorded the eluting species, as measured at a wavelength of 254 nm.

The glass transition temperatures of the dried polymers were measured by differential scanning calorimetry (DSC). Apparent glass transition temperatures were recorded at heating rates of 5, 10, 15, and 20 °C/min, and extrapolated to 1 °C/min.

A Rheometrics mechanical spectrometer, Model 605, was used to collect dynamic mechanical and stress relaxation data using parallel plate geometry for all of the samples. Samples were molded at temperatures up to 240 °C while the top tool was jogged to exclude air. In both types of test, the applied strain was 5%, which is well within the linear viscoelastic response region for all of the samples. Measurements were made under a nitrogen atmosphere to minimize possible sample degradation. Dynamic mechanical data were collected at frequencies between 10^{-2} and 1 rad/s and temperatures between 125 and 215 °C. Stress relaxation data were collected at 170 °C. The step time, which is the time required to achieve full imposition of the test strain, was of the order of 10^{-2} s.

Repeated experiments on already characterized specimens produced duplicate results, indicating that no significant annealing took place during the measurements.

Results and Discussion

Molecular Weight and Residual Solvent Analysis. Table I lists the weight fractions of the components that make up the various blends and the calculated molecular weight averages based on the molecular weights of the starting materials. The samples are coded according to the molecular weights of the narrow fractions that went into a particular blend. For binary blends, the first and last three numbers of the code represent the molecular weights in thousands of the higher and lower molecular weight components, respectively. For the ternary bends, the first, middle and last two numbers represent the molecular weights in tens of thousands of the components ranging from the highest to lowest molecular weights, respectively. For example, the binary blend designated 600208 consists of two narrow polystyrene fractions having molecular weights 600 000 and 208 000. In the other tables and figures presented in this section, the two numbers following the dash represent the concentration, in grams per liter, of the chloroform solutions from which the sample was precipitated.

Table II
Glass Transition Temperatures and Residual Solvent Content of Polystyrene Blends

sample	ethanol,[a] wt %	chloroform, wt %	T_g (1 °C/min), °C
600208-05	0.0019	0.0009	102.2
600208-10	0.0025	0.0010	103.1
600208-20	0.0020	0.0007	102.5
600208-50	NQ	0.0005	102.7
900208-20	NQ	0.0005	102.9
900208-50	NQ	0.0011	103.5
600090-05	0.0171	0.0014	102.5
600090-10	NQ	0.0008	102.2
900090-20	NQ	0.0004	101.7
900090-50	0.0074	0.0014	102.2
602009-05	NQ	0.0007	101.7
602009-50	NQ	0.0006	103.7

[a] NQ, residual solvent content was not quantifiable although some small amount was detectable.

Comparisons of SEC chromatograms (see supplementary material) of samples having the same blend composition, after solution and mechanical treatment, lead to the conclusion that this treatment has not altered the molecular weight distributions of any of the blends.

Residual solvent values can be found in Table II. Unlike the case for narrow fractions reported previously,[1] residual ethanol was present in quantifiable, but minute, amounts in some of the samples. The residual chloroform contents of these blends compare with that of the previously studied narrow fractions. Also listed are the glass transition temperatures of the blends. These are all higher than the glass transition temperature of untreated polystyrene. It is clear that the residual solvent contents of these samples do not significantly influence the glass transition temperature of these samples, since a decrease[3,22] in T_g can be expected with increasing residual solvent content. It is unlikely that the small residual solvent content of these samples influences other physical properties reported here.

Mechanical Data Analysis. (a) Master Curve Construction and Comparison. Frequency shift factors, for time–temperature superposition, were measured empirically from both the loss and storage moduli data, at each temperature, after the moduli had been corrected for temperature and density by the shift factor, $B(T) = \rho_0 T_0/\rho T$. The reference temperature was 125 °C. Densities were estimated from[23] $\rho = -4.97 \times 10^{-4}T + 1.075$, which is independent of molecular weight for the molecular weight range studied here.

The measured shift factors for these blends are plotted in Figure 1 along with the WLF equation[3,24] that was determined from the shift factors for the narrow fractions studied previously.[1] There is excellent agreement between the data and this equation. Fitting the WLF equation to the data of both the narrow fractions and the blends produces the WLF coefficients in eq 1.

$$\log a_t = -9.3\,(T - T_0)/(77 + T - T_0) \qquad (1)$$

Good superposition of the data was achieved, as can be seen from an examination of the master curves, Figures 2 and 3 (see supplementary material as well).

The appearance of multiple plateaus in the storage spectra, and multiple peaks or shoulders in the loss spectra, is consistent with reported spectra of blends consisting of narrow molecular weight distribution components that

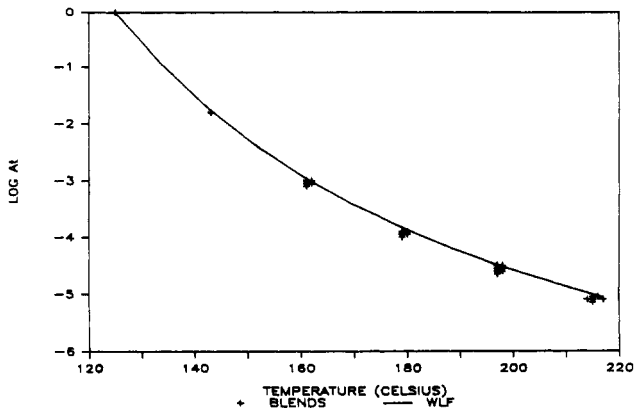

Figure 1. Empirical frequency shift factors as a function of temperature for all of the blends. The solid line is the WLF relationship as described in the text.

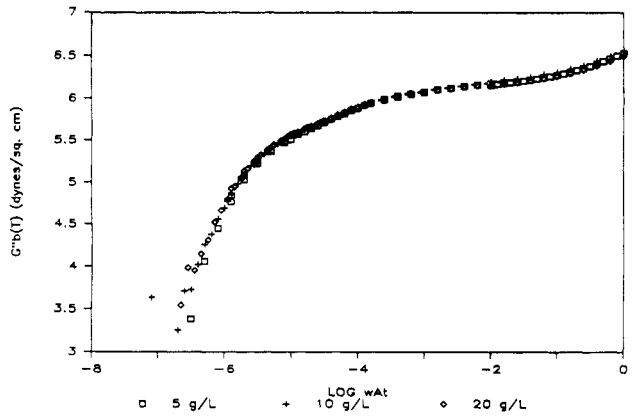

Figure 2. Storage modulus master curves (125 °C) for samples of blend 600208 with difference solution–precipitation histories. The molecular weight distributions of these samples are identical. This solution treatment has produced a small difference in the master curves.

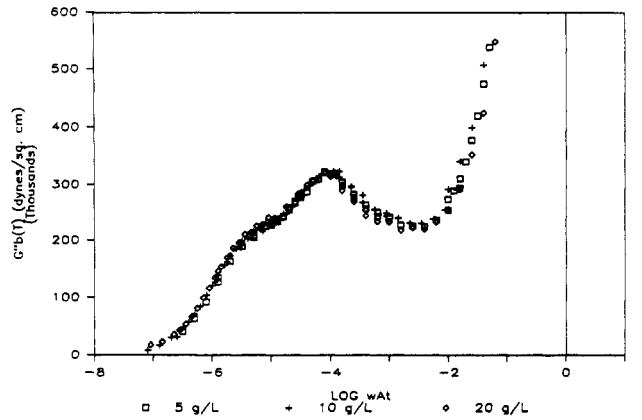

Figure 3. Loss modulus master curves (125 °C), focusing on the terminal peak, for samples of blend 600208 with different solution–precipitation histories. The samples have identical molecular weight distributions. This solution treatment has produced only a small difference between samples.

are well separated in molecular weight, and therefore in relaxation times. Other workers[25–30] have interpreted such spectra in terms of interactions between long chains and long chains, long chains and short chains, and short chains and short chains, within the framework of reptation dynamics. A test of such explanations cannot be convincing here because of the design of our experiment.

Solution treatment, under the conditions used here, has produced little apparent difference in either the storage or loss modulus spectra for samples of identical molecular weight distribution. Differences are most apparent in the loss modulus curve because of the linear ordinate axis. The changes in master curves are small compared to the magnitude of those observed in the previously studied narrow fractions.[1]

Table III
Results of Two-Parameter Power Law Curve Fit With B_2 = 0.694 and B_1 = 0.33

sample	$10^{-4}A_1$	$10^{-6}A_2$	sample	$10^{-4}A_1$	$10^{-6}A_2$
600208-05	2.01	3.71	600090-05	3.84	4.25
600208-10	2.26	3.80	600090-10	4.53	3.78
600208-20	1.96	3.18	900090-20	6.96	3.54
600208-50	2.26	4.04	900090-50	7.79	3.67
900207-20	3.02	4.26	602009-05	3.88	3.53
900207-50	3.13	2.87	602009-50	3.82	4.14

(b) Estimation of Average Entanglement Molecular Weights. The average molecular weight between chain entanglements, M_e, was estimated for each sample by use of eq 2,[3–5] where ρ is the density of the material at temperature T, R is the ideal gas constant, and G_N is the plateau modulus, which is the value of shear modulus associated with the rubbery plateau region of polymer viscoelastic response.

$$M_e = \rho RT/G_N \tag{2}$$

The plateau modulus was estimated from the area under the loss peak for each sample using eq 3[3] from the phenomenological theory of linear viscoelasticity, where G'' is the loss modulus and ω is the test frequency. Power law behavior[31] was assumed to represent the region of overlap between the terminal and transition zones and the data in this region were fitted with eq 4 with $B_1 = 0.33$ and $B_2 = 0.694$.[1]

$$G''(\omega a_t) = A_1(\omega a_t)^{-B_1} + A_2(\omega a_t)^{B_2}$$
$$\text{for } 3(\omega a_t)_{max} < \omega a_t < 10^8 \text{ rad/s} \tag{4}$$

The values of the terminal zone coefficient, A_1, and the corresponding transition zone coefficient, A_2, that were determined in this manner can be found in Table III. The terminal coefficients are plotted bilogarithmically against the number-average molecular weight in Figure 4 along with coefficients determined for polystyrene narrow fractions.[1] The line drawn through the data points was determined by least squares and the same relationship is observed between A_1 and number-average molecular weight of these blends as for polystyrene narrow fractions[1] (eq 5). Our decomposition of the terminal and transition zones is not affected by sample history.

$$G''(\omega a_t)_{terminal} = 7.4 \times 10^{11} M^{-1.3} \omega a_t^{-0.33} \tag{5}$$

Values of the plateau modulus, G_n, for these blends are listed in Table IV and values of the entanglement molecular weight, calculated from these plateau modulus measurements, can be found in Table V. For a given molecular weight distribution, the solution treatment used here has not produced differences outside of experimental error in the plateau modulus. However, it has been established[4,5,32,33] that the plateau modulus of such blends, for samples in the equilibrium entanglement condition, is independent of sample polydispersity. With these solution-precipitated samples, a difference between the plateau moduli of up to 25% is observed between different blends.

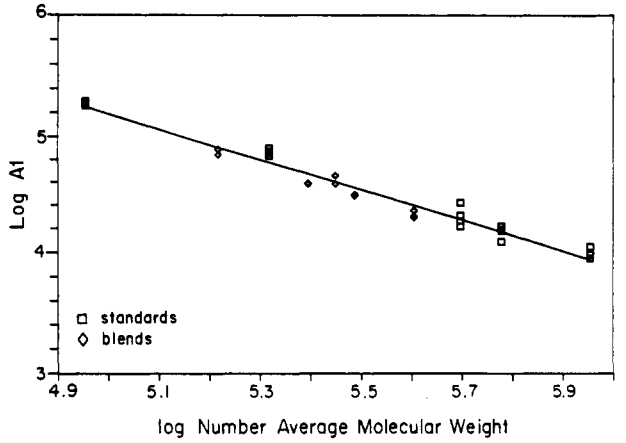

Figure 4. Dependence of the terminal power law curve coefficient, A_1, on the number-average molecular weight. Data for blends and standards are plotted. The solid line, from least-squares analysis, is the same relationship as that observed for polystyrene standards. The resolution of the terminal region that lies under the transition zone is not dependent on sample history.

Table IV
Rheological Parameters of Polystyrene Blends

sample	$10^6 G_n$ (125 °C), dyn/cm²	$10^5 \eta_0$ (170 °C), P	$10^{-6} J_e°$ (125 °C), cm²/dyn	$10^{-6}\delta_0$ (170 °C),[a] dyn·s/cm
600208-05	1.20	3.5	3.0	1.54
600208-10	1.26	4.4	3.0	1.71
600208-20	1.21	4.8	3.0	1.60
600208-50	1.26	3.9	3.0	1.63
900208-20	1.35	2.0	7.1	1.67
900208-50	1.27	2.1	7.1	1.79
600090-05	1.42	5.3	2.9	1.60
600090-10	1.43	5.2	3.0	1.54
900090-20	1.45	2.5	7.1	1.46
900090-50	1.52	2.5	6.6	1.54
602009-05	1.35	3.3	4.5	1.46
602009-50	1.38	3.6	4.5	1.83

[a] Estimated from glass transition data as described in the text.

Table V
Molecular Parameters of Polystyrene Blends Estimated from Rheological Measurements

sample	M_e (170 °C)	$\tilde{N}+1$ (170 °C)	sample	M_e (170 °C)	$\tilde{N}+1$ (170 °C)
600208-05	30 500	4.5	600090-05	25 700	3.1
600208-10	29 000	4.3	600090-10	25 600	3.1
600208-20	30 300	4.2	900090-20	25 200	2.5
600208-50	28 900	4.4	900090-50	24 000	2.5
900208-20	26 900	4.3	602009-05	27 100	3.1
900208-50	28 800	4.3	602009-50	26 500	3.2

No correlation is observed between plateau modulus values and polydispersity of these samples, which leads to the conclusion that the variation in plateau modulus values is a result of solution treatment.

(c) Estimation of Zero Shear Viscosity. The zero shear viscosity was obtained by measuring the area under stress relaxation modulus–time curves observed at 170 °C. Equation 6 from linear viscoelastic theory[3-5] was applied.

$$\eta_0 = \int_0^\infty G(t)\, dt \tag{6}$$

All of the blends (except the ternary blend) have the same weight-average molecular weight. According to the supposition that the zero shear viscosity scales as the 3.4 power of weight-average molecular weight,[3-5] all of the blends should have the same zero shear viscosity.

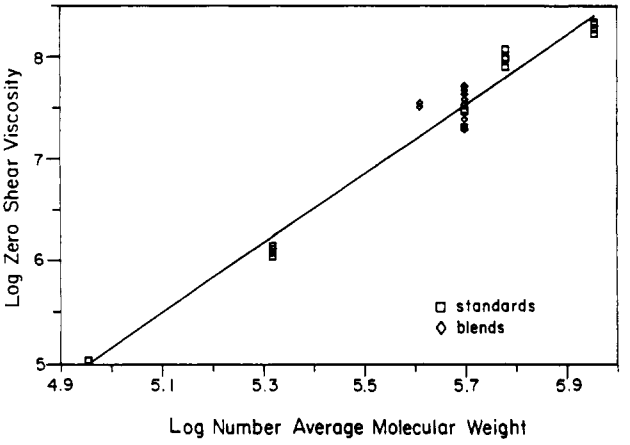

Figure 5. Zero shear viscosity as a function of weight-average molecular weight. Plotted are data for polystyrene standards which give the solid line of slope 3.4 by least squares. Data for blends having the same weight-average molecular weight (498 000) show a half-decade of scatter in the zero shear viscosity.

Viscosities are listed in Table IV. Samples having the same weight-average molecular weight show a variation of approximately 110% in zero shear viscosity. Viscosity differences for samples of identical molecular weight distribution are much smaller. The largest variation occurs with the 600208 series samples and the largest and smallest values of viscosity are different by approximately 35%. If the viscosity is dependent only on the weight-average molecular weight and not on the sample polydispersity, as has been reported by many workers,[3-5] viscosity differences must be attributed to the effects of solution treatment.

Figure 5 is a log–log plot of viscosity against molecular weight. Data for the previously studied[1] polystyrene fractions are plotted along with data from these blends. The line has slope 3.4, determined by least squares for the narrow standards data. The data for the blends of weight-average molecular weight 498 000 show a scatter of half a decade.

(d) Estimation of Steady-State Compliance. The steady-state compliance was estimated from the limiting behavior of the storage compliance according to eq 7.[5] Figure 6 plots log J' against log G' [32] and the storage

$$J_e^0 = \lim_{\omega \to 0} \frac{G'}{G'^2 + G''^2} = \lim_{\omega \to 0} J' \tag{7}$$

compliance attains limiting values at fairly high storage modulus. Values of the steady-state compliance, $J_e°$, are listed in Table IV.

It is well established[5] that the steady-state compliance is very sensitive to sample polydispersity. The exact nature of the correlation between dispersity averages and $J_e°$ is still subject to some uncertainty. Generally, the steady-state compliance of a blend, $J_{eb}°$, is expressed in terms of the steady-state compliance of the corresponding narrow fraction that has the same molecular weight as the weight-average molecular weight of the blend multiplied by a correction factor for polydispersity (eq 8).

$$J_{eb}° = J_e°(M_w)^P \tag{8}$$

There are many theoretical expressions for the parameter P, most of which cannot be adequately tested with these data because of the design of our experiment. There is general agreement[5] that the steady-state compliance correlates with the high molecular weight end of the molecular weight distribution. Proposed forms of the pa-

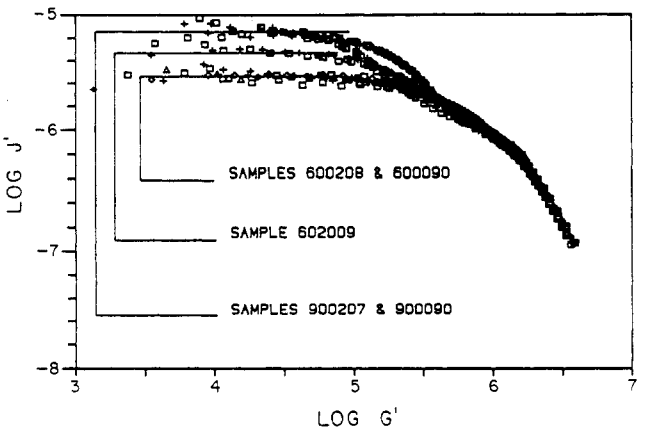

Figure 6. Limiting compliance behavior of solution-treated polystyrene blends at 125 °C. The storage compliance levels out at fairly large values of storage modulus so that limiting values are easily observed. The lines in the figure are meant only as a guide to which data sets correspond to which samples.

rameter P therefore usually involve ratios of the higher molecular weight averages. For example, the modified Rouse[5] model gives

$$P = \overline{M_z}\,\overline{M_{z+1}}/\overline{M_w}^2 \tag{9}$$

Aggarwal[34] proposed

$$P = \overline{M_z}\,\overline{M_{z+1}}/\overline{M_n}\,\overline{M_w} \tag{10}$$

whereas Mills and Nevin[35] observed

$$P = (\overline{M_z}/\overline{M_w})^{3.7} \tag{11}$$

More recently, Zang et al.[36] proposed that the factor P should be expressed in terms of molecular weight moments derived from considerations of proportionalities between the zero shear viscosity and molecular weight, and between the weight-average relaxation time and molecular weight. Their derivation gives

$$P = \sum w_i M_i^a/(\sum w_i M_i)^a = Q_a/Q_1^a \tag{12}$$

The quantity a is the power law exponent that gives the scaling relationship between zero shear viscosity and weight-average molecular weight. This expression has been shown to fit the data for several polymers.[36]

At first glance it would appear to be unreasonable to try to describe our data with this equation, since we have already demonstrated a half-decade of scatter in the viscosity–molecular weight relationship for these solution-treated blends. However, one should expect that the dependence of viscosity on molecular weight should be the same for a series of samples having the same entanglement molecular weight. That is, a comparison of a series of samples with one entanglement molecular weight to a series of samples with another entanglement molecular weight should show two viscosity–molecular weight curves with the same slope, but different intercepts. This has in fact been observed experimentally in another solution modification study[13] in which a series of samples were subjected to the same solution history.

Since the derivation of the above P factor depends only on the exponent of the viscosity–molecular weight power law and not on the intercept, and since no dependence of steady-state compliance on sample history was observed[1] for polystyrene narrow fractions, the expression of Zang et al. should fit our data provided that the steady-state compliance is independent of sample history for these blends as well.

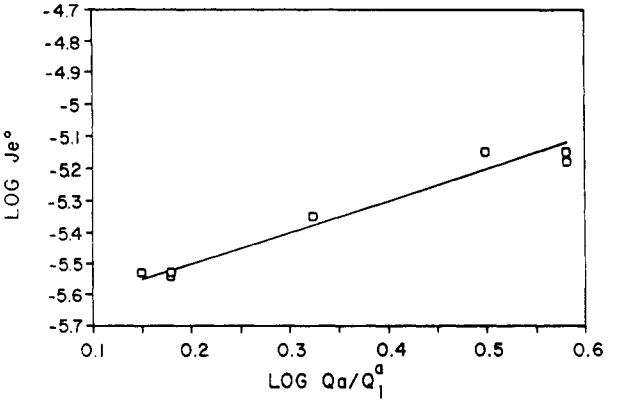

Figure 7. Steady-state compliance as a function of the polydispersity factor Q_a/Q_1^a, described in the text, for solution-treated polystyrene blends. The steady-state compliance appears to be independent of the variation in entanglement spacings observed here and dependent only on sample molecular weight distribution.

Figure 7 is a bilogarithmic plot of steady-state compliance against Q_a/Q_1^a, where $a = 3.4$ for these blends. Linear least squares gives a correlation coefficient of 0.98, a slope of 0.95, and an intercept of −5.68. The slope is in good agreement with the expected slope of 1, and reasonable agreement is obtained between the value of the intercept and the value of the molecular weight limited compliance measured for polystyrene narrow fractions. The steady-state compliance, as for solution-treated narrow fractions, is independent of sample history for the range of properties generated here.

Entanglement and Viscosity. (a) Reptation. The viscosity and entanglement molecular weight data measured for these blends can be used to test the reptation theory scaling prediction.[37] A true test of the scaling relationship requires that comparisons be made for samples with the same friction coefficient.[4] The glass transition data can be used to estimate friction coefficients[3] of the various blends using eqs 13 and 14.

$$\log a_{\Delta T_g} = -C_{1,g}C_{2,g}(T_{g_1} - T_{g_2})/(C_T + (T_{g_1} + T_{g_2}))C_T \tag{13}$$

$$a_{\Delta T_g} = [\xi_0]_{mod}/[\xi_0]_{equil} \tag{14}$$

The estimated values of friction coefficient are listed in Table IV. These values are all greater than the molecular weight limited friction coefficient for equilibrium polystyrene narrow fractions because the glass transition temperatures of these samples are all greater than 100 °C.

Tests of the reptation theory scaling law for polydisperse samples involves use of one of the averages of the sample molecular weight distribution as the correlating parameter for viscosity. Empirically, one is tempted to use the weight-average molecular weight because this parameter is the one usually quoted when correlations between viscosity and molecular weight of broad distribution samples are examined. However, the reptation scaling law that relates viscosity to molecular weight and entanglement molecular weight was arrived at by consideration of the *number* of entanglement points per unit volume.[37] The appropriate average molecular weight parameter for polydisperse systems will therefore be the number-average molecular weight[38] (eq 15).

$$\eta_0 \sim \overline{M_n}^3/M_e^2 \tag{15}$$

Viscosities of the blends were reduced for molecular weight and friction coefficient effects and plotted against

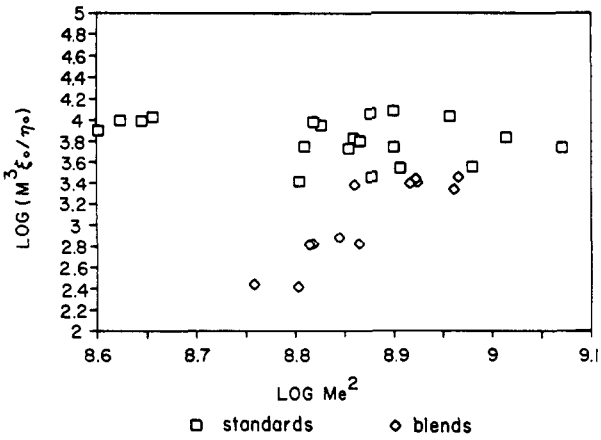

Figure 8. A test of the reptation theory scaling relationship for the dependence of viscosity on the entanglement molecular weight after the molecular weight and friction coefficient dependence of viscosity has been corrected for. Plotted are data for solution-treated polystyrene narrow fractions as well as the data for these solution-treated blends. The expected unique line of slope 1 is not observed.

the entanglement molecular weight in Figure 8 along with the data for the modified narrow fractions previously studied.[1] Lines of slope 1, which are indicative of reptational behavior, have not been added to this plot, but it is not difficult to see that some of the data points could be used to construct such lines. More importantly, it is clear that these data, like those of the narrow fractions, do not demonstrate a unique relationship of slope 1. This leads to the conclusion that the viscosity, corrected for molecular weight and friction coefficient dependence, is not a single-valued function of the entanglement molecular weight for these solution-treated samples.

(b) Coordination Number Model. Recently,[19-21] a statistical mean field approach to the topology of polymer chains in the matrix has been used to investigate the entanglement problem. This model considers the number of other chains surrounding a test chain in a sphere having diameter, D_e, equal to the mean distance spanned by an entangled segment of N_e bonds with characteristic ratio, C_∞, and bond length, l (eq 16).

$$D_e = N_e^{1/2} C_\infty^{1/2} l \tag{16}$$

The number of nontail chains (those that do not end with a tail in the sphere) is the only adjustable parameter in the model, which otherwise offers exact solutions. The average number of nontail chains (hereafter referred to as chains) in the test sphere represents a way of defining the nature of an entanglement coupling on a statistical basis. The number of neighboring chains in the test sphere, called the coordination number, can be viewed as the average number of chains that constitutes a constraint to lateral motions of the test chain, or the number of chains that, on the average, makes up an entanglement coupling.

In the long-chain limit, the coordination number, $\bar{N}$, is expressed by eq 17. Here, ρ is the polymer density, C_∞ is

$$\bar{N} + 1 = (\pi \rho C_\infty^{3/2} l^3 / 6\mu_m) N_e^{1/2} \tag{17}$$

the characteristic ratio, l is the bond length, μ_m is the monomer mass per skeletal bond, and N_e is the number of monomer units between chain entanglements. A survey of the literature data collected on narrow fractions for many polymers suggests that the coordination number is a constant for the "equilibrium" entanglement condition.[21]

The coordination number model can be generalized to include sample polydispersity.[19-21] In the long-chain limit, the relationship between the coordination number and the entanglement molecular weight is independent of polymer molecular weight.

We have previously demonstrated[1] that a modification of this model can be used to rationalize the viscosity behavior of polystyrene narrow fractions having different solution histories. This was achieved by introducing an "effective coordination number" to reflect alterations in chain topology resulting from our precipitation process.

It is probable that our precipitation process has resulted in molecular spatial dimensions that do not conform to the equilibrium situation. The collapse of a polymer chain upon itself, and some preservation of the end-to-end chain distance that existed during precipitation, are examples of situations that are possible with these samples. Other researchers have postulated[17] or measured[15,16,39-42] distortions in the size and shape of the polymer molecular coil as a result of processing.

The coordination number model could be used to describe the polymer chain statistics of samples that do not have equilibrium topologies by measuring changes in the characteristic ratio, for example. It is likely that a number of microscopic physical quantities are being altered by sample history. Since, we have no measurement of these quantities, we have chosen to generalize the model by introducing "effective coordination numbers" for ease of computation.

The coordination number model has been derived strictly from considerations of chain topology in a static system. As described elsewhere,[1] we have incorporated the coordination number scheme into the Rouse model (modified for entanglement interaction) to provide eqs 18 and 19, from which effective coordination numbers can be calculated using our data.

$$\eta_{0COORD}/\eta_{0R} = KM_e^2/(\bar{N} + 1)^4 \tag{18}$$

$$K = \pi \rho^4 C_\infty^6 l^{12} / 6^4 M_0^2 \mu_m^4 \tag{19}$$

Effective coordination numbers are calculated by substituting the experimentally observed values of zero shear viscosity for η_{0COORD} and estimating η_{0R} (modified Rouse model viscosity) using literature constants for polystyrene (ρ = 0.991 g/cm^3 at 170 °C, C_∞ = 9.4, $l = 1.54 \times 10^{-8}$, M_0 = 104, μ_m = 52) and the values of M, M_e, and ξ_0 for these samples. Effective coordination numbers are listed in Table V.

The reptation scaling prediction can be rewritten to accommodate our effective coordination number.[1] The zero shear viscosity scales as $1/M_e^2$, which is equivalent to $1/(\bar{N} + 1)^4$ in the equilibrium case. If we treat both parameters as independent parameters for our nonequilibrium samples, scaling prediction (eq 20) can be written.

The values of effective coordination numbers, and the

$$\eta_0 \sim \frac{M^3 \xi_0}{M_e^2 (\bar{N} + 1)^4} \tag{20}$$

entanglement molecular weights estimated from the plateau modulus, listed in Table V, were used to test this modified scaling law. Plotted in Figure 9 are the data for these blends and for solution-treated polystyrene narrow fractions. The blend data have extended the abscissa by about a decade and these data are consistent with the data for narrow fractions. The line through the points has a slope of 0.95 (least squares), which is in good

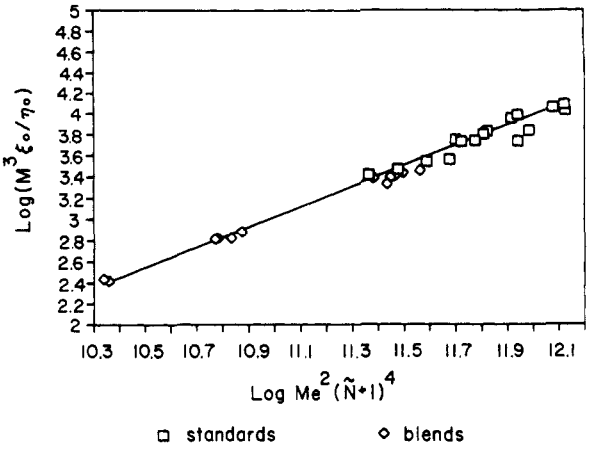

Figure 9. A test of the reptation theory scaling prediction, modified to accommodate a dependence on effective coordination numbers as described in the text. The data of Figure 8 reduce to a unique linear curve. The solid line, determined by least squares, has a slope of 0.95, which is very close to the expected slope of 1.

agreement with the expected slope of unity for reptation dynamics. Use of effective coordination numbers has rationalized the deviation, within the reptation model framework, of zero shear viscosity with the entanglement molecular weight of these samples.

Conclusions

Solution treatment of these blends has resulted in variations of the average entanglement spacings, as measured by plateau modulus, of these samples. The variation in entanglement spacing was not as large as that observed for polystyrene standards. Other properties of the blends have been affected as well.

An increase in the glass transition temperature was observed as a result of solution treatment. This change is not accounted for by the small amounts of residual solvent present because a decrease in the glass transition temperature is expected for diluted polymers.

Zero shear viscosity values varied as much as 110% for samples having the same weight-average molecular weight. This is larger than the variation that was observed in this property for standards that had been treated in the same way. Larger changes in viscosity corresponded to smaller changes in the entanglement spacing than those observed for solution-treated narrow fractions. This implies that the zero shear viscosity is more sensitive to entanglement spacing changes in broad distribution polymers.

The steady-state compliance was independent of the entanglement spacing and was only dependent on sample polydispersity. Good correlation was obtained between J_e° and the ratio of molecular weight moments Q_a/Q_1^a derived by Zang et al.[36]

After viscosities were corrected for molecular weight and friction coefficient differences, a unique reptational scaling dependence on the entanglement molecular weight was not observed. Use of effective coordination numbers, estimated from the data, did provide a unique modified scaling relationship. This analysis implies that solution treatment modifies not only the entanglement spacing, but also the nature of the entanglement. The analysis also implies that the change in the nature of the entanglement for these samples is a result of changing the volume in which the entanglement segment is confined.

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Supplementary Material Available: SEC chromatograms of blends that have undergone solution and mechanical treatment (Figures 1–5), storage modulus master curves of blends with different solution–precipitation histories (Figures 6–9), and loss modulus master curves, focusing on the terminal peak, of blends having different solution–precipitation histories (Figures 10–13) (13 pages). Ordering information is given on any current masthead page.

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