

<연구논문>

저분자량/고분자량 폴리스타이렌 블렌드의 점탄성

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(1991년 4월 2일 접수)

Viscoelastic Properties of Low/High-Molecular-Weight Polystyrene Blends

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(Received April 2, 1991)

요 약

저분자량(분자량 : 1.04×10^4 g/mole)과 고분자량(3.84×10^6) 폴리스타이렌 블렌드를 제조하고 무접촉, 무마찰을 이용한 비틀림 크립장치를 사용하여 점도, 크립 캄플라이언스들을 측정하고 또 지연 스펙트라도 계산해 내었다. 고분자량의 농도는 0, 2, 10, 20, 50, 70, 100 중량 퍼센트였다. 점도는 블렌드의 중량평균 분자량이 임계분자량 이상이면 중량평균의 3.5승에 비례했다. 중량평균 분자량 > 임계분자량 인 블렌드의 경우 정상상태 회복 캄플라이언스는 중량평균의 -2.3승에 비례했다. 지연스펙트라를 검토한 결과 폴리스타이렌의 임계분자량은 38000 g/mole쯤으로 추정되었다.

Abstract—Creep compliance measurements were conducted using a magnetic bearing torsional creep apparatus for polystyrene/polystyrene blend-like solutions whose high-molecular-weight polymer concentrations were 0, 2, 10, 20, 50, 100 wt%. For the blends whose weight-average-molecular-weight (M_w) is larger than the critical molecular-weight (M_c), the zero-shear viscosities were proportional to $(M_w)^{3.5}$. When $M_w > M_c$, the steady state recovery compliance J_e showed -2.3rd power dependency to the M_w . The critical molecular weight M_c for polystyrene was found to be 38000 g/mole from analysis of the retardation spectra.

Keywords: Polystyrene, Blends, Creep, Retardation spectrum

1. Introduction

Many theories[1-5] have been suggested to predict the viscoelastic properties of polymer melts and solutions. Among them Doi-Edwards tube model[3] seems to be in good success in explaining some fundamental properties concerning polymer rheology. On the other hand there has been another approach[6,7] to interpret the experimental results through the concept of the molecular entanglements. Much emphasis was focused on the more detailed geometry and quantitative description of entanglements and their interactions.

Kotliar *et al.*[8] reported that the apparent viscosity of atactic polystyrene that is initially in the disentangled state increases as time passes. They confirmed that the entanglement concentration increases by the reptation-like diffusion of molecules, which are initially in the disentangled state.

It has been known that polymeric liquids start to show the entanglement effects in viscosity when the molecular weight (MW) exceeds a certain critical value M_e . More often the molecular weight between "the entanglements" M_e is used as a good measure to indicate the degree of entanglements for a polymer system.

Binary blends of narrow molecular weight distribution (MWD) polymers can be recommended as the simplest model system which is appropriate to test the validity of the proposed theories. This system has only short (S) and long (L) species of the same polymer. Let their MW's be M_S and M_L , respectively.

This system provides us with several different situations[9]:

1) it can be treated as an undiluted system with bimodal MWD.

2) several definitive MW's can be calculated from the compositions.

3) if $M_S < M_e$, the short species plays the role of a solvent and the system is a solution. (according to the composition, it will be a diluted or a concentrated solution).

4) the system remains in the θ -condition even at different temperatures[10].

5) actually it is a blend system, therefore blending laws can be deduced from the experimental results.

There are some publications on the binary blends of the same polymers.

Watanabe and Kodaka and their colleagues[11-15] conducted systematic experimental work for polystyrene (PS) and summarized their results. Their PS samples have MW's larger than M_e ($= 1.8 \times 10^4$ g/mole for PS)($M_S/M_e = 0.3 \sim 9.5$ and $M_L/M_e = 17.5 \sim 156.1$).

Struglinski and Graessley[16] discussed viscoelastic effects of polydispersity with binary mixtures of nearly monodisperse polybutadiene (PB) ($M_e = 1.85 \times 10^3$ for PB). Their samples have MW's of $M_S/M_e = 21 \sim 98$ and $M_L/M_e = 98 \sim 243$.

Lin[9, 17-21] proposed a theory to explain the line shape of the stress relaxation experiments and adapted his theory for the binary PS/PS blends. His samples cover $M_S/M_e = 0.57 \sim 5.55$ and $M_L/M_e = 3.78 \sim 43.1$ MW ranges.

Doi *et al.*[22] classified the rheological properties of the homopolymer mixtures in terms of three parameters, i.e. M_L , M_S and ϕ_L , which is the volume fraction of the long-species. They differentiated six different situations, which contain 3 different degrees of tube dilation (no, restricted, and free tube dilation) and 2 different line shapes of the stress relaxation measurements (box or wedge shape).

Choi *et al.*[23] proposed a blending law using their equivalent primitive chain model with some rheological measurements on PS binary mixtures. Their PS samples have $M_S/M_e = 5.37$ and $M_L/M_e = 29.3$.

Meister[24] formulated a theory to predict the rheological behavior of entangled linear polymers. He thought out a new mechanism of the "forced segmental reptation" which is applicable only when a polymer assembly is placed under stress. His theory describes the realistic picture of the molecular dynamics quite well.

The aim of this work is to report the experimental results concerning the viscoelastic properties of binary MWD PS/PS blend-like solutions. The creep compliance measurements were con-

cted for the PS/PS blends consisting of the low-MW ($M_S/M_e=0.57$) and high-MW ($M_L/M_e=211$) components. The reduced creep compliance curves and their retardation spectra were deduced using the time-temperature equivalence principle. Colby[25] recently reported that the empirical principle of the time-temperature superposition is found to fail for miscible polymer blends. So the problem should be raised and solved to establish the reason why the time-temperature principle is applicable for some polymer systems.

2. Experimental

2.1. Materials

The component polystyrene samples were nearly monodisperse. Their specifications are summarized in Table 1.

Entanglement index was calculated on the basis of $M_e=18000$ g/mole[7]. For the low-molecular-weight component, the molecular entanglements cannot be formed, but for the high-molecular-weight component, many can.

2.2. Preparation of PS/PS blends[26]

Solutions with a polymer concentration of about 1 weight percent were prepared by slow mixing of the directly weighed components and benzene. The solutions were allowed to equilibrate at room temperature for several days. The solutions were then freeze dried overnight. After the freeze-drying, the material was molded with a stainless molding assembly and a press to give a disk-shape sample with a thickness of about 1.5~2.0 mm. Total sample weight was about 50~150 mg.

2.3. Torsional creep and recovery measurements.

All the creep and recovery data were obtained

by using a magnetic-bearing torsional creep apparatus (MBTCA)[27]. This instrument has a magnetically suspended rotor, to which a given torque is applied by an electrical induction mechanism. The deformation of the sample is measured via a light lever which consists of a laser light source and a set of mirrors attached to the rotor. The beam displacement was recorded by a modified strip chart recorder which has a light detecting circuit and photocells. A vacuum and an inert gas line are connected to the machine. For this work the parallel plate type viscoelastic measurement was made.

After the pre-molded sample was inserted into the machine, the sample chamber was evacuated to a pressure of less than 0.01 Torr and heated to a temperature of ca. 120°C for 2~4 hrs to remove residual solvent, moisture, and entrapped gas. Samples were then heated in nitrogen to a temperature at which the viscosity was $10^5\sim 10^6$ P and reevacuated, at which point the remaining residual moisture etc. cause the sample foam. The shape of the sample then manipulated into cylindrical form by varying the elevation of the lower platen. A step torque was applied and the sample displacement was recorded with the known timer pulses. Most measurements of recovery were made using Leaderman's technique of achieving steady-state creep in a fairly short time by using a relatively high temperature, lowering to the temperature desired for recovery while under load, and then removing the applied load.

The maximum instrument sensitivity allowed absolute compliances of the order of 10^{-8} cm²/dyn to be measured. For compliances below this, the sample was drawn in situ into a thin-waisted rod. In order to measure the compliances using the drawn sample, an empirical shape factor was determined by remeasuring the compliance at a reference temperature, and matching the data for the drawn sample and the undrawn sample.

2.4. Calculations of compliance and viscosity conversions[28]

Let's think to perform a torsion on a linear elastic cylinder, then the required torque about the

Table 1. Component polystyrene specification

Component PS/MW	Low	High
Designation	F-1	F-380
Nominal MW of supplier	1.03×10^4	3.84×10^6
Entanglement Index(MW/M _e)	0.57	213
Polydispersity	1.02	1.04
Manufacturer	TOYO Soda Mfg. Co.	

axis applied to the ends of the cylinder is

$$(\text{torque}) = KG\phi$$

where G is the shear modulus and ϕ is the relative displacement in angle at the outer surface between end surfaces, K is the form factor ($=\pi R^4/(2h)$), R is the radius of the cylinder and h is cylinder height. So the creep compliance J becomes

$$J = K\pi(\text{torque}) = (m^2\pi\rho^2h^3\phi)/(\text{torque})$$

where m is the mass and ρ the density of the sample, and $\phi/(\text{torque})$ is predetermined constant depending on the kinematics of the instrument and testing conditions. The values were already known by calibrating the rotor part with some standard wires.

Densities were calculated with the expression of Fox and Loshaek[29]:

$$1/\rho = 0.767 + 5.5 \times 10^{-4} T + 643 \times 10^{-4} T/M$$

where T is the sample temperature in degrees in K and M is the number average MW.

If the above cylinder is made of a Newtonian fluid, a continuous twisting of the cylinder governs following equation:

$$(\text{torque}) = K\eta(d\phi/dt)$$

where the η is the viscosity coefficient and t the time. Hence the viscosity can be obtained as follows:

$$\eta = (\text{torque})/(Kd\phi/dt) \text{ at long time}$$

The viscosity at a given temperature is calculated from the terminal velocity immediately preceding the removal of the load.

2.5. Calculation of retardation spectra

The retardation spectrum $L(t)$ was calculated from $J(t)$ by a numerical procedure. Using a computer program, the smoothed line drawn through the set of reduced data is fitted by a spline function from which the second approximation to the retardation spectrum was calculated using the Leaderman expression. A second spline function fitted to the second approximation was then used

for the L to evaluate numerically the integral in the expression:

$$J_r(t) |_{\text{calc}} = J_g + \int_{-\infty}^{\infty} L(\lambda)(1 - \exp(-t/\lambda)) d(\ln \lambda)$$

where λ is the retardation time. In several iterations, the approximation to L is changed by our own judgement, until the recoverable compliance curve calculated by the above equation reproduces the experimentally determined curve to within 0.01 logarithmic units.

3. Results and Discussion

The creep recovery and viscosity of the binary PS/PS blends ranging from 0 to 100 weight percent of F380 (higher MW component) in F1 (lower MW component) were measured at several different temperatures. Using the common notation of linear viscoelasticity, $J_r(t)$ is given by the expression:

$$J_r(t) = J(t) - t/\eta = J_g + J_d\psi(t)$$

where $J(t)$ is the shear creep compliance, t is time, η is the limiting low rate of shear viscosity, J_g is the glassy compliance, J_d is delayed recoverable compliance, and $\psi(t)$ is the normalized retardation function, a continuous function defined so that $\psi(0) = 0$ and $\psi(\infty) = 1$. The recovery data for 2% solution are plotted in Fig. 1. From the blend compositions, the number-average and the weight-average MW (M_n , M_w respectively), polydispersity, and entanglement index (M_w/M_n) can be calculated by assuming that both components are truly monodisperse. From the number-average MW of the PS, the T_g can be estimated by using the correlation developed by Altares *et al.*[31]:

$$T_g = 98.0 - 1.02 \times 10^5 M_n \text{ in } ^\circ\text{C}$$

All these values are tabulated in Table 2.

Viscosities of the blends at each test temperature are listed in Table 3.

To construct a reduced recovery curve (complete recovery creep compliance-time behavior at a constant temperature), the time-temperature correspondence principle was applied to each of the

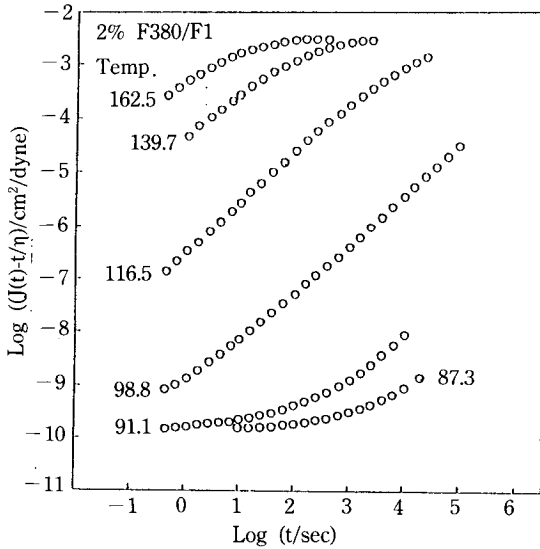


Fig. 1. Plots of the logarithm of the recoverable compliance vs. the logarithm of time t for 0.02 PS/PS solution measured at the indicated temperatures in $^{\circ}\text{C}$.

creep curves. Reduction temperatures were chosen at T_g of each blends to compare all the data at an iso-free-volume-fraction state. No vertical shift were made. The horizontal shift factors a_T 's are determined by manual superposition of the data. As T approaches T_g , the a_T 's become very uncertain. To avoid this pit the a_T 's are plotted in terms of the Vogel equation[23]:

$$\log a_T = \log A + (C/2.303)/(T - T_{\infty})$$

where A , C , and T_{∞} are characterizing parameters. The values of the parameters found for each of

Table 3. Zero-shear viscosities for the PS/PS blends

Blend	$T^{\circ}\text{C}$	$\log \eta_P$	Blend	$T^{\circ}\text{C}$	$\log \eta_p$
0%	121.9	5.799	2%	162.5	4.144
	111.6	7.007		139.7	5.464
	104.6	8.171		125.0	6.214
	99.0	9.004		116.6	7.112
	97.0	9.716		98.8	9.870
	93.4	10.656		91.2	11.842
	183.0	2.16*		188.0	3.51*
10%	177.4	6.181	20%	213.2	6.501
	152.5	7.185		138.3	8.813
	137.2	8.200		108.6	11.108
	123.5	9.329	190.0	6.85*	
	112.5	10.021	50%	199.0	7.980
189.0	5.75*	179.0		8.794	
70%	201.6	8.658		134.9	11.329
	215.6	8.216		193.0	8.22*
	148.1	11.060	100%	198.0	*9.31*
195.0	8.57*				

*Extrapolated values.

the blends are listed in Table 4. The a_T 's and the lowest test temperatures are estimated by extrapolating the above linear relationship.

The reduced recovery curves with their reference temperature (T_0) of T_g are shown in Fig. 2. Most amorphous polymers exhibit the Andrade creep at short times, i.e. a recoverable creep compliance which is linear with the cube root of time:

$$J_r(t) = J_A + \beta t^{1/3}$$

Table 2. Calculated informations about the PS/PS blends and homopolymers

Composition (wt%F380/F1)	M_n	M_w	$\frac{M_w}{M_n}$	$\frac{M_w}{M_c}$	$\frac{\phi M_w}{M_c}$	T_g ($^{\circ}\text{C}$)
0%	1.03×10^4	1.03×10^4	1*	0.57	0	88.1
2%	1.05×10^4	8.69×10^4	8.3	4.83	4.3	88.3
10%	1.14×10^4	3.89×10^5	34.1	21.6	21.6	89.0
20%	1.29×10^4	7.76×10^5	60.2	43.1	42.7	89.9
50%	2.05×10^4	1.93×10^6	94.1	107.2	106.7	92.8
70%	3.41×10^4	2.69×10^6	78.9	149.4	149.3	94.8
100%	3.84×10^6	3.84×10^6	1*	213.3	213.3	98.0

*Each component was assumed to be really monodisperse.

Table 4. Parameter values for the Vogel equation and Andrade creep

Blend	C	T_{∞} (°C)	J_g	β	J_e	$\log J_e$
0%	921	60	6.90×10^{-11}	6.83×10^{-11}	6.407×10^{-8}	-7.193
2%	1103	55	1.09×10^{-10}	1.59×10^{-11}	2.972×10^{-3}	-2.527
10%	891	60	9.21×10^{-11}	5.06×10^{-11}	2.296×10^{-4}	-3.639
20%	1382	50	7.48×10^{-11}	1.71×10^{-11}	5.419×10^{-5}	-4.266
50%	1046	60	2.90×10^{-11}	3.88×10^{-11}	7.707×10^{-6}	-5.113
70%	554	70	5.80×10^{-12}	2.93×10^{-11}	3.751×10^{-6}	-5.426
100%	721	72	2.28×10^{-10}	4.78×10^{-11}	1.644×10^{-6}	-5.798

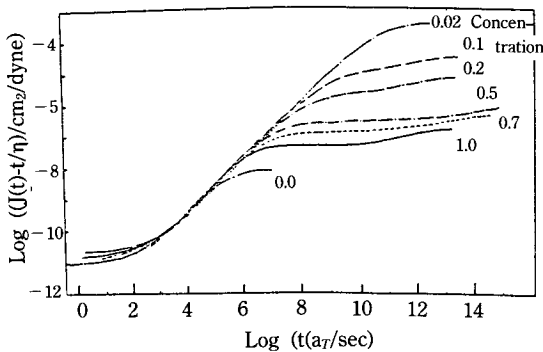


Fig. 2. Logarithmic curves of the reduced recoverable compliance $J_r(t)$ of 7 PS/PS solutions of the indicated concentration (F380 in F1) against the logarithm of the reduced time scale at a reference temperature of T_g .

at temperatures near to and below T_g . In such cases, J_A may be identified with J_g and β is another material characterizing parameter. These values and the steady-state recoverable shear compliance J_e of the blends are shown in Table 4.

The reduced creep compliance data are superposed in Fig. 2. The whole feature of this Figure is very similar to that for the binary PS/PS blends whose both components have MW larger than M_c . The degree of superposition at shorter times is not good because the experimental temperatures for this time scale are at near T_g . The effect of physical aging at around T_g makes the measurement for the shift factor a_T uncertain.

Our PS/PS blend system ranged from a low-MW PS solvent to a high-MW monodisperse polymer and blend-like solutions in the intermediate concentrations. Hence the results can be interpreted both as a blend system and a polymer solution

system. The S-chains have a MW less than M_c and they act like a solvent, especially the theta-solvent. The L-polymers show entanglements at a critical polymer concentration of $(\phi_L)_c = M_c/M_L = 3.1 \times 10^4 / 3.84 \times 10^6 = 0.01$. So our blends are all concentrated solutions. For PS the volume fraction of L-component is nearly equal to the weight fraction of it.

The steady-state recoverable creep compliance J_e

The steady-state recoverable creep compliance J_e increases rapidly at low polymer concentrations. The values of J_e as a function of M_w are plotted in Fig. 3. At higher concentrations the J_e 's have a slope of -2.3 to the M_w or ϕ_L (In terms of concentration, $\phi_L = M_w/M_L$ and $\text{Log } \phi_L = \text{Log } M_w + \text{Log } M_L^{-1}$).

Watanabe and Kodaka summarized their results for PS/PS blends as follows:

$$J_e \propto c^{-1} M \text{ for } M < M_c; J_e \propto c^{-a'} M^b \text{ for } M > M_c$$

where c is the concentration, $c = \rho\phi$, and $a' = 2-2.3$ for many polymers and diluents. In this study $a' = 2.3$, which is nearly the same value of 2.24 for PB blends.

The zero shear viscosity η_0

The zero-shear viscosities at a temperature of $T_g + 100^\circ\text{C}$ for the blends are plotted in terms of the M_w in figure 4. They show an excellent linear relationship of 3.5th power dependency to the M_w except that for the S-polymer. Viscosity for melts is usually expressed in terms of the M_w :

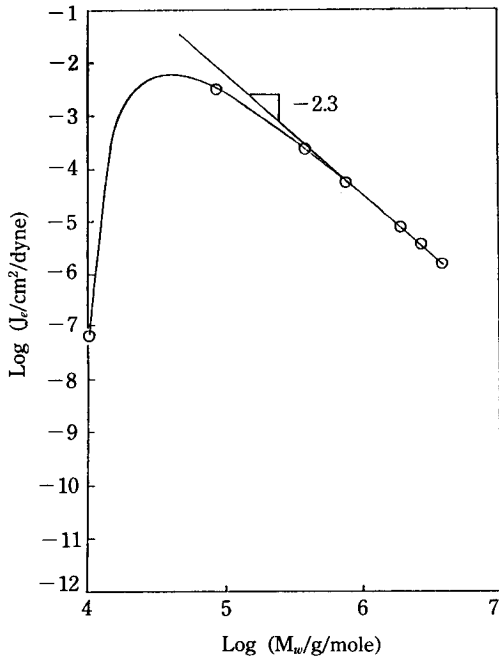


Fig. 3. Log-Log plot of the steady-state compliance against the average M_w of the PS/PS blends.

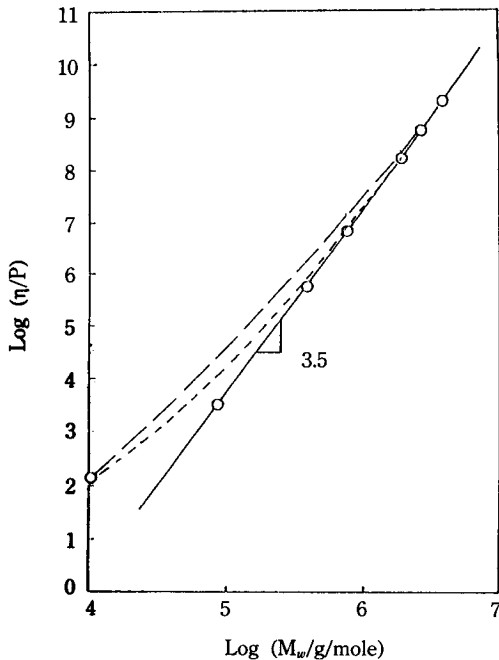


Fig. 4. Comparison of the experimental and theoretical logarithmic zero-shear viscosities of the PS/PS solutions against the logarithm of the average $M_w = \phi_L M_L$. The dotted line and long-dashed line are predictions (see text).

$$\eta_o = KM_w^a$$

where $a=3.3-3.5$ and

$$M_w = \phi_L M_L + \phi_S M_S = \phi_L M_L$$

For solutions:

$$\eta_o = \phi_L M, \text{ for } M < M_c; \eta_o = c^d M^a \text{ for } M > M_c$$

where $d=4.5-5$. The slope of 3.5 starts from the critical concentration $(\phi_L)_c$, where the L-chains start to entangle each other. The presence of the S-component does not change the 3.5th power dependency, i.e., they acts as a θ -solvent. The broken line is the curve calculated from the following equation:

$$\eta_o = (\phi_S (\eta_{oS})^{1/a} + \phi_L (\eta_{oL})^{1/a})^a$$

as Struglinski and Graessley[16] suggested. That line only fits well at higher concentrations. A maximum deviation occurs at $(\phi_L)_c$. The long dashed line is the calculated result from the theory of Meister (See ref.[24], eq (61)). The result is further away from the experiment than that of simple weight-average dependence (the broken line).

The retardation spectrum

The retardation spectra for 7 different blends are superposed in Fig. 5. To describe the features that can be seen in the retardation spectrum, we are going to use the nomenclatures adopted by Berry and Plazek[33]. In their opinion, there are four principal contributions, L_O , L_A , L_B , and L_C , corresponding, respectively to the short-time behavior for which $L_O(\lambda) = \lambda^{1/3}$, the intermediate peak with maximum at time $\lambda_{A, max}$, the next peak with maximum at $\lambda_{B, max}$, and the terminal peak, with maximum at time $\lambda_{C, max}$. Of course, $L(\lambda) = L_O(\lambda) + L_A(\lambda) + L_B(\lambda) + L_C(\lambda)$. Peak A appears in the spectrum for 2% blend as a shoulder. The 0% pure low-MW PS sample shows only peak A. The position of peak A for this sample may be in error. The creep recovery curve at T_g for the 0% sample was estimated by guessing the peak position and shape based on our experiences. At measuring temperature near T_g , the A peak position changes dramatically as shown by Berry and Plazek[33]. Hence this peak should be shifted to a lower time

around that of peak A for 2% sample.

Peaks B and C were associated with the L-component. The general features of retardation spectra are also very similar to those of PS/PS blends with their components' MW higher than M_e . As the concentration of the L-component increases the peaks decreases in height, with peak B shifting to shorter times, and peak C to longer times and attaining a constant value at higher concentrations. The peak A is not detectable at higher concentrations except the 2 wt% sample. The blend system consists of concentrated solutions which only has the L-L entanglements. The S-chains act like a viscous solvent.

For narrow MWD PS with their MW's higher than M_e and PS solutions in Tricresyl Phosphate, the retardation spectra show only 2 peaks B and C[34]. As shown in Figs. 5, 6 the peak B's do not change their positions and peak C's are shifted to longer times as a limiting value and the peak B changes its position to shorter times. This seems to be the special feature of the θ -state PS solutions. We can summarize the results about retardation spectrum as follows: at higher concentrations,

$$\lambda_B \propto M_w^{-3.5}; \lambda_C = \text{constant}$$

and for all concentrations over the $(\phi_L)_c$,

$$\lambda_C/\lambda_B \propto M_w^{3.5}$$

For $\phi_L < (\phi_L)_c$, the topological entanglement con-

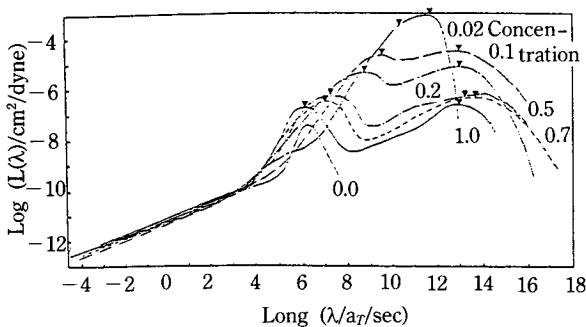


Fig. 5. Bilogarithmic plot of the retardation spectra $L(\lambda)$ of PS/PS solutions with the indicated concentrations as functions of the reduced retardation time $\lambda_r = \lambda/a_T$, where a_T is the temperature reduction factor.

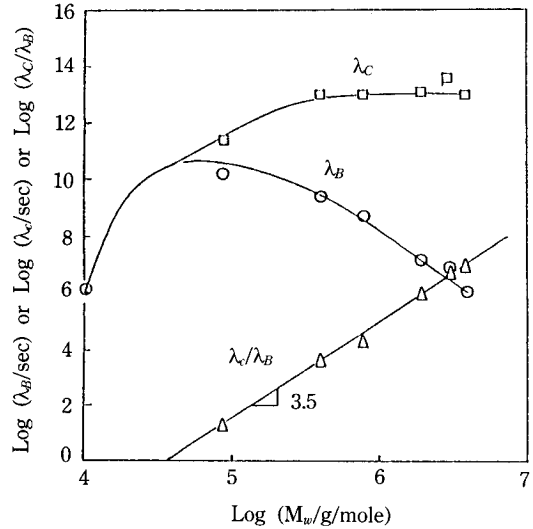


Fig. 6. Logarithms of the retardation times λ_B , λ_C and the ratio of λ_C/λ_B as a logarithmic function of the average of $M_w = \phi_L M_L$.

straints do not dominate $L(\lambda)$, and only a single peak A remains, along with the contribution $L_0(\lambda)$. For $\phi_L > (\phi_L)_c$, $L(\lambda)$ resolves into two peaks, B and C with the separation of these increasing proportional to $M_w^{3.5}$, as is shown in Fig. 6. The two peaks merge at M_e of $\log(4.58) = 38000$, which corresponds to the MW at which entanglements start to enhance the viscosity and is at about ϕ_L of 0.01. M_e of 38000 g/mole is somewhat larger than usual value of 31000(g/mole)[5, 13]. But Watanabe and Kodaka[11] suggested M_e of 36000 from dynamic rheological measurements for the PS/PS blends whose pure components have MW's higher than M_e . To investigate the effect of polydispersity of blends, some monodisperse polymer samples which have the same MW of the blends should be prepared, like what Struingsinski and Graessley did for PB[16]. Comparisons between the results of blends and corresponding monodisperse samples can be used to investigate the effect of polydispersity.

4. Conclusion

Creep recovery compliance measurements using a magnetic bearing torsional creep apparatus were

conducted for PS/PS blend-like solutions whose solute is a high MW (3.84×10^6) PS and solvent is a low MW (1.03×10^4) PS. The concentrations were 0, 2, 10, 20, 50, 70, 100 wt%. The general features of the blends are very similar to those of PS/PS blends whose components have MW's higher than M_c . For the blends with $M_w > M_c$, the zero shear viscosity is proportional to $M_w^{3.5}$. The steady state recovery compliance J_e approaches -2.3 rd power dependency to M_w at high L-polymer concentrations. The critical MW for our high/low-MW PS/PS blends seems to be 38000 g/mole by estimation from the retardation spectra.

Acknowledgement

The authors thank to the Korea Research Foundation for financial assistance.

References

- J.D. Ferry, "Viscoelastic Properties of Polymers", 3rd ed., Wiley, New York, 1980
- P.G. de Gennes, "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, NY, 1979.
- M. Doi and S.F. Edwards, "The Theory of Polymer Dynamics", Oxford University Press, Oxford, 1986.
- F. Bueche, "Physical Properties of Polymers", John Wiley & Sons, New York, 1962.
- W.W. Graessley, *Adv. Poly. Sci.*, **47**, (1982).
- W.W. Graessley, *J. Chem. Phys.*, **47**, 1942 (1982).
- T.A. Kavassalis and J. Noolandi, *Macromolecules*, **22**, 2709 (1989).
- A.M. Kotliar, R. Kumar and R.A. Back, *J. Polym. Sci.: Polym. Phys. Ed.*, **28**, 1033 (1990).
- Y.H. Lin, *Macromolecules*, **20**, 885 (1987).
- J.E. McAdams and M.C. Williams, *Macromolecules*, **13**, 858 (1980).
- H. Watanabe and T. Kotaka, *Macromolecules*, **17**, 2316 (1984).
- H. Watanabe, T. Sakamoto and T. Kotaka, *Macromolecules*, **18**, 1008 (1985).
- H. Watanabe, T. Sakamoto and T. Kotaka, *Macromolecules*, **18**, 1436 (1985).
- H. Watanabe and T. Kotaka, *Macromolecules*, **19**, 2520 (1986).
- H. Watanabe and T. Kotaka, *Macromolecules*, **20**, 535 (1987).
- M.J. Struglinski and W.W. Graessley, *Macromolecules*, **18**, 2630 (1985).
- Y.H. Lin, *Macromolecules*, **17**, 2846 (1984).
- Y.H. Lin, *Macromolecules*, **18**, 2779 (1985).
- Y.H. Lin, *Macromolecules*, **19**, 159 (1985).
- Y.H. Lin, *Macromolecules*, **19**, 168 (1985).
- Y.H. Lin, *Macromolecules*, **19**, 1108 (1985).
- M. Doi, W.W. Graessley, E. Helfand and D.S. Pearson, *Macromolecules*, **20**, 1900 (1987).
- K.-S. Choi, I.J. Chung, and H.Y. Kim, *Macromolecules*, **21**, 3171 (1988).
- B.J. Meister, *Macromolecules*, **22**, 3611 (1989).
- R.H. Colby, *Polymer*, **30**(7), 1275 (1989).
- S.J. Orbon and D.J. Plazek, *J. Polym. Phys.: Polym. Phys. Ed.*, **17**, 1871 (1979).
- D.J. Plazek, *J. Polym. Sci., Pt. A-2*, **6**, 621 (1968).
- H. Markovitz, "Linear Viscoelasticity; an Introduction", Lecture note, Carnegie-Mellon University, pp. 1-10 (1985).
- J.G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
- H. Leaderman, R.G. Smith, and L.C. Williams, *J. Polym. Sci.*, **36**, 233 (1959).
- T. Altares, Jr., D.P. Wyman, and V.R. Allen, *J. Polym. Sci., A-2*, 4533 (1964).
- M.L. Williams, R.F. Landel, and J.D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
- G.C. Berry and D.J. Plazek, "Glass: Science and Technology", ed. by D.R. Uhlmann and N.J. Kreidl, Vol. 3: Viscosity and Relaxation, Academic Press INC., New York, 1986, Chapter 6.
- E. Riande, H. Markovitz, D.J. Plazek and N. Raghupathi, *J. Polym. Sci.: Sympo. No. 50*, 405 (1975).