

## Master Curves for Some Amorphous Polymers

M. TAKAHASHI, M. C. SHEN, R. B. TAYLOR, and A. V. TOBOLSKY,  
*Department of Chemistry, Princeton University, Princeton, New Jersey*

### Synopsis

Master curves for polystyrene, poly(methyl acrylate), and poly(methyl methacrylate) in stress relaxation are reported. The method used to obtain a wide range in modulus is to combine torsional creep data for high modulus regions with direct stress relaxation data for low moduli. The composite curves obtained are compared with existing literature data. The master curve for polystyrene obtained by a ball indentation method is also reported. Characteristic viscoelastic parameters derived from the data are tabulated.

### INTRODUCTION

The object in this investigation was to study the viscoelastic behavior of some amorphous polymers and to obtain the master curves by two methods. The first was to use a combination of torsional creep and stress relaxation and the second to use a ball indentation method to cover the full range of modulus.

The polymers studied by the first method were polystyrene, poly(methyl methacrylate) and poly(methyl acrylate). Polystyrene was also studied by the ball indentation method. The results obtained were compared with those already published in the literature and good agreement was obtained. Some characteristic viscoelastic parameters were also determined for these polymers.

### EXPERIMENTAL

#### Materials

Methyl acrylate monomer was obtained from Borden Chemical Company. Polymerization was conducted between glass plates in front of a G. E. RS sun lamp for 48 hr. Benzoin (Matheson) was used as the photosensitizer. Polymer sheets were heated at 100°C. under high vacuum for 3 days to complete the polymerization and remove any unreacted monomer. Polystyrene and poly(methyl methacrylate) were kindly provided by Rohm and Haas Company. All samples were annealed at 110°C. for 6 hr. in a desiccator.

### Viscoelastic Measurements by Torsion and Stress Relaxation

Rectangular strips were cut from polymer sheets. Isothermal modulus-time curves were made in a temperature range that covers all the viscoelastic regions. The glassy region and the upper transition region, where moduli were greater than  $10^9$  dynes/cm.<sup>2</sup>, were measured by a Clash-Berg<sup>3</sup> apparatus. The rubbery region and the lower transition region, where moduli were less than  $10^9$  dynes/cm.<sup>2</sup>, were measured by a stress-relaxation balance.<sup>4</sup> Tenney environmental equipment (model TSU 100-350) was used to achieve constant temperature. By adapting a bimetallic thermoregulator and a supersensitive relay (American Instrument Company), temperature control was accurate to  $\pm 0.1^\circ\text{C}$ .

Trays of calcium chloride were placed in the instruments to remove moisture. These precautions were taken because the absorption of water is known to swell the sample and cause a change in modulus measurements.<sup>5</sup> The sample was again annealed in the instrument at a temperature above its  $T_g$ , and then allowed to cool slowly to the temperature of measurement. Sufficient time (approximately 6 hr.) was given to reach thermal equilibrium. Sample lengths were measured by a Fischer cathetometer accurate to  $\pm 0.01$  cm.

### Viscoelastic Measurements by Ball Indentation Method

The apparatus consisted of a beam having a weight pan at one end and a counterpoise at the other. The indenter terminates in a steel sphere, and several indentors having spheres of different diameters were made in order to increase the range over which the compliance could be measured. The polystyrene sample was pressed into the form of a short cylinder approximately 2.5 in. in diameter and  $3/8$  in. thick. The distance of penetration was measured by a Starrett gauge and could be estimated to  $10^{-4}$  in. The indenter and sample were enclosed in a chamber in which the air temperature was controlled by means of a Tenney environmental air chamber.

The apparatus was calibrated for bending and movement of the metal parts by measuring the apparent indentations observed on using a steel plate as the sample under various loads. The indentation of the sample by the sphere was measured as a function of time at several temperatures.

It has been shown, that for such an experimental procedure, the time-dependent shear compliance  $J(t)$  may be calculated from the equation<sup>1,2</sup>

$$J(t) = \frac{16[d(t)]^{3/2}R^{1/2}}{3F} \quad (1)$$

where  $d(t)$  is the indentation,  $R$  the radius of the sphere, and  $F$  the applied force. This relationship is applicable up to  $d(t)$  approximately 10% of the ball diameter.

Throughout this paper we have used  $3G$  instead of  $E$  to indicate the modulus. It is well known that the Young's modulus ( $E$ ) is related to the shear modulus ( $G$ ) by the following relationship:<sup>6</sup>

$$E = 2(1 + \sigma)G \quad (2)$$

where  $\sigma$  is the Poisson's ratio.  $\sigma$  is also related to the bulk modulus ( $B$ ) by

$$\sigma = \frac{1}{2}[1 - (E/3B)] \quad (3)$$

Since  $B$  for most materials is approximately  $10^{10}$  dynes/cm.<sup>2</sup>, and for  $E < 10^9$   $\sigma = 1/2$ , therefore

$$E_r(t) = 3G_r(t) \quad (4)$$

For moduli above  $10^9$ ,  $\sigma < 0.5$ . The Clash-Berg method or the ball indentation method measures the shear creep compliance  $J_c(t)$ . This may be transformed to the shear relaxation modulus by the equations:<sup>7</sup>

$$G = 1/J \quad (5a)$$

or

$$G_r(t) = \sin m\pi / m\pi J_c(t) \quad (5b)$$

where  $m$  is the negative slope of the double logarithmic plot of modulus versus time. Over the whole range of moduli, therefore, the quantity

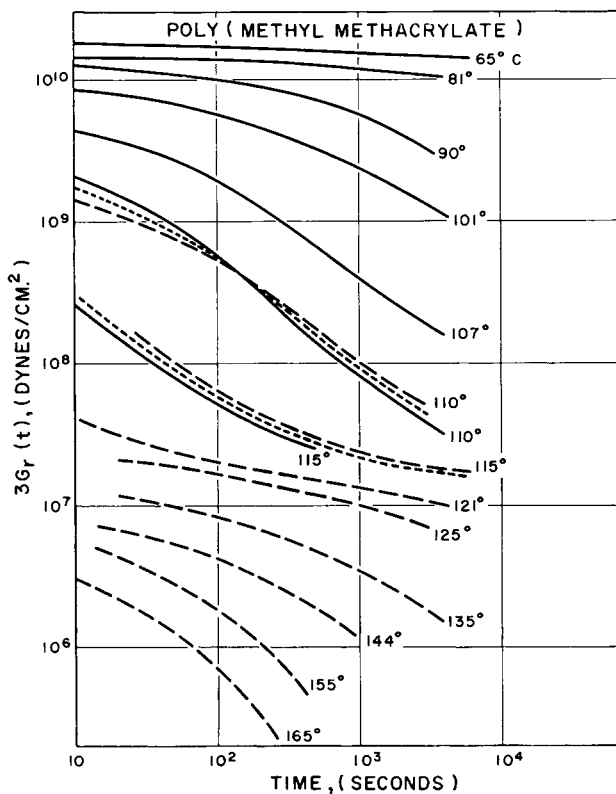


Fig. 1. Log  $3G_r(t)$  vs. log  $t$  for poly(methyl methacrylate) between 65°C. and 165°C.: (—) data by torsion; (---) data by simple extension; (- -) the average of these data.

$3G_r(t)$  is used, since this enables the results obtained from the two types of measurement to be combined.

### Construction of Master Curves

Modulus-time data for three polymers studied are presented in Figures 1-3. These curves were shifted along the time axis to fit into a continuous curve. The distance shifted along  $\log t$  is the logarithm of the parameter  $k(T)$ . At the reference temperature,  $k(T)$  is unity by definition. A more suitable parameter that is often used to characterize the viscoelasticity of amorphous polymers is the characteristic relaxation time  $K(T)$ . It is defined for any temperature  $T$  as the time required to relax to a value of  $\log 3G(t) = 10^9$  dynes/cm.<sup>2</sup>. The function  $K(T)$  is linearly proportional to  $k(T)$ , but, whereas the absolute magnitude of  $k(T)$  depends on the value chosen for the reference temperature,  $K(T)$  is uniquely defined for each polymer by experimental modulus measurements. The shear compliance curves at various temperatures are shown in Figure 4 and were treated as above to yield a master curve in shear compliance at 100°C. which is shown as curve 1 in Figure 5. This curve was transformed to the

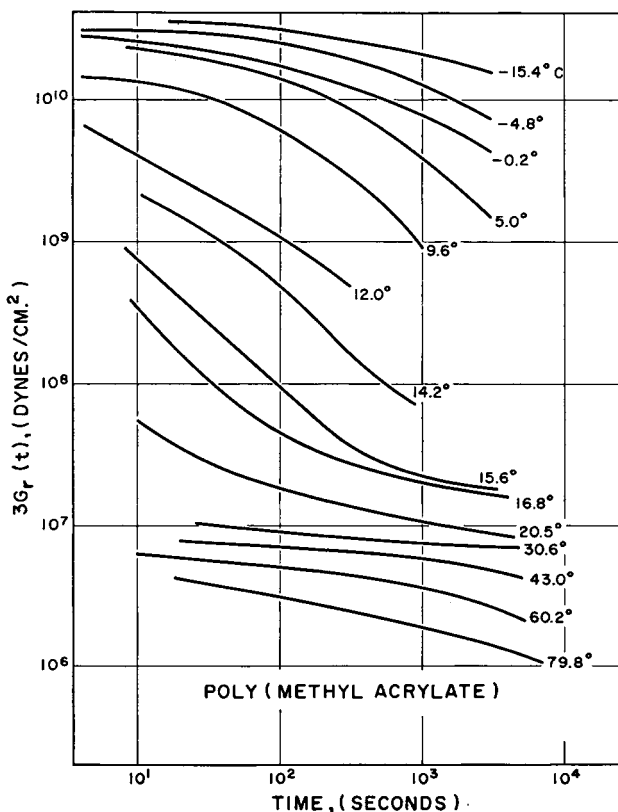


Fig. 2.  $\log 3G_r(t)$  vs.  $\log t$  for poly(methyl acrylate) between  $-15.4^\circ\text{C}$ . and  $79.8^\circ\text{C}$ .

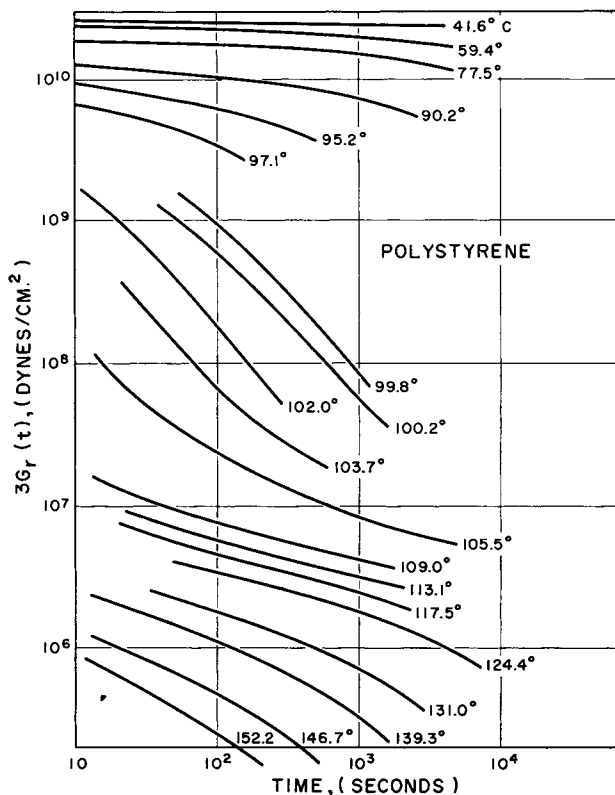


Fig. 3.  $\log 3G_r(t)$  vs.  $\log t$  for polystyrene between  $41.6^\circ\text{C}$ . and  $152.2^\circ\text{C}$ .

relaxation modulus by using eq. (5b), and the resulting master curve (curve 2, Fig. 5) obtained is shown. For comparison the master curve obtained by a combination of stress relaxation and torsional creep is also shown (Fig. 5, curve 3) after correction to  $100^\circ\text{C}$ .

### Modulus-Temperature Measurements

Ten-second torsion modulus measurements were carried out by converting those from two instruments. Clash-Berg apparatus was used in the high modulus region, and Gehman apparatus<sup>8</sup> in the low modulus region. Dow-Corning silicone fluid was used as temperature bath. The rate of heating was  $1^\circ\text{C}/\text{min}$ . Good agreement was obtained between data from these instruments. In order to define some very simple parameters to characterize these curves, we have selected  $3G = 10^9$  dynes/cm.<sup>2</sup> as an arbitrary point of reference for the moduli, and 10 sec. as an arbitrary reference time. Hence the inflection temperature  $T_i$  is the temperature at which the modulus is  $10^9$  dynes/cm.<sup>2</sup>, and  $s$  is the slope of the tangent of the curve at that point (Fig. 6).  $T_i$  is known to be closely related to  $T_g$ .<sup>4</sup> Values of these parameters are given in Table I.

TABLE I  
Viscoelastic Characteristic Parameters

Polymer	$T_g$ , °C.	$T_i$ , °C.		$n$	$p$	$np$	$s$	$\alpha_g \times 10^4$	$\alpha_r \times 10^4$	$T_g(\alpha_r - \alpha_g)$	Reference
		SR <sup>a</sup>	T-M <sup>b</sup>								
Poly(methyl methacrylate)	106	109	111	0.62	0.27	0.17	0.14	2.7	5.4	0.102	
	100							1.9	3.6	0.063	14
	105							2.2	4.6	0.091	18
	105							3.1	5.0	0.115	26
	105	113			0.54	0.33	0.18				5
Poly(methyl acrylate)	111			0.58	0.25	0.14					19
	119			0.52	0.29	0.15					20
	118		107	0.53	0.31	0.16	0.14				8
	8	15	14	0.84	0.29	0.24	0.20	1.9	5.6	0.104	21
Polystyrene (atactic)	9		17	1.58	0.28	0.44	0.23				22
	99	103	104	0.91	0.29	0.26	0.21	2.7	5.6	0.082	8
	100							2.5	5.8	0.122	24
	100							2.4	6.0	0.134	26
Polystyrene (isotactic)	93		94	0.87	0.26	0.22	0.17	2.6	5.5	0.108	14
	98										15,16
	100							1.9	5.5	0.134	23
	95							2.5	5.5	0.112	24
96							2.1	4.4	0.085	25	
							2.4	5.4	0.111	0.085	26
										0.111	17

<sup>a</sup> From stress relaxation curves.

<sup>b</sup> From modulus-temperature curves.

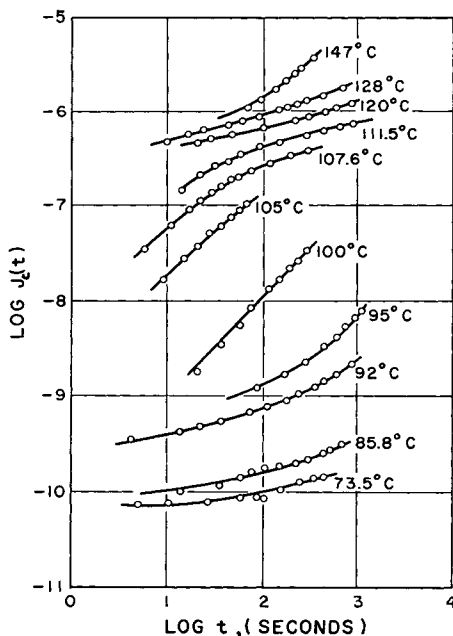


Fig. 4. Shear compliance curves,  $J(t)$ , as a function of time at various temperatures for polystyrene by ball indentation method.

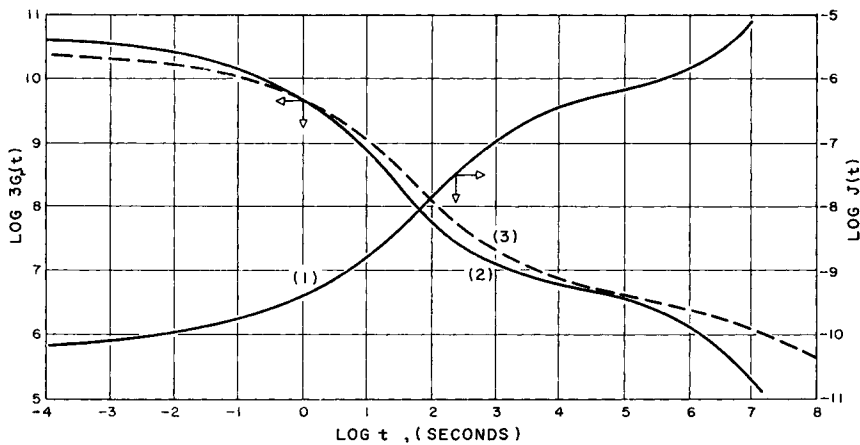


Fig. 5. Master curves obtained for polystyrene at 100°C.: (1)  $\log J(t)$  vs.  $\log t$ ; (2)  $\log 3G_r(t)$  vs.  $\log t$ ; (3)  $\log 3G_r(t)$  vs.  $\log t$  by combination of stress relaxation and torsional creep.

### Specific Volume-Temperature Measurements

Specific volume-temperature curves were determined by displacement method in silicone oil. Weight changes were followed by a Mettler automatic balance. Volumes of the samples under study were calculated from the specific volumes of silicone oil at each temperature. The tem-

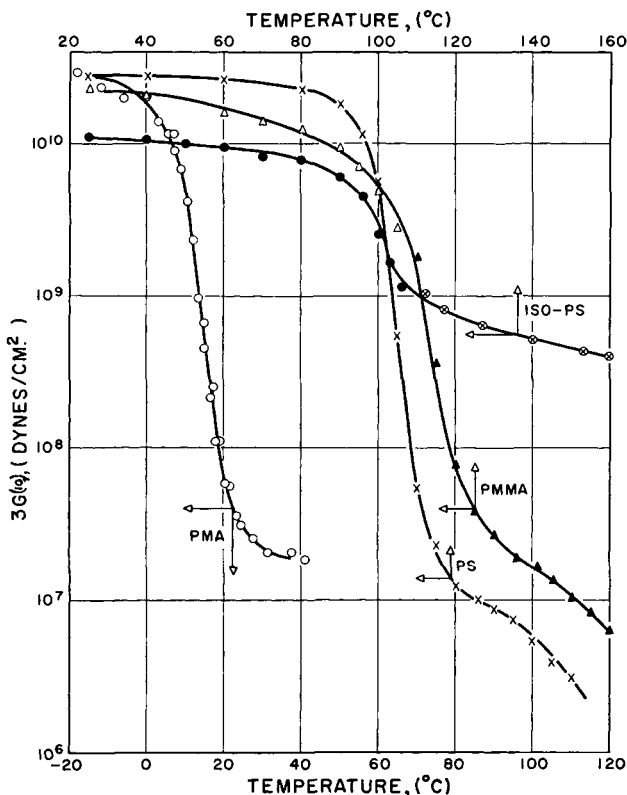


Fig. 6. Log  $3G(10)$  vs. temperature for poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), polystyrene (PS), and isotactic polystyrene (iso-PS).

perature at which a sudden break in the  $V_{sp} - T$  curve occurs was taken to be the glass transition temperature of the polymer (Fig. 7). Data are collected in Table I.

## RESULTS AND DISCUSSION

From Figure 1 it is clear that moduli measured by creep and stress relaxation show good agreement. Master curves obtained from them are presented in Figure 8. Those obtained from literature are also included for the sake of comparison. Considering the diversified methods of sample preparation and measurements, the agreement must be considered satisfactory. Only the poly(methyl acrylate) curve shows appreciable deviation from that reported by Fujino et al.<sup>9</sup> It appears that the modulus measured by these workers is exceptionally low for the glassy region.

The master curves obtained for polystyrene by the two methods indicate similar behavior in all but the low modulus region. The rapid decrease in modulus obtained by the ball indentation method may be attributable to some degradation in the sample produced by the several pressings above



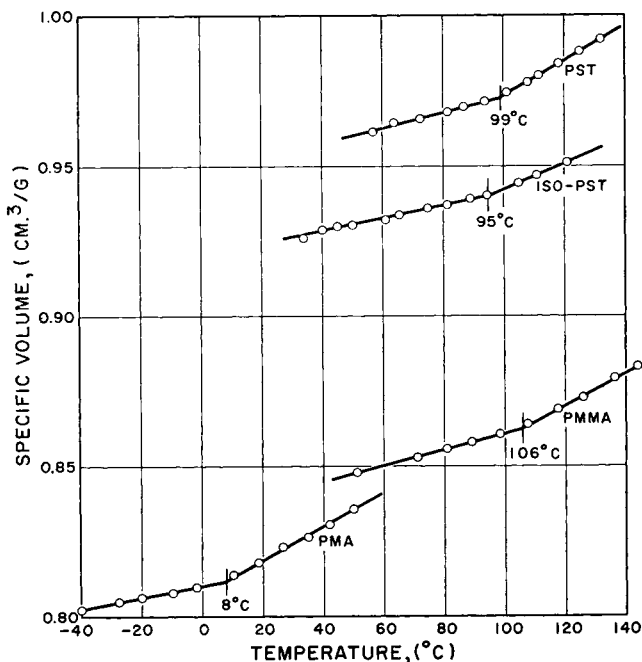


Fig. 7. Specific volume-temperature curves for poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), polystyrene (PS), and isotactic polystyrene (iso-PS).

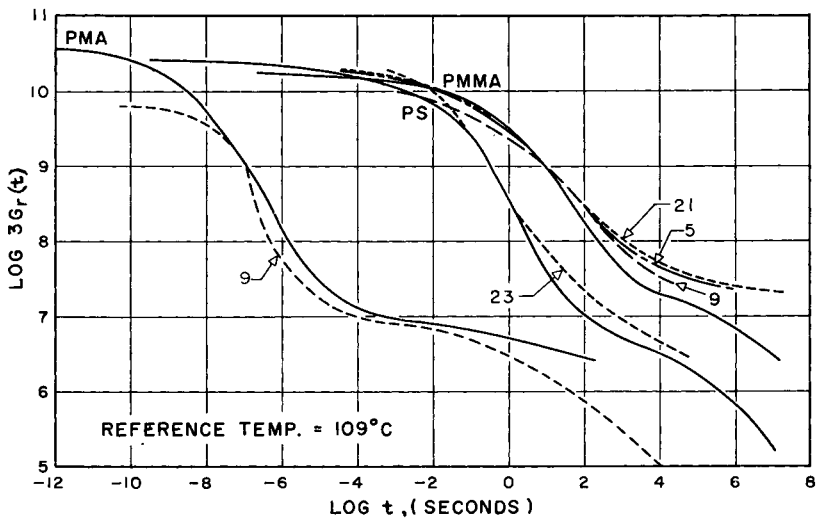


Fig. 8. Master curves for poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), and polystyrene (PS). Solid curves are those obtained in this work. Other curves were taken from references as indicated.

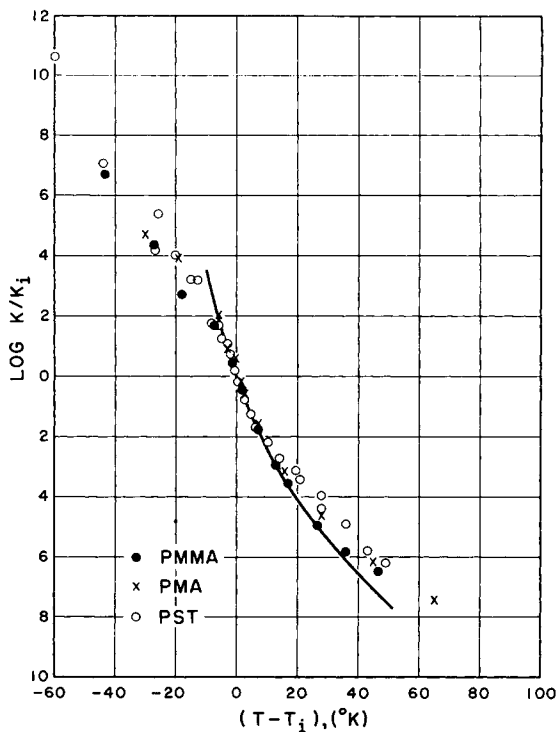


Fig. 9.  $\log K(T)/K(T_i)$  vs.  $T - T_i$  for poly(methyl methacrylate) (PMMA), polyacrylate) (PMA), and polystyrene (PS). Solid curve represents the WLF equation.

100°C. necessary to obtain a uniform sample of the required dimensions. Alternatively, the difference between the curves at low values of modulus may be a reflection of the inaccuracy of the ball indentation method due to the small forces being applied and to the short times for which measurements may be made.

The applicability of superposition principle usually finds its support in exact matching of the shapes of adjacent curves. That this is achieved is already discussed in the preceding section. Another criterion is that the temperature dependence of  $K(T)$  must have a reasonable form with no gross fluctuations or irregularities. An expression was proposed by Williams, Landel, and Ferry<sup>10</sup> to relate these variables. As modified by Tobolsky and Catsiff,<sup>11</sup> it assumes the following form:

$$\log K(T)/K(T_d) = -16.14 (T - T_d)/(56 + T - T_d) \quad (6)$$

where  $T_d$  is a characteristic temperature. Table II tabulates  $\log K(T)/K(T_i)$  at each temperature for the three polymers. Figure 9 shows the curve of eq. (6) and the experimental points. Here the inflection temperature is taken to be close to the characteristic temperature. A good fit is obtained for both the torsional creep and simple extension data, where  $T - T_i$  values are higher than  $-20$ . Below this value the points deviate

TABLE II  
Dependence of Relaxation Times  $K(T)$  on Temperature

Polymer	$T$ , °C.	$T - T_i$ , °C.	$\log K(T)/K(T_i)$	
Torsion-Relaxation Method				
Poly(methyl methacrylate)	65	-44	6.88	
	81	-28	4.51	
	90	-19	2.85	
	101	-8	1.81	
	107	-2	0.59	
	109	0	0.00	
	110	1	-0.30	
	115	6	-1.64	
	121	12	-2.84	
	125	16	-3.41	
	135	26	-4.78	
	144	35	-5.85	
	155	46	-6.34	
	Poly(methyl acrylate)	-15.4	-30.4	5.19
		-4.8	-19.8	4.40
-0.2		-15.2	3.82	
5.0		-10.0	3.35	
9.6		-5.4	2.56	
12.0		-3.0	1.43	
14.2		-0.8	1.17	
15.0		0.0	0.00	
15.6		0.6	-0.30	
16.8		1.8	-0.70	
20.5		5.5	-1.66	
30.6		15.6	-3.25	
43.0		28.0	-4.73	
60.2		45.2	-6.30	
79.8		64.8	-7.55	
Polystyrene	41.6	-61.4	10.64	
	59.4	-43.6	7.14	
	77.5	-25.5	5.39	
	90.2	-12.8	3.29	
	95.2	-7.8	2.34	
	97.1	-5.9	1.69	
	99.8	-3.2	1.09	
	100.2	-2.8	0.79	
	102.0	-1.0	0.24	
	103.0	0.0	0.00	
	103.7	0.7	-0.16	
	105.5	2.5	-0.76	
	109.0	6.0	-1.71	
	113.1	10.1	-2.21	
	117.5	14.5	-2.71	
124.4	21.4	-3.31		
131.0	28.0	-4.41		
139.3	36.3	-4.91		
146.7	43.7	-5.81		
152.2	49.2	-6.21		

(continued)

TABLE II (continued)

Polymer	$T_i$ , *C.	$T - T_i$ , °C.	$\log K(T)/K(T_i)$
	Ball Indentation Method		
Polystyrene	73.5	-26.5	4.203
	80	-20.0	4.00
	85.2	-14.8	3.275
	92	-8.0	1.719
	95	-5.0	1.175
	100	0	0.000
	105	5.0	-1.825
	107.5	7.6	-1.734
	111.5	11.5	-2.180
	120	20.0	-3.056
	128	28.0	-3.533
	147	47.0	-4.117

appreciably from the curve for the glassy region characteristic relaxation times. The WLF equation was derived from the Doolittle viscosity equation,<sup>12,13</sup> which is based on the free-volume concept. Below the transition temperature, there is presumably no further collapse of free volume, hence application of the equation is probably meaningless.

The results on the temperature dependence of the processes obtained by the ball indentation method are in agreement with the above except in the region of high temperatures indicating the limitation of this instrument for measuring low modulus behavior.

Values of  $T_g$ ,  $T_i$ , and  $s$  are given in Table I. Good agreement is obtained when compared with literature values. We have also included expansion coefficients in the rubbery ( $\alpha_r$ ) and the glassy ( $\alpha_g$ ) states. They were used to calculate the constant  $K_1$  proposed for all amorphous polymers by Simha and Boyer:<sup>26</sup>

$$K_1 = (\alpha_r - \alpha_g)T_g \quad (7)$$

In conclusion, we can say that one may circumvent the usual experimental difficulties in extension measurements of high moduli by using torsional creep, which is simple to perform, requires little attention during the experiment and yields satisfactory results.

This study indicates, too, that the ball indentation method provides an alternative means of obtaining such viscoelastic data although at low modulus values the results may be less accurate than those obtained by stress relaxation.

### References

1. Larrick, L., *Phys. Rev.*, **57**, 358 (1940).
2. Pocklington, H. C., *Proc. Camb. Phil. Soc.*, **36**, 507 (1940).
3. ASTM Standards Designation D1043-51 (1953).
4. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960.
5. McLoughlin, J. R., and A. V. Tobolsky, *J. Colloid Sci.*, **7**, 555 (1952).

6. Kittel, C., *Introduction to Solid State Physics*, 2nd Ed., Wiley, New York, 1956.
7. Leaderman, H., in *Rheology*, Vol. II, F. R. Eirich, Ed., Academic Press, New York, 1958.
8. ASTM Standards Designation D1053-58 (1958).
9. Fujino, K., K. Senshu, and H. Kawai, *J. Colloid Sci.*, **16**, 262 (1961).
10. Williams, M. E., R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
11. Tobolsky, A. V., and E. Catsiff, *J. Polymer Sci.*, **19**, 111 (1956).
12. Doolittle, A. K., *J. Appl. Phys.*, **22**, 147 (1951).
13. Doolittle, A. K., and D. B. Doolittle, *J. Appl. Phys.*, **28**, 901 (1957).
14. Martin, G. M., S. S. Rogers, and L. Mandelkern, *J. Polymer Sci.*, **20**, 581 (1956).
15. Fox, T. G., and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).
16. Fox, T. G., and P. J. Flory, *J. Polymer Sci.*, **14**, 317 (1954).
17. Natta, G., F. Danusso, and G. Moraglio, *Makromol. Chem.*, **28**, 166 (1958).
18. Rogers, S. S., and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
19. Strella, S., *J. Appl. Polymer Sci.*, **7**, 569 (1963).
20. Gall, W. G., and N. G. McCrum, *J. Polymer Sci.*, **50**, 489 (1961).
21. Nakane, H., M. Hidejima, and S. Iwayanagi, *J. Sci. Res. Inst. Japan*, **32**, 111, 140 (1956).
22. Bueche, F., *J. Appl. Phys.*, **26**, 738 (1955).
23. Fujita, H., and K. Ninomiya, *J. Polymer Sci.*, **24**, 233 (1957).
24. Tobolsky, A. V., and M. Takahashi, *J. Appl. Polymer Sci.*, **7**, 1341 (1963).
25. Ueberreiter, K., and G. Kanig, *J. Colloid Sci.*, **7**, 569 (1952).
26. Simha, R., and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).

### Résumé

On a déterminé les courbes maîtresses de relaxation de la tension du polystyrène, du polyacrylate de méthyle et du polyméthacrylate de méthyle. Pour déterminer le module dans un large domaine on a combiné des résultats obtenus par des études de déformation à poids constant par cisaillement avec des mesures de relaxation à la tension. Les courbes composites qui ont été obtenues sont comparées avec les données de la littérature. On présente également la courbe maîtresse du polystyrène obtenue par une méthode de pénétration. On a catalogué les paramètres viscoélastiques caractéristiques qui peuvent être calculés à partir de ces résultats.

### Zusammenfassung

Die verallgemeinerten Spannungsrelaxationskurven von Polystyrol, Polymethylacrylat und Polymethylmethacrylat werden beschrieben. Die zur Beschreibung eines weiten Modulbereiches angewandte Methode besteht in einer Kombination von Torsionskriechdaten bei hohen, und direkten Spannungsrelaxationsdaten bei niedrigen Moduln. Die so ermittelten zusammengesetzten Kurven werden mit den in der Literatur vorliegenden Daten verglichen. Ausserdem wird die mittels einer Kugeleindrückmethode bestimmte verallgemeinerte Spannungsrelaxationskurve von Polystyrol beschrieben. Aus den experimentellen Daten abgeleitete charakteristische viskoelastische Parameter wurden tabelliert.

Received August 5, 1963