

Viscoelastic Behavior of the Polycarbonate of Bisphenol A

J. P. MERCIER,* J. J. AKLONIS, M. LITT,† and A. V. TOBOLSKY,
Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Synopsis

The viscoelastic properties and thermal expansion properties of bisphenol A polycarbonate have been studied in the neighborhood of the major glass transition temperature. A discussion is given of the possible relation of these properties to the unusual impact resistance of this polymer in the glassy state.

Introduction

Polycarbonates are a class of polyesters in which carbonic acid is substituted for the usual bifunctional organic acids. Some polycarbonates possess very interesting thermomechanical properties, characterized especially by high impact resistance over a broad temperature range below the glass transition temperature, great rigidity, and very good dimensional stability. Among these the polycarbonate 2,2'-bis(4-hydroxyphenyl)propane (bisphenol A) is the most known because it combines ease of synthesis with the most useful mechanical properties.¹

This work is devoted to the study of the viscoelastic behavior of the polycarbonate of bisphenol A. One of our motivations for this study was the hope of contributing toward an explanation of the high impact strength of this polymer at room temperature and below, even though its major glass transition temperature is about 150°C. In this respect it contrasts with most amorphous polymers which are brittle in their glassy states and become impact resistant only above their glass transition temperature.

Other workers have studied the viscoelastic properties near the secondary glass transition or γ -transition which occurs at low temperatures and which they believe may relate to the unusual impact strength.² Our studies have been carried out in the vicinity of the major glass transition temperature in order to see whether any unusual effects could be found in this region.

* Present address: Chargé de Recherches au F. N. R. S. (Belgium).

† Present address: Central Research Laboratories, Allied Chemical Company, Morristown, New Jersey.

Materials

The two bisphenol A polycarbonate (Lexan) samples used in this work were kindly supplied by the Polycarbonate Research and Development Division of the General Electric Company. Their intrinsic viscosities measured in dioxane were 0.60 and 1.0. Wineman³ has given an expression to relate the weight-average molecular weight of unfractionated polycarbonate to its intrinsic viscosity:¹

$$[\eta] = 4.80 \times 10^{-4} \bar{M}_w^{0.67} \quad (1)$$

According to this relationship the weight-average molecular weights of the two polymers were 40,000 and 90,000, respectively. The samples were pressed into sheets under conditions similar to commercial compression-molding practice, with rapid cooling from the melt. Before testing, the polymers were annealed for 3 hr. at 160°C. ($\bar{M}_w = 40,000$) and for 24 hr. at 173°C. ($\bar{M}_w = 90,000$). Preliminary experiments showed that this treatment was necessary to insure good reproducibility of the measurements.

Experimental Procedure

The variation of modulus with time was studied by tensile stress relaxation and by creep.^{3,4} At higher temperatures, modulus-time studies were conducted by using a relaxation balance³ which gives accurate results up to a Young's modulus of 10^9 dyne/cm.². At lower temperatures modulus-time studies were determined by shear creep experiments with a Clash-Berg torsion tester⁵ slightly modified to fit into an air bath. Special care was taken to keep the bearing friction to a minimum. A Tenney environmental test chamber (model T.S.U. 50) was used to achieve constant temperature.

The modulus-temperature curves (at a fixed time of 10 sec.) were measured in the high modulus region ($3G > 10^9$ dyne/cm.²) with a Clash-Berg apparatus.⁵ A Gehman torsion tester⁶ was used for lower values of modulus. Good agreement was obtained between data from both methods.

The variation of specific volume as a function of temperature was measured according to a buoyancy procedure.⁷ Dow-Corning 200 Fluid (silicone oil) was used as the liquid medium for both modulus-temperature and volume-temperature experiments.

Modulus-Time Studies

The modulus time data for the two molecular weights studied are presented in Figures 1 and 2. The weight-average molecular weights were 40,000 and 90,000 respectively. The curves above a modulus of 10^9 dyne/cm.² are shear creep data which show the variation of $3G_c$ with time at several temperatures. Curves below this value are results of tensile stress relaxation experiments. Shear creep modulus can be con-

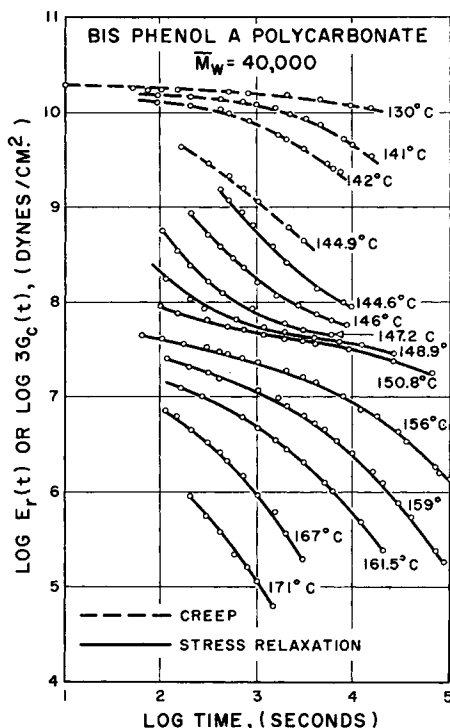


Fig. 1. Torsional creep and stress relaxation of the polycarbonate of bisphenol A, $\bar{m}_w = 40,000$.

verted to relaxation modulus by using an approximation described elsewhere.⁸ Curves at different temperatures can be superposed by the application of lateral shifts along the time axis to form a master relaxation curve^{3,8} at 150°C.

When utilizing both shear and tension results, we use $3G$ instead of E to indicate the modulus. The relationship between Young's modulus E and the shear modulus G is

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

When the Young's modulus is below 10^4 dyne/cm.⁻² the Poisson ratio σ is very close to 0.5, so that $E = 3G$. In the glassy region however, σ is smaller than 0.5, and E lies somewhere between $2G$ and $3G$.

The results for the stress relaxation master curves and for the approximate distribution of relaxation times are shown in Figures 3 and 4. The relaxation master curves have the following characteristics: a glassy region ($3G_1 = 10^{10.3}$ dyne/cm.⁻²), a transition region, a rubbery plateau ($3G_2 = 10^{7.7}$ dyne/cm.⁻²) and a flow region, all of which are characteristic of typical amorphous materials. It should be emphasized that there is a difference of more than one logarithmic cycle between the master curves

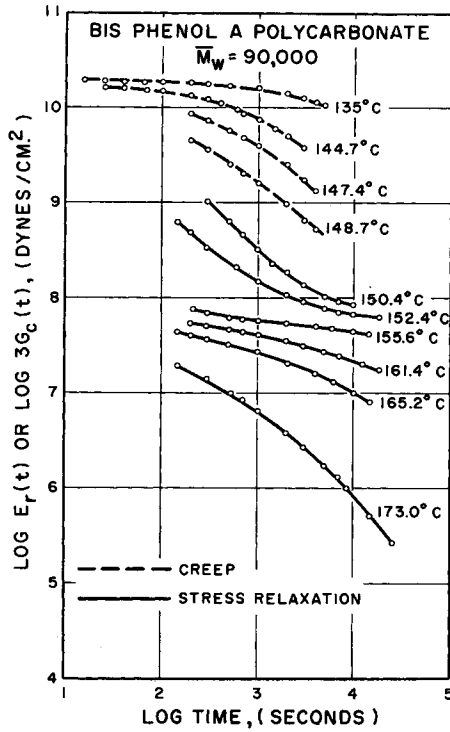


Fig. 2. Torsional creep and stress relaxation of the polycarbonate of bisphenol A, $\bar{M}_w = 90,000$.

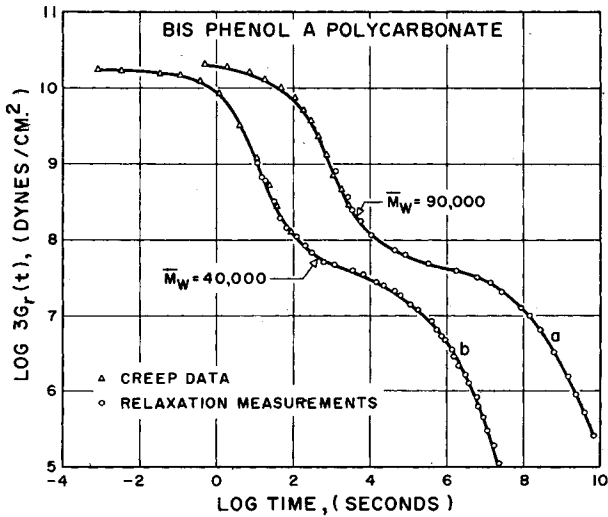


Fig. 3. Stress relaxation master curves reduced to 150°C.

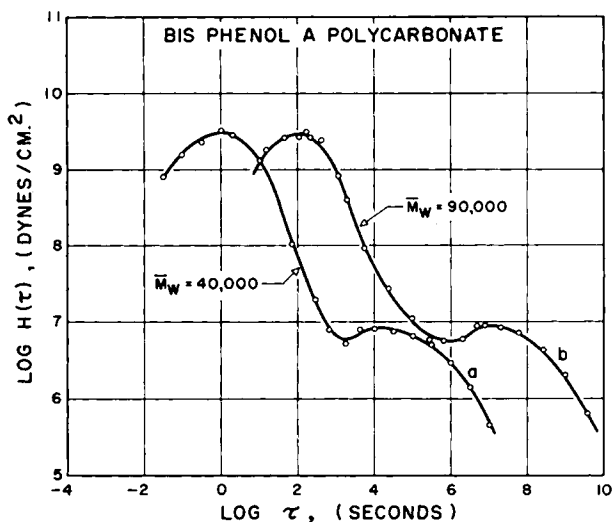


Fig. 4. Relaxation spectra of the polycarbonate of bisphenol A determined by using the first approximation method from the master curves (Fig. 3) reduced to 150°C.

of the samples of different molecular weight, not only in the flow region, but also in the transition region.

At any temperature we can define⁴ the characteristic relaxation time $K(T)$ as the time required to relax to a value of $3G_r(t) = 10^9$ dyne/cm.². The most important parameter of a polymer is the characteristic temperature T_i which is the temperature at which the characteristic relaxation time is 10 sec. T_i differs from the usual characteristic temperature T_g , which is defined in terms of volume-temperature measurements and which does not depend upon an arbitrary choice of 10 sec. For an amorphous polymer the two characteristic temperatures T_g and T_i are closely related. For bisphenol A polycarbonate, the characteristic temperatures T_i from stress relaxation measurements are 150 and 155°C. for the 40,000 and 90,000 molecular weight polymers, respectively.

In addition to $3G_1$, $3G_2$, and T_i , another characteristic parameter for the transition region is n , the negative slope on the plot of $\log 3G_r(t)$ versus $\log t$ at the value of $3G_r(t) = 10^4$ dyne/cm.². For other amorphous polymers it has been found^{3,4} that n varies between 0.5 and 1.1. For the polymer studied here n is about 1.1, which is as high as any previously

TABLE I
Parameters Characterizing the Stress Relaxation of
Polycarbonate of Bisphenol A

\bar{M}_w	T_i , °C.	$\log 3G_1^a$	$\log 3G_2^a$	n	p
40,000	150	10.25	7.74	1.11	0.29
90,000	155	10.25	7.68	1.12	0.29

^a Modulus expressed in dynes/cm.².

found value. The value of $3G_2$ is also quite high. The values for the characteristic parameters are tabulated in Table I.

Temperature Dependence

In the construction of a master curve, one shifts the experimental logarithmic curves along the time axis to obtain superposition; the distance shifted represents the logarithm of the shift factor $k(T)$ which is proportional to $K(T)$. An empirical equation for the temperature dependence of the shift factor was proposed by Williams, Landel, and Ferry^{9,10} (W.L.F. equation)

$$\begin{aligned}\log k(T) &= \log K(T)/K(T_g) \\ &= -17.44(T - T_g)/(51.6 + T - T_g)\end{aligned}\quad (3)$$

We have used a modification of the original W.L.F. equation using T_i as the reference temperature.¹¹

$$\begin{aligned}\log k(T) &= \log [K(T)/K(T_i)] \\ &= -16.14(T - T_i)/(56 + T - T_i)\end{aligned}\quad (4)$$

This equation has been found to apply to numerous polymers. It should be emphasized that eqs. (3) and (4) are essentially equivalent, provided that the difference $T_i - T_g$ is 4.4°C. In appendix K of reference 3 and also in reference 4 the values of T_i and T_g for several polymers are reported; in general the difference found between these two characteristic temperatures is about 4°C. This fact shows the essential equivalence of T_i and T_g as characteristic temperatures for amorphous polymers.

We define the slope $dk(T)/dT$ at $T = T_i$ as another characteristic parameter p .^{3,4} From eq. (4) it is clear that $p = 0.29$.

Williams, Landel, and Ferry¹⁰ gave a justification of the above empirical relationship starting with the empirical Doolittle equation¹² for the viscosity of liquids employing the free volume concept. The final equation of this treatment is

$$\log \frac{K(T)}{K(T_g)} = \frac{(B/2.303f_g)(T - T_g)}{(f_g/\alpha_2) + T - T_g}\quad (5)$$

B is the Doolittle empirical constant which is usually close to 1; f_g is the fractional free volume at T_g , and α_2 is the coefficient of expansion of the free volume which is equal to the difference between the thermal expansion coefficients above and below T_g . A similar relation has been derived by Bueche¹³ from considerations of local and free volume. The fact that the $K(T)$ values for numerous polymers fit eq. (3) or (4) and that α_2 is roughly constant for numerous polymers has been used as an argument that the glass transition temperature is a state of iso free volume for amorphous polymers. In Figure 5, we compare the experimental shift factor $k(T)$ with the modified W.L.F. equation, eq. (4). The agreement between the

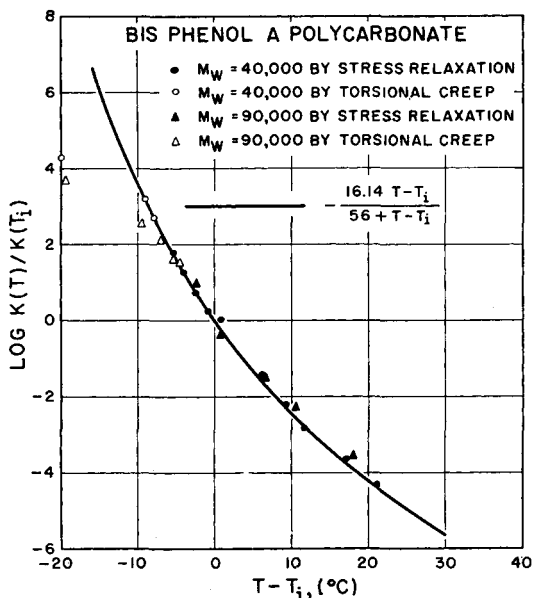


Fig. 5. Plot of $\log K(T_i)/K(T)$ vs. $T - T_i$ for the polycarbonate of bisphenol A.

calculated and the experimental curves is very good except at $T - T_i = -20^\circ\text{C}$., where the time-temperature superposition principle becomes less certain and the W.L.F. equation is probably not applicable. The results for the polymers of the two different molecular weights fall on the same curve.

Viscoelastic Evidences for and against Crystallinity

The polycarbonate of bisphenol A is a crystallizable material.¹⁴ However under the conditions by which our sheets were molded and annealed (see section on materials), the sheets were clear and transparent. In this condition the samples are generally referred to as "amorphous."

It is an *a priori*, possibility that the unusual impact resistance is due to the presence of small imperfect crystallites, or that crystallization occurs during the imposition of stress. We therefore thought it would be interesting to see whether there was any viscoelastic evidence of crystallization in these samples.

The fact that the polymer obeys the W.L.F. equation and the fact that some of the viscoelastic parameters (Table I) fall within the range of other amorphous polymers provides somewhat negative evidence for crystallization. However we have also found that the W.L.F. equation applies reasonably well in the transition region of poly(vinyl chloride), which is a polymer having a slight amount of imperfect crystallinity and small crystallites.

We studied the relaxation of stress for the 40,000 molecular weight sample in the rubbery flow region (167°C .) under various strains (from

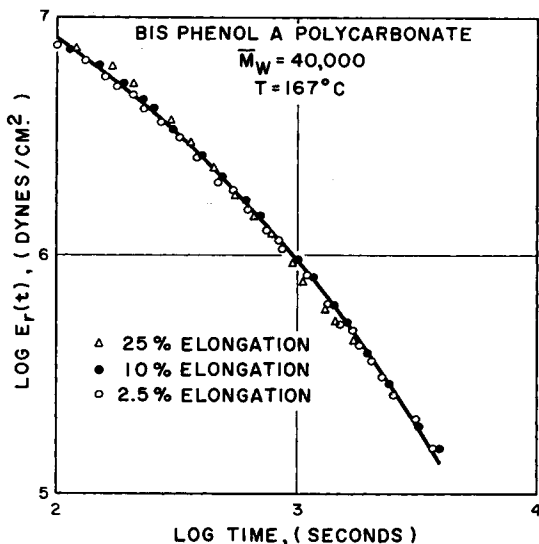


Fig. 6. Stress relaxation of polycarbonate of bisphenol A at various elongations in the rubbery flow region.

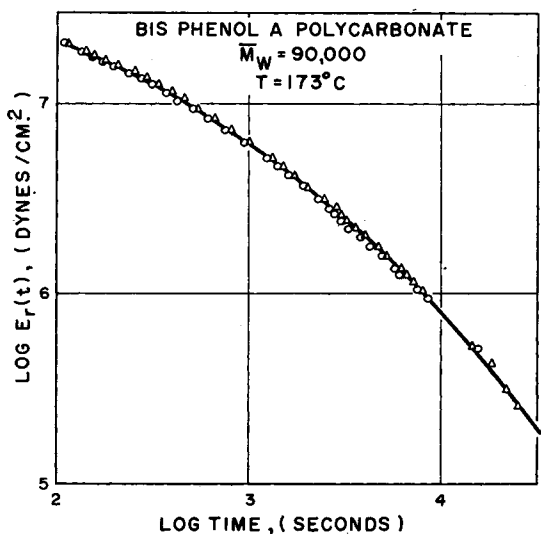


Fig. 7. Two successive stress relaxation measurements of polycarbonate of bisphenol A in the rubbery flow region.

2.5 to 25%). The fact that all the measurements fell on the same line (Fig. 6) demonstrates that there is no strain-induced recrystallization at this temperature as happens in natural rubber at -20°C .¹⁵ The stress relaxation modulus was also unaffected at 173°C . by annealing for 24 hr. at that temperature, indicating no new crystallization (or degradation) occurring under this condition. This is shown in Figure 7.

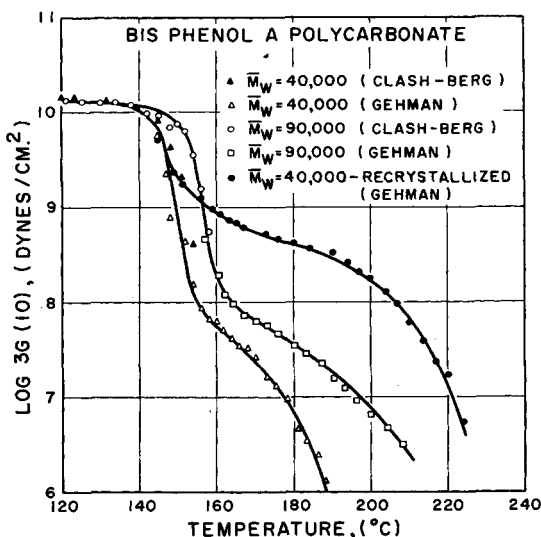


Fig. 8. Variation of the torsional modulus $3G(10)$ with temperature.

We did notice orientation lines forming in the stretched samples in the flow region (156–171°C.). The lines occurred at an angle of 45° with respect to the direction of stretching, which coincides with the plane of principal shearing stress. A similar observation is reported to occur when mild steel is tested in a tension testing machine.¹⁶ The lines which appear at the yield point are known as Luder lines. In steel their origin is attributed to the deformation of microcrystals under the shear stress induced by crystallization. We did find these orientation lines in the 40,000 molecular weight polycarbonate sample during stress relaxation studies in the rubbery flow region. We did not find these lines under similar conditions in polystyrene. The possible association between these lines and microcrystalline structure is speculative when applied to polycarbonate.

We were, however, able to produce definite viscoelastic evidence of crystallization in a sample of the 40,000 molecular weight polycarbonate annealed for 8 days at 190°C. Values of the 10-sec. modulus (measured by the Gehman instrument) versus temperature are shown on Figure 8. There is abundantly clear evidence of the change in the viscoelastic properties associated with crystallization, especially a change in the apparent rubbery plateau modulus $3G_2$.

From the values of $3G_2$ for the unannealed samples, one can obtain a molecular weight between "entanglements" of 2400. This is abnormally small as compared to poly(methylmethacrylate) (6100) and polystyrene (30,000).⁴ This is surprising, since for a "stiff" polymer chain like polycarbonate one might expect a poorly entangled chain and a lower rubbery plateau value, i.e., a higher molecular weight between entanglements.

It is possible that even the unannealed samples have a quite small amount of tiny, imperfect crystallites, and that these, acting as crosslinks (or otherwise) produce a high rubbery plateau value as compared to a truly amorphous polymer of the same material. That this could be true is witnessed by the effect of crystallization shown in Figure 8. However this certainly does not constitute a proof of the hypothesis that the unannealed specimens are semicrystalline.

Volume-Temperature Measurements

We also studied the variation of volume with temperature as shown in Figure 9 and Table II. The T_g values measured for nonrecrystallized polycarbonates were 150°C. for the high molecular weight and 145°C. for the low molecular weight. In both the modulus-temperature and

TABLE II
Coefficient of Expansion and Free Volume of Bisphenol A Polycarbonate

\bar{M}_w	T_g , °C.	$\alpha_s \times$ 10^4 , °C. ⁻¹	$\alpha_1 \times$ 10^4 , °C. ⁻¹	$\alpha_2 \times$ 10^4 , °C. ⁻¹	f_g	$(\alpha_1 - \alpha_s)$ T_g
40,000	145	3.00	5.76	2.76	1.42	0.115
90,000	150	2.82	5.63	2.81	1.45	0.119

modulus-time work, we found that a difference of 5 or 6°C. exists between the values of T_g , which is completely comparable to the difference observed here. This effect can be attributed to the change in the molecular weight of the polymer. A very similar effect was reported for polystyrene.¹⁷ A change from 25,000 to 50,000 in the number-average molecular weight of fractionated polystyrene leads to an increase of 4°C. in T_g . If we assume a ratio between number-average and weight-average molecular weights of $1/2$,¹⁸ we can calculate a number-average molecular weight of 20,000 and 45,000 for our two polycarbonate samples, which is very close to the number-average molecular weights quoted above for polystyrene. A linear relationship between T_g and the inverse of the molecular weight ($1/M$) was found for polystyrene. Postulating such a relationship for polycarbonate, we have calculated a limiting value for T_g of 154°C. (infinite molecular weight). The variation of the glass transition temperature with molecular weight is attributed¹⁷⁻¹⁹ to a change of free volume associated with the relatively mobile terminal units.

The W.L.F. equation previously considered is used to obtain a measure of the free volume at T_g . Identifying eqs. (5) and (3) we find that

$$f_g = 51.6\alpha_2 \quad (6)$$

where α_2 is the coefficient of expansion of the free volume and is equal to the difference between the coefficient of expansion above and below T_g .

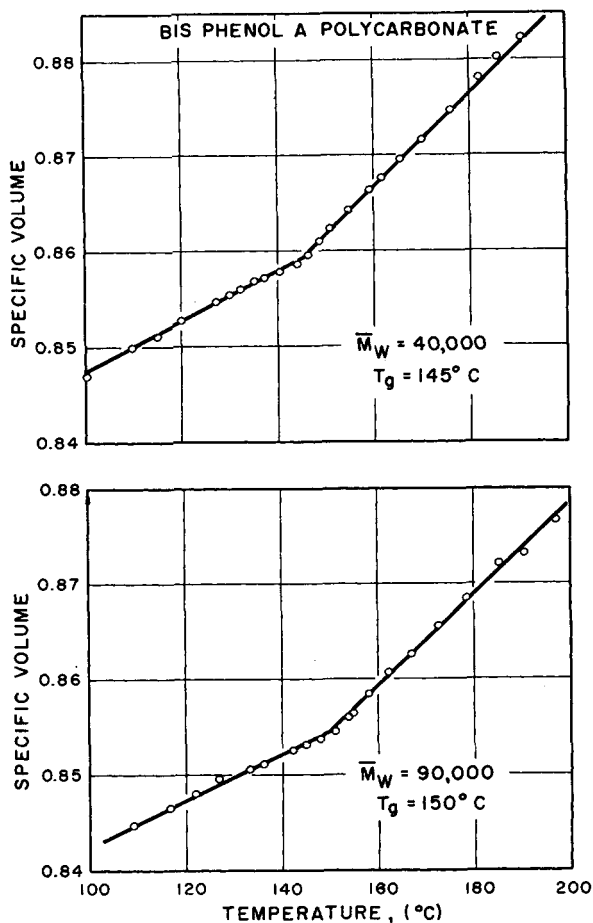


Fig. 9. Specific volume-temperature curves for polycarbonate of bisphenol A.

The value of 1.5% for the W.L.F. free volume at T_g is below the mean value of 2.5% obtained for numerous polymers, but within the range of values obtained by this method. The value of α_s is perhaps somewhat larger than for other polymers without fairly long pendant side chains.

Simha and Boyer²⁰ recently proposed another expression deduced from the concept of iso free volume at T_g . According to them, if a polymer satisfies the hypothesis of iso free volume at T_g , it should fit the expression:

$$(\alpha_s - \alpha_1)T_g = K \quad (7)$$

After considering the results from the literature, Simha and Boyer assigned to K a numerical value of 0.113. The results obtained for polycarbonate (0.115 and 0.119) in this study were in good agreement with this proposed value.

The term "free volume" obviously has numerous meanings depending on its operational definition. Another measure of the "available empty

space" can be defined for crystallizable polymers. This is the percentage difference (at room temperature in this instance) between the specific volume of the wholly amorphous polymer and the specific volume of the wholly crystalline polymer. This is 8% for bisphenol A polycarbonate, a relatively high value. It is 10% for poly(ethylene terephthalate). It is interesting that both of these polymers, when obtained in an "amorphous" condition at room temperature, have high impact resistance even though their T_g values are considerably above room temperature.

It may be that the percentage difference between the specific volumes of the amorphous and crystalline states is an important quantity for predicting which crystallizable polymers will have high impact resistance below T_g .

Conclusions

The viscoelastic parameters and thermal expansion parameters of bisphenol A polycarbonate in the neighborhood of T_g have been measured and tabulated. There is an unexpectedly low calculated "molecular weight between entanglements" arising from a high rubbery plateau modulus. Also there is a rather high coefficient of thermal expansion in the glassy state as compared to other polymers without flexible side chains. The fractional difference between amorphous and crystalline specific volume is quite high. Otherwise the viscoelastic and thermal expansion properties seem similar to those of other amorphous polymers.

The partial support of the Office of Naval Research is gratefully acknowledged.

References

1. Christopher, W. P., and D. W. Fox, *Polycarbonates*, Reinhold, New York, 1962.
2. Neilsen, L. E., *Mechanical Properties of Polymers*, Reinhold, New York, 1962, pp. 187-189.
3. Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960.
4. Tobolsky, A. V., and M. Takahashi, *J. Appl. Polymer Sci.*, **7**, 1341 (1963).
5. *A.S.T.M. Standards*, American Society for Testing Materials, Philadelphia, Designation D1043-61T.
6. *A.S.T.M. Standards*, American Society for Testing Materials, Philadelphia, Designation D1053-58T.
7. Shibukawa, T., V. D. Gupta, R. Turner, J. H. Dillon, and A. V. Tobolsky, *Textile Res. J.*, **32**, 810 (1962).
8. Ferry, J. D., *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, Chap. 4.
9. Williams, M. L., *J. Phys. Chem.*, **59**, 95 (1955).
10. Williams, M. L., R. F. Landel, and J. D. Ferry, *J. Phys. Chem.*, **77**, 3701 (1955).
11. Catsiff, E., and A. V. Tobolsky, *J. Colloid Sci.*, **10**, 375 (1955).
12. Doolittle, A. K., *J. Appl. Phys.*, **22**, 1471 (1952); *ibid.*, **23**, 236 (1952).
13. Bueche, F., *J. Chem. Phys.*, **24**, 418 (1956).
14. Prietzsch, A., *Kolloid-Z.*, **8**, 156 (1958).
15. Tobolsky, A. V., and G. M. Brown, *J. Polymer Sci.*, **17**, 547 (1958).
16. Nadia, A., *Theory of Flow and Fracture of Solids*, 2nd Ed., McGraw-Hill, New York, 1950, Chap. 18.
17. Fox, T. G., and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

18. Baumann, G. F., and S. Steingiser, paper presented to Division of Polymer Chemistry, 142nd Meeting, American Chemical Society, Atlantic City, N. J., September 1962.

19. Kelley, F. N., and F. Bueche, *J. Polymer Sci.*, **50**, 549 (1961).

20. Simha, R., and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1957).

Résumé

On a étudié les propriétés viscoélastiques et le coefficient d'expansion thermique du polycarbonate de bisphénol-A au voisinage du point de transition principale. On discute de la possibilité d'une relation de ces propriétés avec la résistance à l'impact exceptionnelle de ce polymère à l'état vitreux.

Zusammenfassung

Die viskoelastischen Eigenschaften und das thermische Expansionsverhalten von Bisphenol-A-polycarbonat wurde in der Umgebung der Hauptglasumwandlungstemperatur untersucht. Eine Diskussion der Möglichkeiten einer Beziehung dieser Eigenschaften zu der ungewöhnlichen Stossfestigkeit dieses Polymeren im Glaszustand wird gegeben.

Received February 13, 1964