Elastic Moduli of Glassy Polymers at Low Strains

I. W. GILMOUR, A. TRAINOR, and R. N. HAWARD, *Centre for Material Science, The University of Birmingham, Birmingham B15 2TT, United Kingdom*

Synopsis

The short time moduli of polystyrene, poly(methyl methyacrylate), and polycarbonate have been measured in the glassy state. The main methods used were as follows: (1) The Young's modulus of a strip was derived by extrapolating to infinite length. (2) A bidirectional strain gauge was used for Young's modulus and Poisson's ratio. (3) A unidirectional bulk modulus was measured by the method of Warfield. The results obtained made it possible to determine all the isotropic moduli including the bulk modulus, and these are compared with those reported in the literature. Poisson's ratio (ν) was found to increase with temperature in all cases. For poly(methyl methacrylate), where results reported in the literature vary widely, our values agreed with the lower reported figures ($\nu < 0.36$). The Young's modulus of poly(methyl methacrylate) is found to be more dependent on temperature and frequency than with the other two polymers.

INTRODUCTION

In a previous paper[1] we have measured the reversible temperature change that takes place when a glassy polymer is subjected to a stress within the elastic range. This temperature change dT, which is directly proportional to the applied stress, is related to the other material constants by the classical Joule-Thompson equation[2-4]

$$\frac{dT}{d\sigma} = \frac{-\alpha T}{\rho C_p}$$

where T is the absolute temperature, ρ is the density, α is the coefficient of linear expansion, and C_p is the specific heat at constant pressure.

An advantage of this measurement is that it is closely related to the Grüneisen constant γ_T.[5,6] So that

$$\gamma T = \frac{3B_s}{T} \; \frac{dT}{d\sigma}$$

where B_s is the adiabatic bulk modulus. However, for most plastics within the elastic range B_s is very close to B, the isothermal bulk modulus, so that the latter may be substituted in the above equation without serious error.

Thus, in order to derive a Grüneisen constant from a measurement of $dT/d\sigma$ we need only measurements of B carried out within the time scale of a thermoelastic experiment (a few minutes). Initially, we expected to obtain such figures from the literature either directly or by calculation from other moduli using Poisson's ratio (ν). However, a study of the literature showed that this was not really possible and that, in addition, measurements of Poisson's ratio over a range of temperatures were not readily available. Furthermore, there was an unexplained scatter in the values of ν for poly(methyl methacrylate)

Journal of Applied Polymer Science, Vol. 23, 3129–3138 (1979)

0021-8995/79/0023-3129$01.00

(PMMA) even at room temperatures. The results of our literature survey are given in the Appendix. No doubt many of the differences recorded are, at least in part, owing to the use of different grades of polymer. We therefore set out to make measurements on the three materials in which we were mainly interested, using readily available techniques. These could then be compared with each other and with the published data. In carrying out this work, several factors of more general interest came to light.

MATERIAL AND METHOD

Polystyrene

Extruded sheet made from Carinex H.R. polystyrene was supplied by Shell Chemical Co. (U.K.) Ltd. This is a relatively pure polystyrene containing <0.1% of monomer and no added lubricants. Since it has been shown that the moduli of polystyrene are not greatly affected by orientation,[7] we felt that the extruded sheet would be quite suitable for our work. No differences were observed in moduli measured parallel or perpendicular to the line of extrusion.

Polymethyl Methacrylate

Standard perspex sheet as supplied by I.C.I. Ltd. Total additives <0.1%.

Polycarbonate

Bayer Makrolon sheet was used in all experiments. Total additives <1.0%. Further details of these materials are given elsewhere.[1]

METHODS OF MEASUREMENT

Rheovibron Model D.D.V. II

This instrument measured the Young's modulus (E) at 3.5 Hz. However, in spite of the shorter measurement time compared with the other tests, the values of E obtained were low[8] and are not reported here. However, the variation of E with temperature is recorded and compared with other results.

Young's Modulus from Extension of a Strip

Strips of plastic of different lengths (up to 60 cm) were measured in an Instron Tester, and the results were extrapolated to infinite length according to the equation

$$\frac{1}{E_m} = \frac{1}{E} + \frac{K}{L}$$

where E_m is the measured value for a specimen of length L, and E is the true modulus. K is a "gripping constant." The method was used only at 23°C.

Use of Strain Gauge

A strain gauge was attached to the cleaned and slightly abraded surface of a polymer strip by a very thin layer of epoxy adhesive initially held in position by Sellotape.[8]

The Instron environmental chamber enabled a range of temperatures to be used, but limited the length of the strip to 25 cm. This was, however, considered to be quite satisfactory for the measurement of strain in the middle section. Bidirectional gauges made it possible to measure ν and E together.

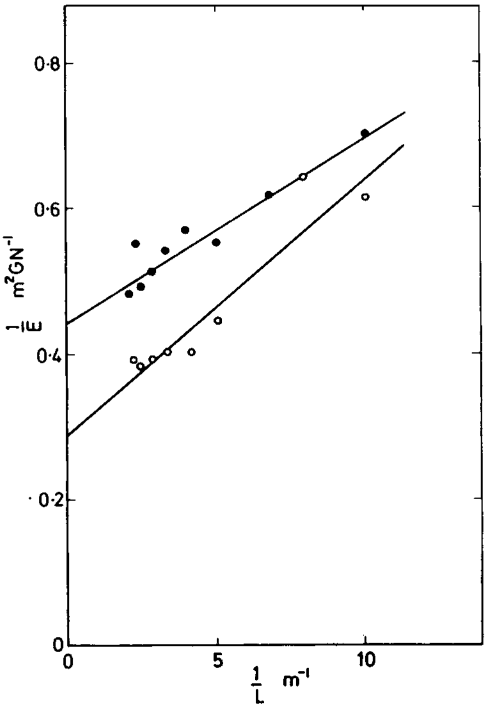

Fig. 1. Reciprocal plots of modulus against length for polystyrene (○) and polycarbonate (●) at 23 °C.

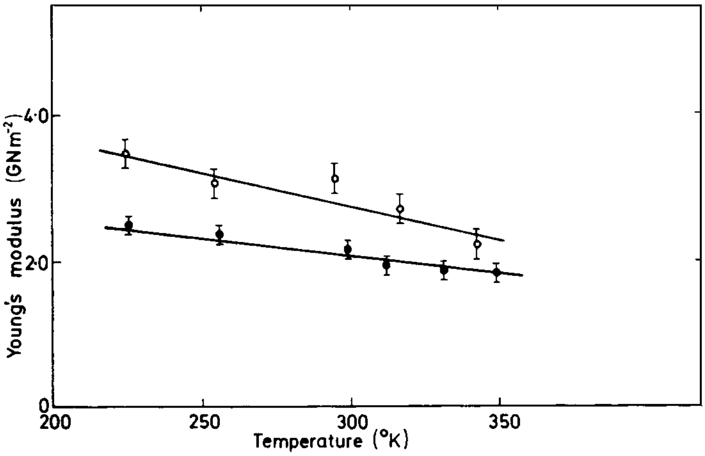

Fig. 2. Young's modulus against temperature for polystyrene ○ and polycarbonate ●.

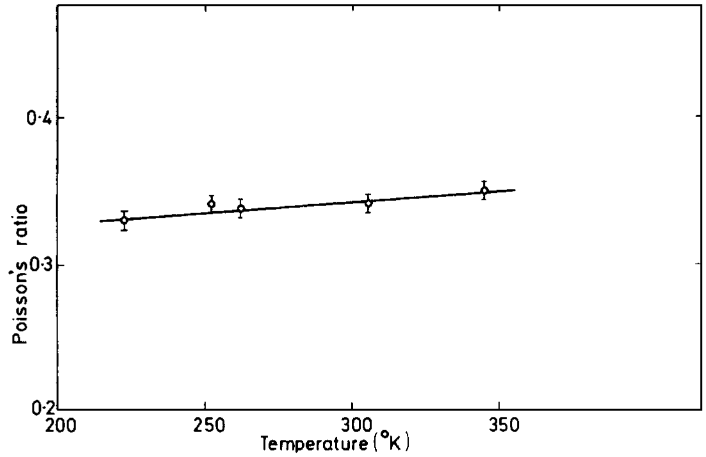

Fig. 3. Poisson's ratio as a function of temperature for polystyrene.

Warfield Compression Test

The apparent (unidirectional) bulk modulus B_a was measured directly by the method of Warfield.[9,12] A compression moulded cylindrical test-piece is placed in a close fitting metal cylinder and the linear compression is measured by an accurate clock gauge.[8] B_a is related to the true bulk modulus B by the equation[11]

$$B_a = 3B\left(\frac{1-\nu}{1+\nu}\right)$$

TABLE I
Young's Modulus of Polymers at 295 K (23 °C)

Material	E from strips (GN m^{-2})	E from strain gauge (GN m^{-2})
Polystyrene	3.19 ± 0.10	2.65 ± 0.020
PMMA	2.95 ± 0.095	2.96 ± 0.020
Polycarbonate	2.35 ± 0.090	2.12 ± 0.010

TABLE II
Regression Constants for Young's Modulus Measured from a Strain Gauge (GN m^{-2})

Material	Young's modulus equation (220–350 K)	r^2	Slope from Rheovibron
Polystyrene	$Y = 5.55 - 0.00928T$	0.94	$-0.010T$
Polystyrene[a]	$Y = 5.73 - 0.00956T$	0.99	
PMMA	$Y = 8.18 - 0.01770T$	0.98	$-0.0190T$
Polycarbonate	$Y = 3.95 - 0.00621T$	0.92	$-0.00672T$

[a] Results of Moll and Lefevre.[12]

TABLE III
Poisson's Ratio from Strain Gauge Measurements

Material	Poisson's ratio (295 K)	Equation of line (220–350 K)	$\hat{r}^2$
Polystyrene	0.342 ± 0.010	$Y = 0.3005 + 0.00013T$	0.88
PMMA	0.333 ± 0.010	$Y = 0.221 + 0.00038T$	0.91
Polycarbonate	0.313 ± 0.010	$Y = 0.242 + 0.00024T$	0.92

EXPERIMENTAL RESULTS

Extension of Strip

Reciprocal plots showing the relation between measured modulus and strip length are given in Figure 1 from which it will be seen that the end correction is comparatively large. The values obtained, together with the standard deviations obtained for least squares fits, are given in Table I.

Measurements with the Strain Gauge

These results at 259 K are compared with measurements from the strips in Table I. As the measurement could be used over a range of temperatures the results obtained, both for the Young's modulus and Poisson's ratio, could be plotted against temperature as in Figures 2 and 3. For numerical purposes the results are best represented by the equations of the lines obtained (Tables II and III). Values of the "coefficient of determination" $\hat{r}^2$, which measures the goodness of fit are also given ($\hat{r}^2 \rightarrow 1$ for perfect straight line).

Measurement of the Apparent Bulk Modulus and the Calculation of Bulk Modulus

Results for PMMA obtained by the Warfield method[9,10] are given in Fig. 4, and the equations for the regression line are given in Table IV.

From the several different measurements it is possible to obtain the true bulk

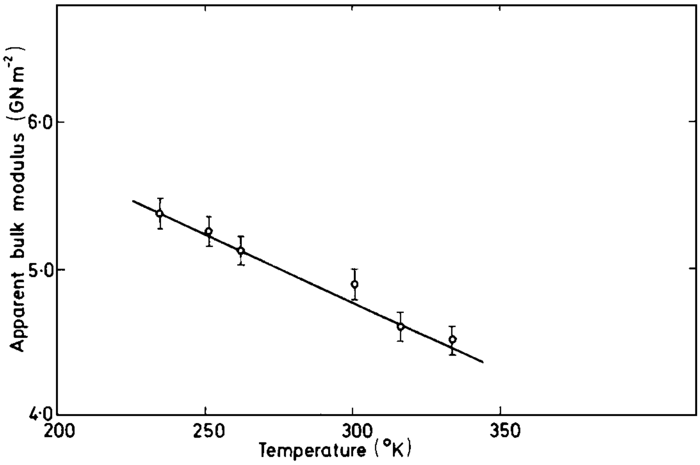

Fig. 4. Apparent bulk modulus as a function of temperature for PMMA.

TABLE IV
Apparent Bulk Modulus

Material	B_a (295 K)	Equation of line	r^2
Polystyrene	4.79 ± 0.40	$Y = 6.99 - 0.00645T$	0.99
PMMA	4.94 ± 0.30	$Y = 7.67 - 0.00958T$	0.96
Polycarbonate	3.18 ± 0.33	$Y = 6.03 - 0.00965T$	0.78

modulus from the Young's modulus and the apparent bulk modulus according to the standard equations:

$$B = \frac{E(1-2\nu)}{3} = \frac{B_a(1+\nu)}{3(1-\nu)} \tag{1}$$

from which it will be seen that the two methods depend on ν in opposite senses. Furthermore, the sensitivity of results calculated from E to variations in ν is greater than that for the results derived from B_a. The actual values obtained for the bulk modulus are given in Table V.

Comparison of these values with the literature suggested that the results derived from B_a were, as expected, the most accurate and these were used for the derivation of Grüneisen constants.[13]

Poisson's Ratio Calculated from Moduli

The determination of E and B_a makes a separate calculation of the Poisson's ratio possible from eq. (1), which can also act as a check on the validity of the methods used (Table VI).

DISCUSSION

The results presented here may be compared with literature values summarized in the Appendix. For polystyrene we find a rather low value of E from the strain gauge measurements, but the strip measurement agrees well with several recent results, e.g., Pugh *et al.*[14] and Lainchbury and Bevis.[15] Confirmation that the strain gauge moduli may be slightly low for polystyrene is also given by

TABLE V
Calculated Value for the Bulk Modulus for Glassy Polymers (GN/m^2)

		Temperature		
	Method[a]	240 K	295 K	340 K
Polystyrene	(a)	3.43 ± 0.38	3.26 ± 0.35	3.14 ± 0.32
	(b)	3.32 ± 0.33	2.80 ± 0.28	2.70 ± 0.27
	(c)		3.32 ± 0.40	
PMMA	(a)	3.42 ± 0.40	3.21 ± 0.35	3.02 ± 0.35
	(b)	3.50 ± 0.35	2.94 ± 0.30	2.34 ± 0.24
	(c)		2.93 ± 0.35	
Polycarbonate	(a)	2.29 ± 0.30	2.02 ± 0.28	1.79 ± 0.25
	(b)	2.08 ± 0.20	1.89 ± 0.19	1.73 ± 0.17
	(c)		2.09 ± 0.28	

[a] (a) From apparent bulk modulus. (b) From Young's modulus measured by strain gauges. (c) From Young's modulus measured by extrapolation and from ν by the strain gauge.

TABLE VI
Poisson's Ratio at 295 K from Modulus Measurements

Material	E/B_a[a]	ν (calc)	ν (expt; from strain gauge)
Polystyrene	(a) 0.55	0.375	0.342
	(b) 0.67	0.332	
PMMA	(a) 0.60	0.355	0.333
	(b) 0.60	0.355	
Polycarbonate	(a) 0.67	0.327	0.313
	(b) 0.74	0.300	

[a] (a) From strain gauge; (b) from strip (these values are, of course, completely independent of strain gauge results).

the high Poisson's ratio obtained in this case (Table VI). The temperature coefficient agrees well with Moll and Lefevre[12] and reasonably well with the Rheovibron.

The Young's moduli for PMMA generally agree with a number of literature values, which also furnish support for the observation that this polymer is more sensitive to temperature than the other two. This higher temperature dependence might be expected to correlate with a greater time sensitivity in the moduli. This may be checked by comparisons of our values of the compression modulus and the very accurate ultrasonic results of Asay *et al.*[16,17] (see Appendix) who reported a 25°C figure of 5.87 for PMMA and 3.73 for polystyrene. These are further supported by other ultrasonic measurements carried out by the British Rubber and Plastics Research Association (RAPRA) whose values closely agree with those of Asay *et al.*[16,17] and whose Young's modulus figures were generally in line with our own (possibly less accurate) measurements made on their equipment (see Appendix). Taken together these results clearly support the view that the greater temperature sensitivity of PMMA is accompanied by similar frequency effects. The difference in time and temperature sensitivity between PMMA and polystyrene is not accompanied by a difference in the coefficient of expansion.[1,18] This difference in behavior was also recorded by Bondi in his survey of the earlier literature.[46]

Our values for the bulk modulus are generally lower than those reported in the literature. However, the published results are also unsatisfactory in several cases. If, for example, we accept a value of E for polystyrene of 2.9–3.4 GN m^{-2} and a Poisson's ratio of 0.33 then bulk moduli similar to E would follow from eq. (1). This argument supports the lower values of B reported elsewhere (see Appendix) as well as our own results.

The values of Poisson's ratio measured here show that it increases with temperature in all cases as might be expected. With the single exception of the result obtained from the strain gauge value of E and B_a for polystyrene, all values lie between 0.30 and 0.36. Thus, our results support the lower values of ν reported in the literature for poly(methyl methacrylate).

We would like to thank Professor F. Danusso for supplying experimental results and a number of useful references, and the Rubber and Plastics Research Association for the use of their ultrasonic equipment. We also received assistance from Dr. A. Barker, Department of Chemical Engineering, Birmingham, in carrying out the strain gauge experiments.

Appendix

Literature Values of Elastic Constants for Polystyrene

Ref.	Polymer source (if stated) or other comments	Temperature (°C) (if stated)	Young's modulus E (GN m^{-2})	Bulk modulus B (GN m^{-2})	Poisson's ratio ν
19		Room Temp	3.45		
20		R.T.	3.0	3.0	0.33
14	Shell Carinex HR		3.03		
15		R.T.	3.10		
		80°C	2.69		
12		−50	3.62		
		20	2.97		
		70	1.86		
21	Dow Styron additive free		3.17		
22			3.40		0.33
23			3.58	3.81	0.344
9			3.40	4.40	0.37
10			3.60	5.40	
24				4.0	
25[a]	specially annealed	27	4.59		
	specially annealed	49	4.31		
	specially annealed	80	3.73		
26					0.33–0.36
27	Shell Ltd.	45		3.13	
		75		2.78	
28		R.T.	3.10		
29		R.T.	3.10		
30		30°C	3.31		
7		R.T.	2.68		
31	Ultrasonic			4.21	
17	Cadillac Plastic Co.	25	3.73		
	Ultrasonic	55	3.52		
	Ultrasonic	75	3.38		
45	Ultrasonic	23	3.69	3.76	0.336
This paper	Ultrasonic (see text)	24	3.76		

[a] Dr. F. Danusso states that values of E close to his own are given in refs. 48–51.

Literature Values of Elastic Constants for Poly(methylmethacrylate)

Ref.	Polymer source (if stated) and other comments	Temperature (°C) (if stated)	Young's modulus E (GN m^{-2})	Bulk modulus E (GN m^{-2})	Poisson's ratio ν
19	Rohm and Haas Plexiglas	R.T.	2.76		
20		R.T.	4.15	4.10	0.33
32			2.94		
		70	1.96		
		80	1.62		
14	Diakon M.G. (ICI)		2.99		
22			3.7		
9			3.2	5.1	
10			3.2	5.1	
33	Rohm and Haas	55	2.6		

	Plexiglas II UVA	5	3.8		
		−45	5.0		
34*	Rohm and Haas Plexiglas II UVA	80	1.86		
		100	1.68		
35	States "with internal stresses removed"		4.50		
			4.17		
36			2.90		0.39
37					0.37–0.45
38	ICI Perspex	20	3.08		0.372
		50	2.31		0.391
		80	1.75		0.420
39	Rohm and Haas Plexiglas				0.40
40			2.97		0.35 ± 0.02
41	Rohm and Haas		3.22 (10^{-3} Hz)		0.30
28			2.90		
29			2.90		
30			2.76		
7	ICI Perspex	R.T.	2.90		
31	ultrasonic			6.49	
16	Cadillac Plastics	25	5.87		
Ltd. Cast Rod		55	5.45		
	Ultrasonic	75	5.19		
45	Ultrasonic	23	5.93	6.02	0.33
This paper	Ultrasonic (see text)	24	5.95		

Literature Values of the Elastic Constants of Polycarbonate

Ref.	Polymer source (if stated) and other comments	Temperature (°C) (if stated)	Young's modulus E (GN m^{-2})	Bulk modulus B (GN m^{-2})	Poisson's ratio ν
42	Unoriented Bisphenol "A"	−50	3.299		
		0	2.924		
		25	2.712		
		70	2.21		
43	Bayer Makrolon	R.T.	2.16		
44	GEC Lexan	R.T.	2.40		0.38
20		R.T.	2.40	2.40	
45	Ultrasonic	23	3.53	3.00	0.304
47	U/V stabilized Lexan sheet Low strain values. Strain rate 0.78%/min	−65	2.77	–	0.39
47	As above	26	2.28	–	0.40
47	As above	65	2.23	–	0.36
This paper	Ultrasonic (see text)	24	3.15		

---

* These workers clearly observed the increased dependence of E on temperature for PMMA compared with polycarbonate. However, accurate figures for polycarbonate are not readily obtained from this paper.

References

1. I. W. Gilmour, A. Trainor, and R. N. Haward, *J. Pol. Sci.* (*Phys.*), **16,** 1277 (1978).
2. W. Thompson, *Trans. R. Soc. Edin.*, **20,** 261 (1853).
3. J. P. Joule, *Philos. Mag.*, **14,** 226 (1857).
4. J. R. Benton, *Phys. Rev.*, **16,** 11 (1903).
5. E. Grüneisen, *Ann. Phys.*, **10,** 211 (1908).
6. E. Grüneisen, *Ann. Phys.*, **10,** 393 (1908).
7. H. Wright, C. S. N. Faraday, E. F. T. White, and L. R. G. Treloar, *J. Phys. D.*, **4,** 2002 (1971).
8. I. W. Gilmour, thesis, University of Birmingham, U.K., October 1976.
9. R. W. Warfield, J. E. Cuevas, and F. R. Barnet, *Rheol. Acta.*, **9**(3), 439 (1970).
10. R. W. Warfield, J. E. Cuevas, and F. R. Barnet, *J. Appl. Polym. Sci.*, **12,** 1147 (1968).
11. I. W. Gilmour, A. Trainor, and R. N. Haward, *J. Polym. Sci.* (*Phys.*), **12,** 1939 (1974).
12. H. Moll and J. W. Lefevre, *Ind. Eng. Chem.*, **40,** 2172 (1948).
13. I. W. Gilmour, A. Trainor, and R. N. Haward, *J. Poly. Sci. Phys. Ed.*, **16,** 1291 (1978).
14. H. Pugh, E. Chandler, L. Holliday, and J. Mann, *Polym. Eng. Sci.*, **11,** 463 (1971).
15. D. L. G. Lainchbury and M. Bevis, *J. Mater. Sci.*, **11,** 2222 (1976); see also D. L. G. Lainchbury, thesis, University of Liverpool, 1975.
16. J. R. Asay, D. L. Lamberson, and A. H. Guenther, *J. Appl. Phys.*, **40,** 1768 (1969).
17. D. L. Lamberson, J. R. Asay, and A. H. Guenther, *J. Appl. Phys.*, **43,** 976 (1972).
18. G. Martin, S. S. Rogers, and L. Mandelkern, *J. Polym. Sci.*, **20,** 579 (1956).
19. A. E. Lever and J. A. Rhys, *Properties and Testing of Plastic Materials,* Temple Press, London, 1968.
20. D. W. Van Krevelen, *Properties of Polymers,* Elsevier, Amsterdam, 1972.
22. L. E. Nielsen, *Mechanical Properties of Polymers,* Rheinhold, New York, 1962.
23. H. W. Turner (private communication).
24. D. S. Hughes and J. L. Kelley, *Phys. Rev.*, **92,** 1145 (1953).
25. A. Pavan, M. Rink, G. Blundo, and F. Danusso, *Polymer,* **15,** 773 (1974).
26. L. E. Nielson, *Trans. Soc. Rheol.*, **9,** 243 (1965).
27. H. Khan, Ph.D. thesis, Imperial College, London, 1965.
28. K. Matsuskige, S. Radcliffe, and E. Baer, Tech. Rep. 270, Case Western Res. Univ., 1975.
29. R. G. Saba, D. A. Morrow, and J. A. Sauer, *Bull. Am. Phys. Soc.*, **13,** 372 (1968).
30. B. Maxwell, *J. Polym. Sci.*, **20,** 559 (1956).
31. B. Hartman, *U.S. National Ordnance Lab. Tech. Rep.*, **72,** 267 (1972).
32. W. J. Roff and J. R. Scott, *Fibres, Films, Plastics and Rubber,* Butterworths, London, 1971.
33. A. T. Benedetto and K. L. Trachte, *J. Appl. Polym. Sci.*, **14,** 2249 (1970).
34. D. H. Ender, *J. Appl. Phys.*, **39,** 4877 (1968).
35. N. V. Rapp, *Sov. Plast.*, **9,** 52 (1962).
36. P. Benham and D. MacCammond, *Plast. Polym.*, **39,** 130 (1971).
37. J. M. Powers and R. M. Cadell, *Polym. Eng. Sci.*, **12,** 472 (1972).
38. M. Darlington (private communication).
39. J. S. Rinehart, *Nature,* **194,** 369 (1962).
40. E. Hoff, *J. Appl. Chem.*, **2,** 441 (1952).
41. J. Koppleman, *Rheol. Acta.*, **1,** 20 (1958).
42. R. E. Robertson and J. Wilson, *J. Polym. Sci. Polym. Lett.*, **3,** 427 (1965).
43. "Makrolon" Sheet. May and Baker Ltd. Dagenham, Essex U.K. 1/1/73 (D.I.N. 53457).
44. D. R. Cunan, D. A. Shockey, and L. Seaman, *J. Appl. Phys.*, **44,** 2025 (1973).
45. R.A.P.R.A. Members Journal, Sept. 1974, p. 225.
46. A. Bondi, *Molecular Liquids, Crystals and Glasses,* Wiley, New York, 1967, Tables 13.9, 13.10. This compilation also contains some further references to the early literature.
47. M. H. Litt and S. Tarp, *Ind. Eng. Prod. Res. Develop.*, **11,** 357–363 (1972).
48. H. Keskkula, in *Encyclopédia of Polymer Science and Technology,* Vol. 13, H. F. Mark and N. G. Gaylord, Eds., Wiley, New York, 1970, p. 396.
49. *Modern Plastics Encyclopedia 1969–1970,* Vol. 46, Sidney Gross, Ed., McGraw-Hill, New York, 1969.
50. S. Strella, in *High Speed Testing,* Vol. 1, A. G. Dietz and F. R. Eirich, Eds., Interscience, New York, 1960.
51. V. A. Matonis, in *Polymer Handbook,* 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, Chap. VIII-1.

Received October 25, 1977