Ultrasonic Studies of Polycarbonate, Polysulfone, and Polyether Sulfone

D. W. PHILLIPS, A. M. NORTH, and R. A. PETHRICK, *Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, Glasgow G1 1XL, Scotland*

Synopsis

Ultrasonic attenuation and velocity measurements are reported for samples of polycarbonate, polyether sulfone, and polysulfone over a temperature range from 10° to 80°C and over a frequency range from 5 to 35 MHz. Observed relaxations are ascribed to short-range motions of the polymer backbone—here designated the α process. The amplitude of the absorption initially decreased with increasing draw ratio, but after two years returned to the values characteristic of undrawn samples. The longitudinal wave velocity increased with draw ratio in a manner consistent with the creation of molecular order and remained constant over two years. Differences in the attenuation properties between the three polymers studies are discussed in terms of the chemical structure and the macroscopic morphology of the samples.
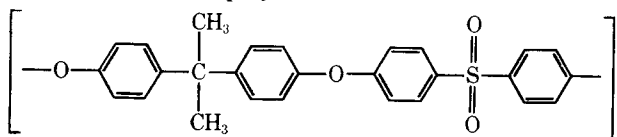
INTRODUCTION

The three polymers studied in this paper form a group of widely used high-temperature thermoplastics. These polymers all possess similar paraphenylene groups and have the molecular structures shown below:
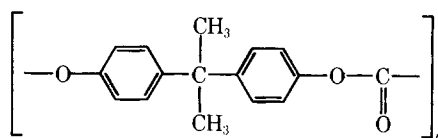
polycarbonate
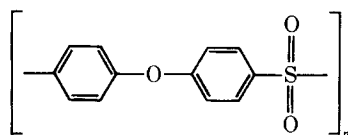
polyether sulfone

polysulfone

All the polymers exhibit similar relaxation features,[1–6] with at least two principal relaxation regions. The higher-temperature process is associated with

1859

the glass transition, and corresponds to the large-scale motion of chain segments. The lower temperature process is more difficult to assign, particularly since it may be water sensitive. The current consensus view is that it arises in a librational movement of chain segments, possibly facilitated by the special rotational freedom of specific chemical groupings within each segment.

Although the mechanical and dielectric relaxation characteristics of polycarbonate have been studied extensively,[3,7-9] those of polyether sulfone and polysulfone have received less attention.

In this paper, acoustic attenuation and velocity measurements are reported in an attempt to characterize further the molecular origins of the lower temperature relaxation process.

EXPERIMENTAL

The polycarbonate–poly(4,4'-dioxydiphenyl-2,2'-propane carbonate) samples were prepared from commercial material, Bayer Makrolon. The samples of polysulfone and polyether sulfone were supplied by ICI Ltd. The undrawn samples of polycarbonate were either injection or compression molded at 190°C into sheets or disks of 2-mm thickness and were acoustically identical. The drawn samples were prepared by pulling out 4-mm-thick extruded sheets at 160°C at a rate of 3.8 mm/sec.

The measurements of attenuation and velocity of longitudinal waves in the range 5 to 35 MHz were obtained using an immersion technique similar to that reported by Watermann.[10] Measurements were made on predried samples (24 hr in a vacuum oven at 25°C followed by storage *in vacuo*). Since the rate of water uptake on immersion is only 0.36% in 12 days,[11] no change occurred during the 5-mm measurement. No acoustic variation could be detected after measurements performed with varying periods of immersion.

The drawn samples of polycarbonate were measured with the stretch direction perpendicular to the wave vector.

The glass transition temperatures were determined using a Perkin–Elmer DSC-1 at a heating rate of 8°C/min. Densities were measured (±0.2%) by a liquid immersion method.[12] The birefringences of thin sections of the drawn sample were determined in the near-infrared and with white light. The molecular weights were obtained using gel permeation chromatography, the values being uncorrected for the finite resolving power of the columns.[13] Thus, the true distribution may be narrower than reported in Table I.

TABLE I
Physical Characteristics of the Polymers

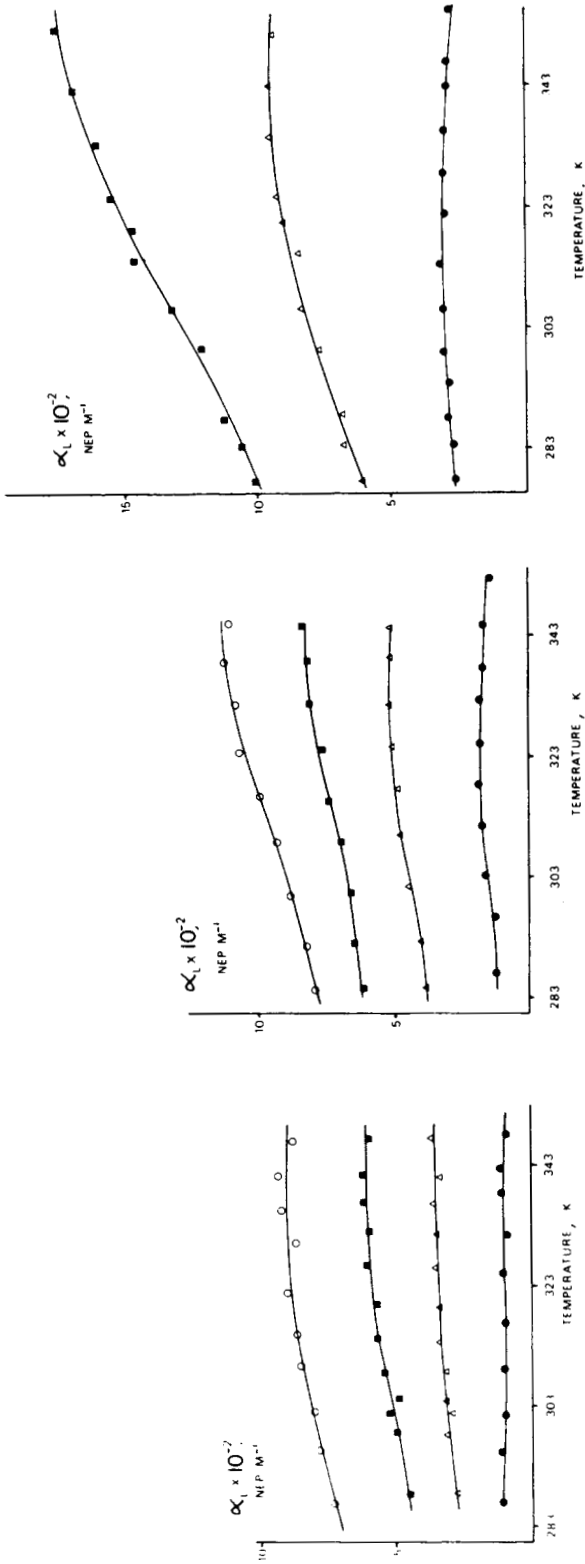| Polymer	Density kg/m^3	T_g, °C	Crystallinity, %	Draw ratio	Birefringence	$M_n \times 10^3$	M_w/M_n
Polycarbonate	1192	143	0	1.0	0.0	7.22	2.45
	1196	—	4	1.5	0.021	—	—
	1199	—	6	2.1	0.027	—	—
	1206	—	12	2.4	0.030	—	—
Polysulfone	1235	198	—	—	—	23.77	2.43
Polyether sulfone	1373	237	—	—	—	—	—

Fig. 1. Attenuation characteristics for polysulfone, polyether sulfone, and polycarbonate. Frequency of observation: (●) 5.0 MHz; (△) 15.0 MHz; (■) 24.9 MHz; (○) 24.9 MHz.

RESULTS AND DISCUSSION

Transition Nomenclature

Considerable confusion exists in the literature concerning the designation of relaxation processes and associated transitions. Some authors name the highest temperature transition known at the time as α, and then list all lower temperature transitions in sequence β, γ, δ, etc. On the other hand, many authors refer the transitions to accepted molecular mechanisms. The main glass transition in amorphous polymers (or amorphous regions in semicrystalline polymers) is designated the α process, and the closely related process shown in *all* polymers (although it may be resolved from the α process only at very low frequencies of observation or at high pressures) is designated β. Intermediate or higher temperature transitions associated with such phenomena as molecular order in melts, crystallite melting, molecular processes in crystalline regions, or motion of impurities are indicated by superscripts plus, minus, or prime. These authors support the trend toward the second procedure, despite the necessity of identifying the two primary transitions. Thus, in this work, and for polycarbonate, the main transition, $+140°C$ at 10 Hz, is designated α, and the transition occurring around $-100°C$ at 10 Hz is designated β. The intermediate transition ($+70°C$ at 10^3 Hz) is shown only by partially crystalline or oriented polymer, and is designated β^+.

Relaxation Properties

Attenuation

The temperature dependences of the ultrasonic attenuation of undrawn samples of the polymers are presented in Figure 1 and all exhibit molecular relaxation characteristics. The differential scanning calorimetry measurements (Table I) indicate that the glass transition temperatures of all these polymers occurred above $140°C$, and therefore the associated molecular movement should not be significant at the temperatures and frequencies of this study.

Dielectric and low-frequency mechanical measurements[14-16] of polycarbonate have shown two major relaxation processes: the α process, having a high-frequency activation energy of 450 kJ/mole, and the β process, with an activation energy of 45 kJ/mole. An additional relaxation process (β^+) observed in certain samples of polycarbonate has been attributed to either changes in morphology or relaxation of strained regions within the sample.[17-18]

The close similarity in the appearance of the relaxation process (Fig. 1) and in the structures of the three polymers studied suggests that similar molecular motions are operative in each case. Calculation of the specific attenuation (the attenuation coefficient divided by the density) at $50°C$ and 15 MHz (Table II) shows that the relaxation has the largest amplitude in polycarbonate and decreases through polyether sulfone to polysulfone. The amplitude of acoustic relaxation caused by an internal rotational process correlates approximately with the energy difference between stable rotational states. The dependence is direct for small rotational energy differences, but becomes inverse at higher energy differences. However, the observed sequence of amplitude cannot be compatible

TABLE II
Ultrasonic Properties of the Polymers

	Poly-carbonate	Polyether sulfone	Polysulfone
Normalized attenuation $\alpha_{50^\circ C}$	1.9	1.3	1.0
Density, $\rho_{20^\circ C} \times 10^{-3}$, kg/m^3	1.192	1.373	1.235
Specific attenuation α/ρ	1.59	0.95	0.81
Normalized $\alpha/\rho/(\alpha/\rho)_{polysulfone}$	1.96	1.17	1.0

with the ease of rotational motions of the kind responsible for the glass transition. However, the sequence is in line with a mechanism in which the β process is associated primarily with the motion of relatively small elements of the backbone.[17,18]

The relaxation frequencies in this study compare well with those reported for the β relaxation in polycarbonate, (Fig. 3) and lead to activation energies of 40 ± 4 kJ/mole for polycarbonate, 13.1 ± 4 kJ/mole for polyether sulfone, and 16.6 ± 4 kJ/mole for polysulfone. The latter values were estimated in conjunction with previously published data[7] and contain a large error due to the relative weakness of the process and the limited frequency range available. The activation energies for the β process in these polymers are consistent with an origin in coupled motion of the phenylene group with the polar linking units.[17,18]
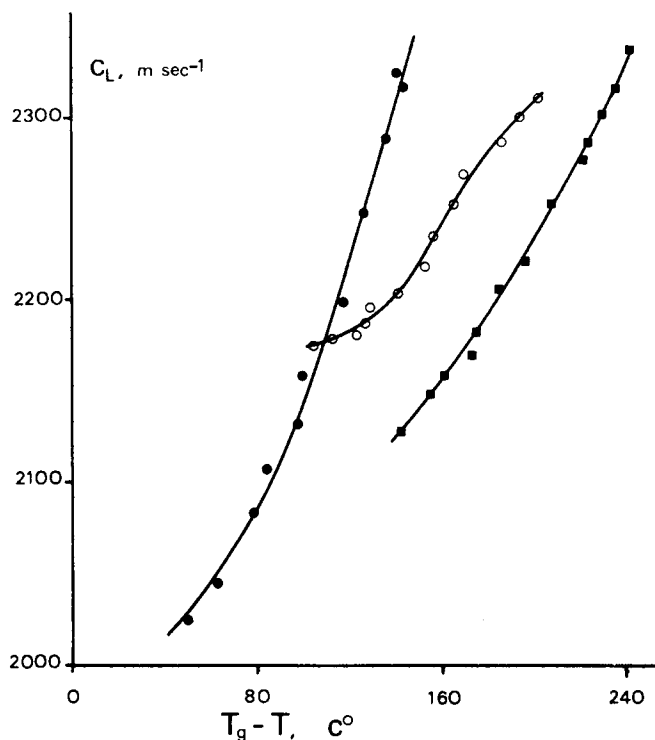

Fig. 2. Velocity of propagation of longitudinal waves at 5 MHz normalized to the glass transition temperature: (●) polycarbonate; (○) polysulfone; (■) polyether sulfone.
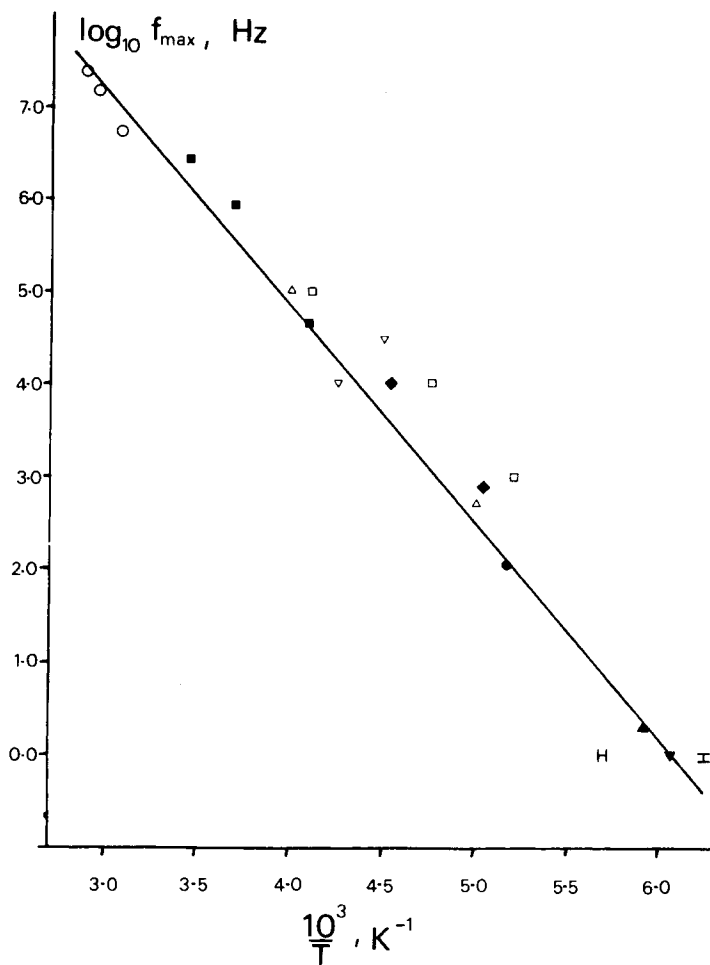
Fig. 3. Activation energy plots for β relaxation: (O) this work; (■) dielectric;[15] (△) dielectric;[9] (●) mechanical;[9] (▲) mechanical;[21] (▼) mechanical;[22] (H) mechanical;[18] (I) mechanical;[23] (◆) mechanical;[7] (□) dielectric.[16]

Velocity

The temperature dependence of the ultrasonic velocity at 5 MHz (Fig. 2), normalized to the glass transition, indicates that both the polycarbonate and the polyether sulfone possess similar molecular relaxation characteristics. In contrast, the polysulfone either has a much higher sound velocity (and modulus) in the rubbery state or, more probably, undergoes another relaxation (with associated decrement in sound velocity) between 90°C and the glass temperature. The latter possibility is supported by low-frequency mechanical measurements. The consequent lower mobility of the polysulfone chains at room temperature partially accounts for the low value of the specific attenuation in this polymer. These phenomena indicate that the polymer has a partially crystalline structure.
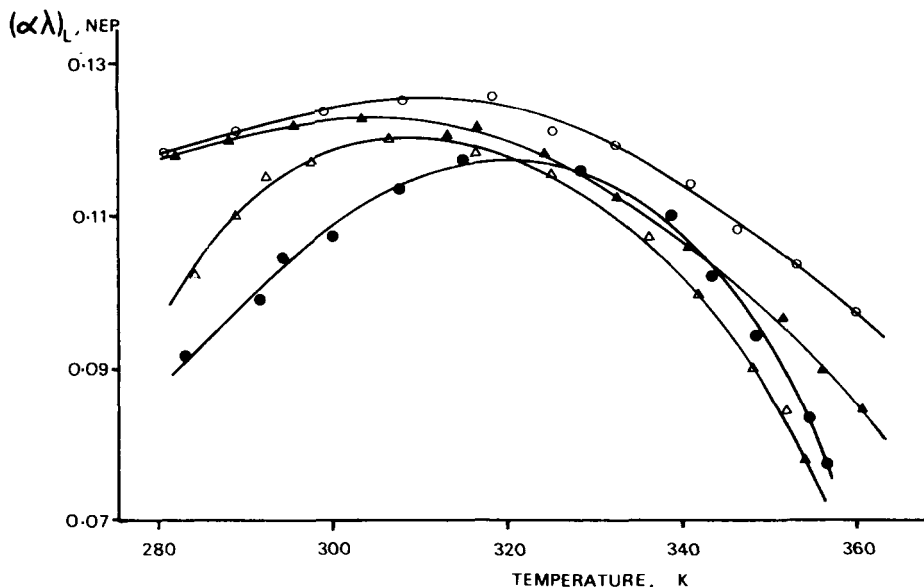
Fig. 4. Effect of draw on attenuation $(\alpha\lambda)_L$ of ultrasound in polycarbonate (measured at 5 MHz): (O) undrawn; (▲) draw ratio 1.5; (△) draw ratio 2.1; (●) draw ratio 2.4.

Effects of Draw on the β Process

Samples of polycarbonate were studied with varying draw ratios, Figure 4, where the relaxation peak is seen more clearly by presentation as $\alpha\lambda$. Increasing the draw ratio narrows the relaxation peak and lowers its amplitude. The dependence of the attenuation on stretching is closely parallelled by the variation of the yield stress.[19] At low draw ratios, the molecular environment is not changed significantly, but for ratios of two and above, significant increases in density and crystallinity are observed as a consequence of alignment and close packing of the polymer chains. The associated morphologic changes damp the motions of the polymer backbone and reduce the amplitude of the acoustic attenuation.

Dielectric[20] and low-frequency mechanical[21] studies of the effect of draw ratio on the β relaxation also indicate that the amplitude of the process is decreased on drawing.

The velocity data for drawn and undrawn polycarbonate (Fig. 5) show two distinct trends. At low draw ratios, the velocity appears to drop. This may be associated with extension and orientation in the direction of draw of the amorphous regions. At higher draw ratios, the molecular ordering in these regions increases with a consequent rise in the volume fraction of oriented chains.

The effect of draw on the high-frequency transition temperature is not so distinct as in lower-frequency dielectric studies,[20] although an increase at intermediate ratios and a reduction at the highest extension is indicated. The dielectric and acoustic techniques are thus sampling slightly different aspects of the total motion of the polymer. The initial drawing of the polymer will bring the polar groups into closer proximity while not significantly altering the van der Waals interactions. As a result, electrostatic interactions will hinder rotation
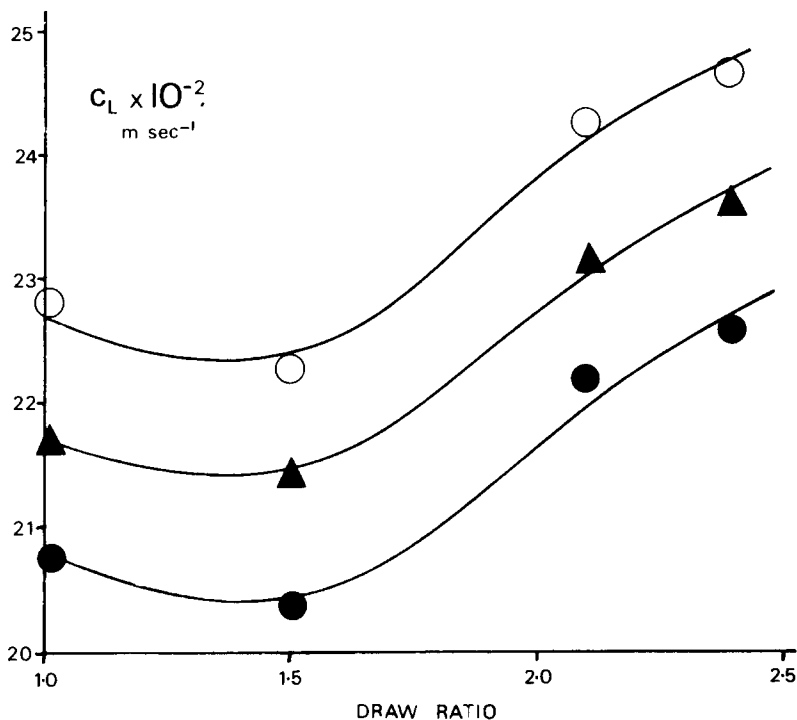
Fig. 5. Effect of draw on velocity of ultrasound in polycarbonate (measured at 5 MHz): (O) 27°C; (▲) 57°C; (●) 87°C.

of the carbonyl dipole while leaving motion of the phenylene units relatively unchanged. A further increase in the draw ratio should raise the rotational barrier for both motions.

CONCLUSIONS

The studies of the three polymers indicate that polycarbonate and polyether sulfone behave as amorphous polymers with relaxations reflecting the relative mobilities of the molecular chains. Polysulfone appears to exhibit properties of a partially crystalline polymer in which the relaxation process is influenced by the anchoring effect of regions of ordered polymer chains. It appears from these studies that the β process arises from a combination of phenylene and heteroatom motion. This hypothesis is consistent with the effects of temperature and stretching on the relaxation as monitored by various techniques.

References

1. R. F. Boyer, *Polym. Symposia,* 14, 3 (1966).
2. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids,* Wiley, London, 1967.

ULTRASONIC STUDIES   1867

 3. G. S. Y. Yeh, *Crit. Rev. Macromol. Sci.* **1,** 173 (1972).
 4. M. Baccaredda, E. Butta, V. Frosini, and S. de Petris, *J. Polym. Sci. A-2* **5,** 1296 (1967).
 5. J. E. Kurz, J. C. Woodbrey, and M. Ohta, *J. Polym. Sci. A2,* **8,** 1169 (1970).
 6. F. S. Myers and J. O. Brittain, *J. Appl. Polym. Sci.,* **17,** 2715 (1973).
 7. G. Allen, J. McAinsh, and G. M. Jeffs, *Polymer,* **12,** 85 (1971).
 8. H. Schnell, *Chemistry and Physics of Polycarbonates,* Wiley-Interscience, New York, 1964.
 9. K. Neki and P. H. Geil, *J. Macromol. Sci.,* **B-8,** 295 (1974).
10. H. A. Waterman, *Kolloid-Z.,* **192,** 1 (1963).
11. W. Hechelhammer and G. Peilstocker, *Kunstoffe,* **49**(3), 93 (1959).
12. J. B. Jackson, P. J. Flory, and R. Chiang, *Trans. Faraday Soc.,* **59,** 1906 (1963).
13. A. Yamamoto, I. Noda, and M. Nagasowa, *Polym. J. (Japan,* **1,** 304 (1970).
14. I. I. Perepechko and O. V. Startsev, *Soviet Phys. (Acoustics),* **20,** 456 (1974).
15. M. P. Eidelnant and G. P. Mikhailov, *Vysokomol. Soedin.,* **2,** 287 (1960).
16. K. Huff and F. H. Müller, *Kolloid-Z.,* **164,** 34 (1959).
17. F. Krum and F. H. Müller, *Kolloid-Z.,* **164,** 8 (1959).
18. H. Breuer and K. H. Illers, *J. Colloid Sci.,* **18,** 1 (1963).
19. E. Ito and T. Hatakeyama, *J. Polym. Sci., Polym. Phys., Ed.,* **13,** 2313 (1975).
20. E. Ito, Y. Shinogawa, S. Okajuna, K. Sawamura, and S. Saito, *Rep. Progr. Polym. Phys., Japan,* **15,** 161 (1972).
21. J. A. Faucher, F. P. Reding, and R. D. Whitman, *J. Polym. Sci.,* **54,** 556 (1961).
22. C. I. Chung and J. A. Sauer, *J. Polym. Sci. A2,* **9,** 1097 (1971).
23. L. E. Neilson, *Mechanical Properties of Polymers,* Reinhold, New York, 1962.