Effects of Molecular Weight and Strain Rate on the Flexural Properties of Polycarbonate

J. H. GOLDEN, B. L. HAMMANT, and E. A. HAZELL,
*Explosives Research and Development Establishment,
Ministry of Technology, Waltham Abbey, Essex, England*

Synopsis

The effects of changes in molecular weight (7000 to 22,000) and strain rate (0.0001 to 4 min.$^{-1}$) on the flexural properties of polycarbonate have been examined in detail with the use of specimens of different molecular weight prepared by high-energy electron irradiation. The results have been plotted as surfaces which show the dependence of both stress and strain on molecular weight and strain rate, and these surfaces have been described in terms of brittle, transitional, and ductile regions. The relationships between stress or strain and molecular weight in the brittle region have been shown to be hyperbolic. A single failure locus has been found to include all the corresponding stress and strain data obtained at the various molecular weights and strain rates. In the low strength region this locus exhibits a proportionality between stress and strain, while at high strength values, strain becomes a logarithmic function of stress. Stress–molecular weight data obtained at the various rates have been superimposed to form a single composite curve, and the corresponding crossplots of stress–log rate have been treated similarly. It is concluded from these superpositions that an equivalence exists between changes in both molecular weight and strain rate such that a tenfold change in strain rate corresponds approximately to a change of 1000 in molecular weight. Strain–strain rate data obtained at the various molecular weights have also been superimposed in a similar manner. Modulus is shown to increase slowly with decrease in molecular weight and appears to be relatively insensitive to changes in strain rate.

INTRODUCTION

In a previous paper[1] we reported the results of an examination of the effect of molecular weight on the tensile and flexural properties of polycarbonate. We have now extended our earlier study to cover a range of rates of testing, in order to examine interrelationships among molecular weight, strain rate, and flexural properties (yield stress, strain, and modulus).

In this work electron irradiation of polymer specimens has again[1,2] been utilized as a convenient method for the production of a range of specimens of different molecular weight but having otherwise identical prehistories.

EXPERIMENTAL

Preparation of Specimens

Makrolon grade S (Farbenfabriken Bayer) poly [2,2-propane bis(4-phenyl carbonate)] was used. Bars (nominally 4 × 0.5 × 0.125 in.) were machined from extruded sheet.

Irradiation

The bars were irradiated in an evacuated aluminum container (10^{-3} mm.), with external water cooling, as described previously.[2] A linear accelerator electron beam (4 M.e.v.) was employed at a dose rate of 1 Mrad/min. Under the conditions used, uniform degradation of the material was obtained.

Test Methods

Specimens were tested after a conditioning period of not less than 2 weeks ($20 \pm 1°$C./$70 \pm 2\%$ R.H.) after irradiation.

Molecular Weight Measurements. The intrinsic viscosity of the polycarbonate bars in methylene chloride at 20°C. was determined by using a modified dilution viscometer.[3] Molecular weights $\bar{M}_v$ were calculated from the relationship

$$[\eta] = 1.23 \times 10^{-5} M^{0.83} \qquad (1)$$

derived by Schnell.[4] The initial viscometric molecular weight of the polymer was 21,900.

Flexural Measurements. Flexural properties at yield (or break in the case of brittle specimens) were measured by using a three-point loading jig, with a span of 2 in., on a Hounsfield Tensometer. The samples were conditioned, and tested, at $20 \pm 1°$C. and $70 \pm 2\%$ R.H. at strain rates of 4, 1, 0.1, 0.0125, 0.001, and 0.0001 min.$^{-1}$. At the higher strain rates a Sanborn Model 321 hot wire recorder was used in conjunction with a Bytrex load cell in place of the recording equipment of the Tensometer. The maximum yield stress or brittle stress in the absence of yield σ, based on the initial cross-sectional area, was calculated by using eq. (2):

$$\sigma = 3Ml/2bd^2 \qquad (2)$$

where M is the recorded load; b and d are the breadth and depth, respectively, of the specimen and l is the span (2 in. in the present work). The strain at which the above stress obtained was calculated from eq. (3):

$$\epsilon = 6Dd/l^2 \qquad (3)$$

where D is the deflection of the center of the specimen. This equation was also used to calculate the quoted strain rates.

The flexural modulus E was determined from the slope S of the tangent to the load deflection curve at the origin by using the relationship

$$E = Sl^3/4bd^3 \qquad (4)$$

RESULTS

The stress and strain results, each of which represents the mean of three determinations, are shown graphically in Figures 1 and 2. Figure 1 shows a three-dimensional surface illustrating the dependence of stress on both strain rate and molecular weight. Figure 2 shows a similar surface relating
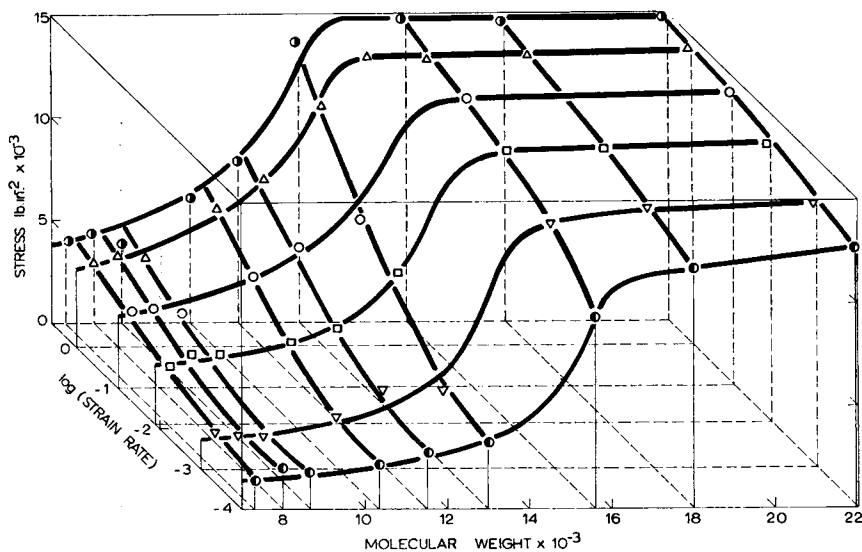
Fig. 1. Flexural yield strength (or brittle strength) vs. log strain rate and molecular weight.
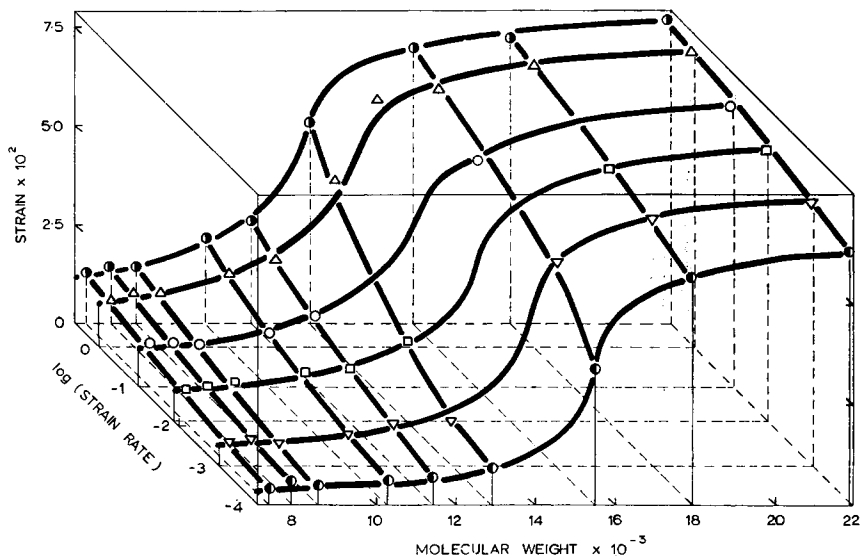

Fig. 2. Strain at yield (or break) vs. log strain rate and molecular weight.

strain, strain rate, and molecular weight. The effects of molecular weight on the stress–strain rate and strain–strain rate relationships are illustrated separately in Figures 3 and 4. The scatter limits for both stress and strain, which have been omitted in the interests of clarity from Figures 1–4, did not exceed ±12% in the upper part of the transition region and ±3% elsewhere.

Data obtained at various strain rates showing the effect of molecular weight on modulus are illustrated in Figure 5.
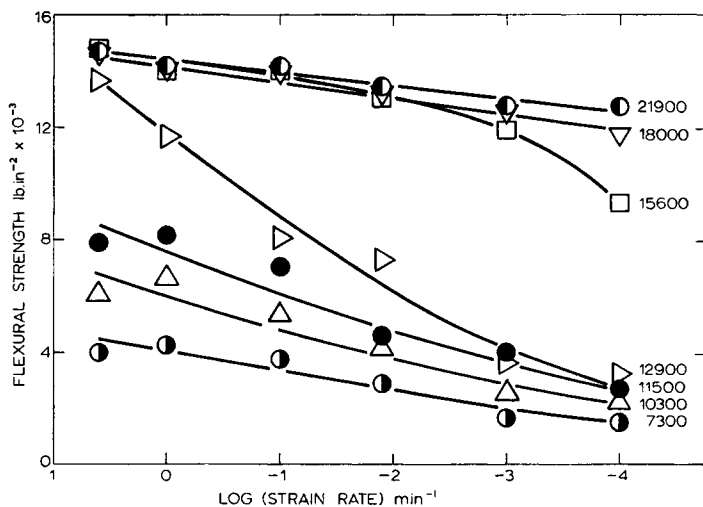
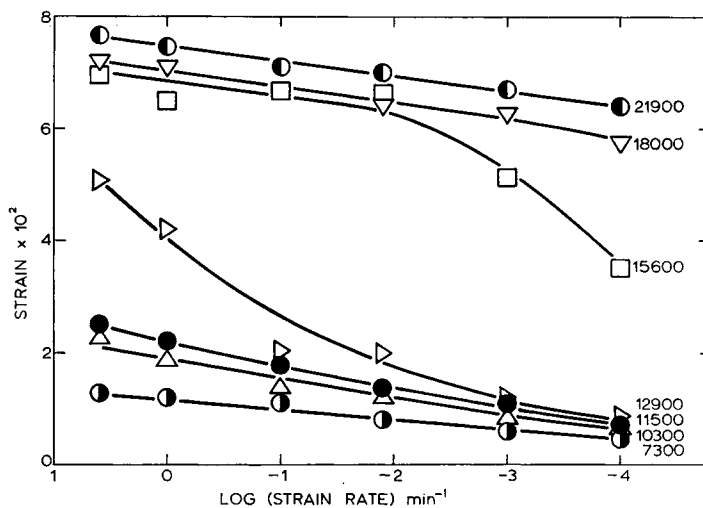Fig. 3. Stress at yield (or break) vs. strain rate for all molecular weights.

Fig. 4. Strain at yield (or break) vs. strain rate for all molecular weights.

DISCUSSION

Stress

The surface showing the dependence of flexural strength on both molecular weight and strain rate (Fig. 1) can be considered in terms of three regions: high strength at high values of molecular weight, a transitional region, in which the strength drops rapidly with decreasing molecular weight and strain rate, and low strength at low molecular weights.

In the high strength region all specimens were ductile and the stresses shown are those obtaining at yield. The stress appears as an essentially
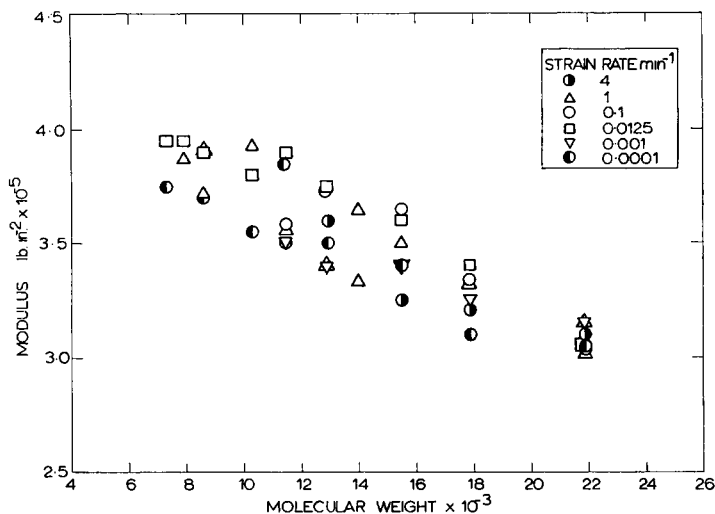
Fig. 5. Dependence of modulus on molecular weight at all strain rates.

linear function of molecular weight decreasing slowly towards the transition in agreement with previously reported data.[1]   There is also a slight upward trend of stress with increasing rate; increases have been described for other thermoplastics[5,6] and have been investigated in an earlier paper.[6]   The limited change in stress observed in the present work is an indication of the low rate dependence of polycarbonate within the range of rates studied.

The decrease in stress with molecular weight in the initial part of the transition down to the plane of inflection indicated that it was consistent with a dependence of stress on reciprocal molecular weight, although the data in this region were insufficient to establish the precise relationship. A dependence of tensile strength on reciprocal molecular weight has been observed for various thermoplastics in the transition region.[1,7]

At lower molecular weights the observed failures are all brittle in character, the brittleness being characterized by low strength.   In this region a very gradual increase in strength occurs with increasing strain rate.

The shape of the stress–molecular weight curves observed from the plane of inflection within the transition region downwards can be represented by a rectangular hyperbola:

$$\sigma \bar{M}_v = p_\sigma + k_\sigma \sigma \tag{5}$$

where σ is flexural stress, $\bar{M}_v$ is viscometric molecular weight, k_σ is the asymptotic value of molecular weight, and p_σ is a constant.

The results plotted in this form for the various values of strain rate (two examples are shown in Fig. 6) exhibit good linearity, supporting the validity of the hyperbolic relationship.

The values of k_σ and p_σ obtained at the various rates of strain are given in Table I.
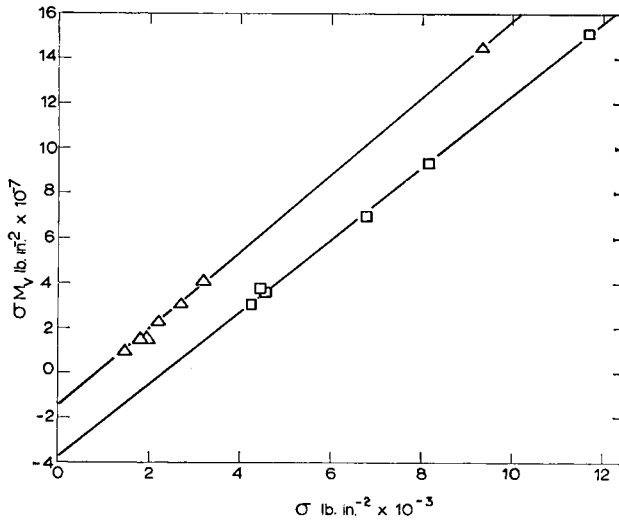
Fig. 6. Relationships between stress and molecular weight in the brittle region at strain
rates of (□) 1 min.$^{-1}$ and (△) 0.0001 min.$^{-1}$.

TABLE I

Calculated Values of the Constants in the Stress–Molecular Weight and
Strain–Molecular Weight Equations, (5) and (6)

Strain rate, in./min.	k_σ	k_ϵ	$p_\sigma \times 10^{-7}$, lb./in.^{2}	p_ϵ	$(p_\sigma/p_\epsilon) \times 10^{-5}$, lb./in.^{2} [a]
4	15800	14800	−3.40	− 90	3.78
1	15900	15700	−3.65	−100	3.65
0.1	16700	16100	−3.45	−106	3.26
0.0125	17500	16800	−3.30	− 84	3.93
0.001	15500	15700	−1.25	− 40	3.13
0.0001	17200	16800	−1.49	− 40	3.75

[a] For comparison, A, determined from the stress–strain locus (Fig. 8), has a value
of 3.6×10^5 lb./in.^{2}.

Strain

The strain surface as a function of molecular weight and strain rate (Fig.
2) is similar in appearance to the stress surface shown in Figure 1, possessing
two levels connected by a transition region. Again, in both ductile and
brittle areas, strain has a low sensitivity to changes in molecular weight and
strain rate, appreciable changes in strain occurring only in the transitional
region.

As with the stress, the strain in the brittle region can be represented by a
hyperbola.

$$\epsilon \bar{M}_v = p_\epsilon + k_\epsilon \epsilon \tag{6}$$

where ϵ is strain and the constants have a similar significance to those in
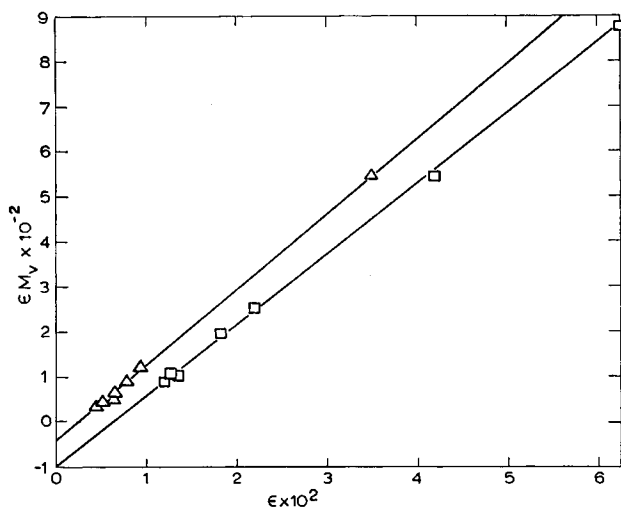eq. (5). Figure 7 shows the results plotted for two strain rates, and the

Fig. 7. Relationships between strain and molecular weight in the brittle region at strain rates of (□) 1 min.$^{-1}$ and (△) 0.0001 min.$^{-1}$.

appropriate values of the constants at all rates examined are given in Table I.

Stress–Strain Failure Locus

Corresponding stress and strain data obtained at yield (or break in the case of brittle failure, for all molecular weights and all rates of strain formed a well defined curve.   This failure locus is analogous to the curves obtained[8] for the rupture strength of rubbers at various strain rates and temperatures.

It can be seen (Fig. 8) that the plot is linear up to a stress value of 6000 lb./in.^{2} and is expressed by the relationship

$$\sigma = A\epsilon \tag{7}$$

The slope A in this region is the secant modulus of the material at break and has a value of 3.6×10^5 lb./in.^{2}.   As the material is essentially Hookean when brittle, this value of the secant modulus approximates to that of the tangent modulus.

Above 6000 lb./in.^{2}, strain is a logarithmic function of stress given by

$$\sigma = 1.4 \times 10^4 \log \epsilon + 3.0 \times 10^4 \tag{8}$$

as illustrated in Figure 9.

In the earlier discussion it was shown that the dependence of stress and strain on molecular weight in the brittle region could be represented by hyperbolic functions [eqs. (5) and (6)].   Since it has been shown in the brittle region [eq. (8)] that the secant modulus to failure is univalued, it is possible to specify the interrelationships between the constants of eqs. (5) and (6).   Substituting for σ [eq. (7)] in eq. (5) we obtain:

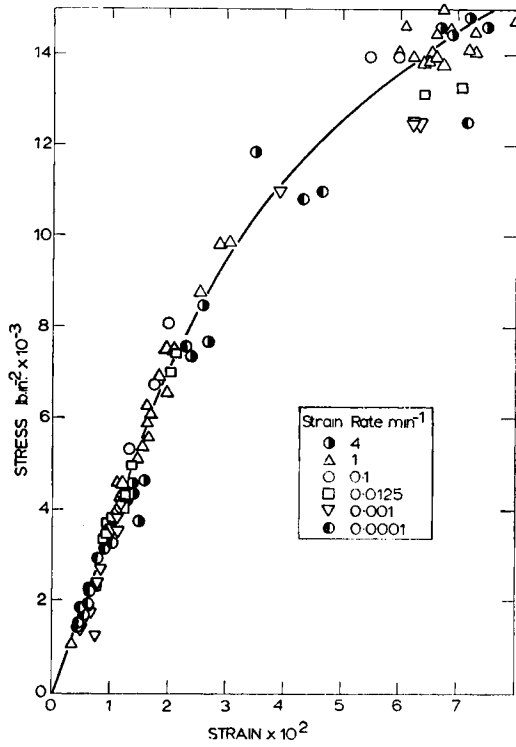$$\epsilon \overline{M}_v = (p_\sigma/A) + k_\sigma \epsilon \tag{9}$$

Fig. 8. Stress vs. strain locus for all specimens over a range of molecular weights (7300–21,900) at various strain rates as denoted in key.
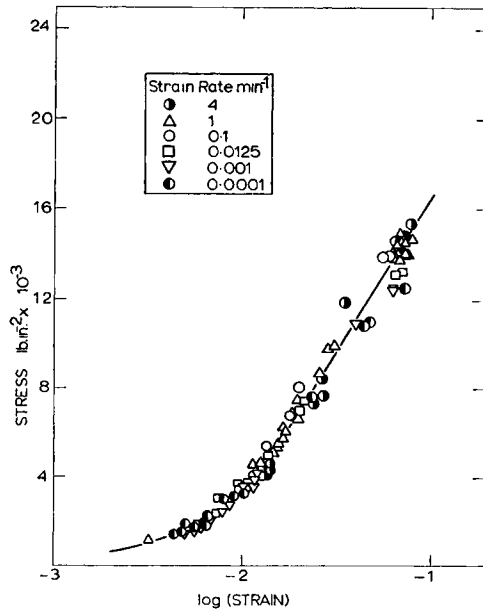

Fig. 9. Stress vs. log strain locus for all specimens over a range of molecular weight (7300–21,900) at various strain rates as denoted in key.

By comparison with eqs. (6) and (7) we have:

$$k_\sigma = k_\epsilon \qquad (10)$$

and

$$A = p_\sigma/p_\epsilon \qquad (11)$$

This equivalence between k_σ and k_ϵ together with the ratios of p_σ/p_ϵ and their equivalence with the previously determined value of A are presented in Table I. Comparison of the experimental values of the constants in eqs. (10) and (11) shows that k_σ and k_ϵ are in close agreement and that the values of the ratio p_σ/p_ϵ are very similar to that of A (Table I).

Modulus

Values of modulus at all strain rates versus molecular weight shown in Figure 5 indicate little or no rate dependence. There is, however, an increase in modulus with decrease in molecular weight, except at the lowest molecular weights. However, the scatter inherent in the method of measurement makes it difficult to define the relationship between the properties. It would consequently, be of interest to re-examine modulus by more precise methods, e.g., dynamic mechanical techniques.

Rate–Molecular Weight Superposition of Stress Data

The shape of the individual plots of stress against strain rate for the various molecular weights, shown in Figure 3, suggest that the curves are amenable to superposition. Accordingly, a tracing of each curve was transposed sufficiently to provide the best fit with adjacent curves. The hori-
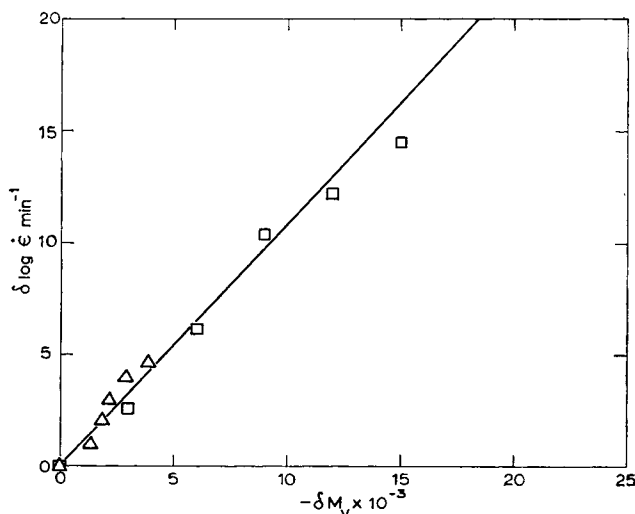

Fig. 10. Relationship between molecular weight and log strain rate shift factors: (□) shift to reference rate of 0.0001 min.$^{-1}$; (△) shift to reference molecular weight of 7300.
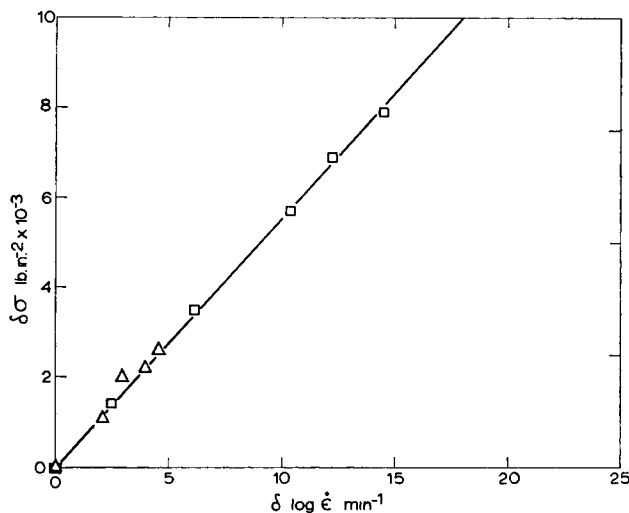
Fig. 11. Relationship between stress and log strain rate shift factors: (□) shift to reference rate of 0.0001 min.$^{-1}$; (△) shift to reference molecular weight of 7300.

zontal ($\delta \log \dot\epsilon$) and vertical ($\delta\sigma$) components of the resultant shifts were measured and plotted as functions of the corresponding changes in molecular weight ($\delta \bar M_v$) with respect to the lowest molecular weight (7300) in Figures 10 and 11. Both components are linear functions of $\delta \bar M_v$ expressed by eqs. (12) and (13).

$$\delta (\log \dot\epsilon) = -1.1 \times 10^{-3} \, \delta \bar M_v \qquad (12)$$

$$\delta\sigma = -0.62 \, \delta \bar M_v \qquad (13)$$

A third relationship [eq. (14)]

$$\delta\sigma = 5.6 \times 10^2 \, \delta (\log \dot\epsilon) \qquad (14)$$

can be obtained by elimination from eqs. (12) and (13) or graphically.

It is a necessary condition of the above treatment that the individual plots of stress against molecular weight for the various strain rates should also be superposable and a similar procedure was employed to effect this. Data obtained thus are also presented in Figures 10 and 11 with respect to a specified strain rate (0.0001 min.$^{-1}$). The results again satisfy eqs. (12)–(14). These equations were used to construct the master curves of stress with respect to strain rate and molecular weight illustrated in Figures 12 and 13. The third axis provided allows the curves to be used at the required value of the reference variable, molecular weight in Figure 12 and log (strain rate) in Figure 13, without reference to the shift equations. This third axis, which is calibrated in terms of the reference variable, is defined as the locus of the point of origin of the other two axes and has a slope given by the resultant of the two shifts required. The development of this third axis in the case of Figure 12 can be considered as follows. Taking the plot of stress against log strain rate (Fig. 3) it is apparent that the effect of pro-
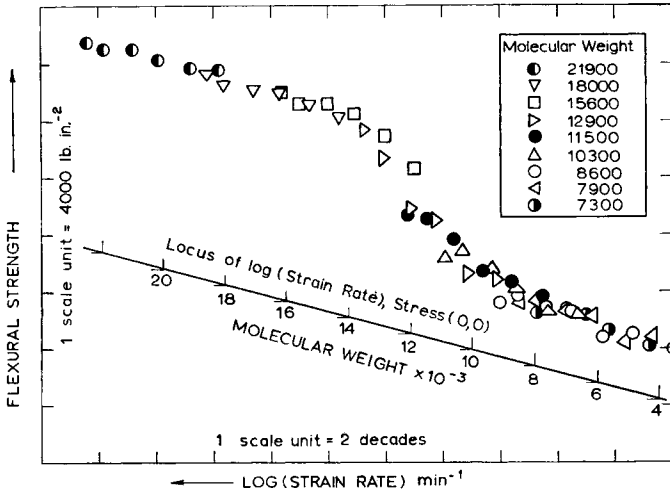
Fig. 12. Master curve of flexural strength vs. log strain rate at all molecular weights.
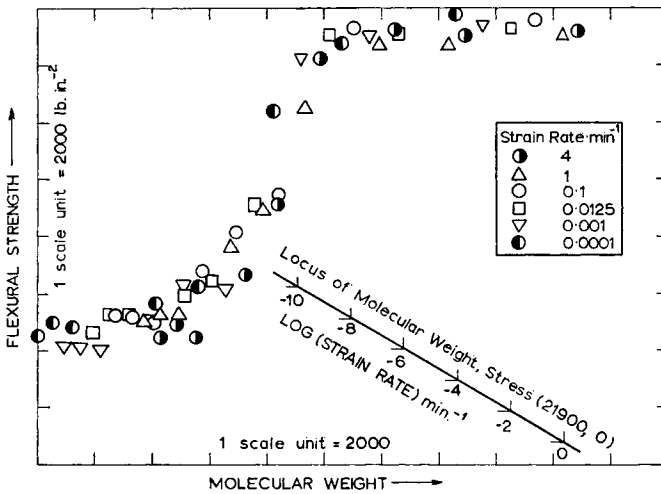

Fig. 13. Master curve of flexural strength vs. molecular weight at the strain rates employed.

gressively changing the molecular weight is to change the position of the defined origin with respect to the curve without affecting the shape of the curve.   The change in position of the origin of these axes, i.e., $\sigma = 0$, log $\dot{\epsilon} = 0$, is proportional to the change in molecular weight as given by eq. (14) and is represented on the master curve as the third axis.   This axis is then calibrated in terms of molecular weight by using eq. (12), which relates a change in molecular weight to an equivalent change in strain rate.

The master curves can conveniently be used to obtain the appropriate flexural strength–log (strain rate) or flexural strength–molecular weight curves at a specified molecular weight or strain rate (Figs. 12 and 13,

respectively) and also extend the ranges of both strain rate and molecular weight for prediction purposes.

As an example of the use of the master curves, suppose that it is required to predict the flexural strength at a strain rate of 10^3 min.$^{-1}$ of polymer having a molecular weight of 16,000. Referring to Figure 12, first locate the point 16,000 on the molecular weight axis. This point is then taken as the origin of the flexural strength and log strain rate axes (0,0), and measurements are subsequently made relative to this origin. The height of the master curve above the log strain rate axis is then determined at a distance representing a strain rate of 10^3 min.$^{-1}$ (i.e., 1.5 scale units of log strain rate) from the origin. This height, 4.125 scale units, i.e., a flexural strength of 16,500 lb./in.^{2}, is then the predicted strength.

It is concluded from the foregoing discussion that there is an equivalence between the effects of rate and molecular weight on the stress properties of polycarbonate. Large changes in strain rate are necessary to produce similar changes in stress to those obtained by comparatively small changes in molecular weight; thus from eq. (12) a change in molecular weight of 1000 has an effect approximately equivalent to a tenfold change in strain rate over a very wide range of strain rates.

Further evidence for interrelationships between mechanical properties, rate (frequency), and molecular weight has been obtained by Oyanagi and Ferry[9] in a study of the effect of molecular weight on the mechanical loss of poly(vinyl acetates).

Rate-Molecular Weight Superposition of Strain Data

The close similarity in form of the stress and strain data with respect to rate and molecular weight (Figs. 1 and 2) suggest that similar superpositions can be achieved for both sets of data and this has been found to be true.
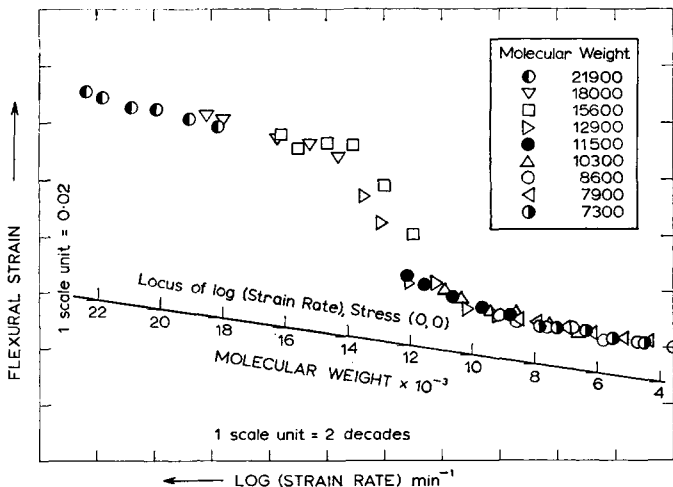

Fig. 14. Master curve of flexural strain vs. log strain rate at all molecular weights.

Figure 4 shows a plot of strain against strain rate for the various molecular weights, comparable to that of stress shown in Figure 3. Horizontal and vertical transpositions of these strain curves permit the construction of a master curve of strain results as shown in Figure 14. The equations defining the appropriate shifts were found to be:

$$\delta (\log \dot{\epsilon}) = -1.1 \times 10^{-3} \, \delta \bar{M}_v \tag{15}$$

$$\delta \epsilon = -1.6 \times 10^{-6} \, \delta \bar{M}_v \tag{16}$$

$$\delta \epsilon = 1.5 \times 10^{-3} \delta (\log \dot{\epsilon}) \tag{17}$$

The master curve of strain versus molecular weight at various rates of strain is not illustrated but can be derived by application of eqs. (15)–(17).

The relationships [eqs. (12) and (15)] derived from the stress and strain transpositions demonstrate that the same equivalence between strain rate and molecular weight exists in both cases.

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