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INFLUENCE OF MOLECULAR WEIGHT ON THE DYNAMIC MECHANICAL PROPERTIES OF POLY(METHYL METHACRYLATE)

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Using a new parallel beam apparatus, the dynamic mechanical properties of poly(methyl methacrylate) were determined over a wide range of molecular weights ($1500 < \bar{M}_n < 600\,000$). Results showed that the modulus (25 °C) was only slightly dependent on chain length, and equalled 2.3×10^9 Pa for the highest molecular weight scanned. Simultaneous acquisition of α- and β-relaxations indicated a decrease in T_α in accordance with Gibbs' relation, while T_β was invariant. Both $T_\alpha^\infty = 111°$ and $T_\beta^\infty = 40°$ corroborated previous results from several sources, including dynamic mechanical measurements. Such modulus and glass transition data are essential to the calculation of fracture toughness and to the assessment of radiation damage of acrylic, respectively.

Background and introduction

During the past five years, the fracture toughness and morphology of poly(methyl methacrylate) (PMMA) were studied at room temperature (25°) as a function of molecular weight ($\bar{M}_n$) [1–3]. From results compiled over nearly the entire solid state region ($1.5 \times 10^3 < \bar{M}_n < 6.0 \times 10^5$), the energy absorbing capabilities of this amorphous, organic glass were transformed from a low energy absorbing, brittle oligomer to a high energy absorbing, ductile polymer [1, 2]. Simultaneously morphological changes were shown that corroborated the physical test results – namely, that a more specular fracture surface was characteristic of limited viscous flow and that the frequencies of the so-called rib markings were inversely proportional to ductility [3].

To complement these efforts, thermal analyses techniques have been used to characterize not only the atactic but also the isotactic PMMA [4–7]. From differential thermal analysis (DTA) and differential scanning calorimetry (DSC) the glass transitions (T_g), melting temperatures (T_m), and heats of fusion (ΔH_u) have been determined. Here T_g decreased as a function of molecular weight according to Gibbs' theory [4], while T_m and ΔH_u indicated not only the chemical but also the physical damage resulting from radiation processing, the former via the Flory equation [5–7].

Now a third thermal analysis technique has been utilized – namely, that of dynamic mechanical analysis (DMA). (An excellent review of the principles of dynamic mechanical testing has been compiled by Koo [8].) In addition to the use

of a wide variety of instrumentation [9–16] and the broad range of temperatures scanned (down to 4.2 K) [10], extensive DMA investigations have been carried out on the effect of α-methyl and methoxycarbonyl substitution onto the methyl methacrylate repeat unit [11]. The resulting changes in chain mobility from these and additional stereoregular modifications [12] have been correlated with shifts in the dynamic processes observed. Using newly available instrumentation, the present objective is to determine the viscoelastic properties of PMMA over this broad range of molecular weights and to evaluate these results within the context of more recent observations.

Experimental

PMMA was prepared (cf Table 1) either by the irradiation degradation [17] of a commercial unplasticized product, Plexiglas G, or by the solution polymerization [18, 19] of the uninhibited monomer (source: Rohm and Haas Co.). Viscometry or vapor pressure osmometry yielded values for $\overline{M}_v$ and $\overline{M}_n$, respectively [2]. Because incident radiation randomizes PMMA's molecular weight distribution, $\overline{M}_v$ could be reduced to $\overline{M}_n$ in a predictable manner [20, 21]. All DMA specimens were machined using a diamond saw (Gillings–Hamco Co.) from the batches of physical test specimens previously evaluated (cf. ref. 1, 2, and 22).

All dynamic mechanical properties were measured using a Dupont 981 Dynamic Mechanical Analyzer. This instrument operates on a compound resonance principle in which the specimen bridges the driven and the passive pivot arms (cf. inset Figure 1). By means of an electromechanical transducer, a forced oscillation amplitude is selected for the driven beam that is periodically maintained

Table 1

Preparation of PMMA

Nominal dose, Mrad	$\overline{M}_n \times 10^{-2}$	Reference
0	5870	22
10	540	22
19	355	22
25	275	22
30	225	22
60	135	22
80	64	1
108[a]	52	2
—[b]	25	2
—[b]	16	2

[a] Precipitated following radiation degradation.
[b] Prepared directly by solution polymerization.

by an electronic feedback system. From the frequency response of the system and the evaluation of the characteristic machine constants, a modulus is calculated either in flexure ($L/T \geq 10$),

$$E = \left[\frac{4\pi^2 f^2 J - K}{2W\left(\frac{L}{2} + D\right)^2}\right]\left(\frac{L}{T}\right)^3\left[1 + 0.71\left(\frac{2T}{L}\right)^2 - 0.1\left(\frac{2T}{L}\right)^3\right], \quad (1)$$

where $\left[1 + 0.71\left(\frac{2T}{L}\right)^2 - 0.1\left(\frac{2T}{L}\right)^3\right] \cong 1$ for $L/T \geq 10$,

or in shear ($L/T \approx 1$) [23],

$$G = \left[\frac{4\pi^2 f^2 J - K}{2W\left(\frac{L}{2} + D\right)^2}\right]\left(\frac{L}{T}\right) \quad (2)$$

where . . .

E = Young's modulus (Pa),
G = shear modulus (Pa),
f = system frequency (Hz),
J = moment of inertia of sample arm (typically $1.45 - 1.65 \times 10^{-3}$ kg · m^2),
K = torsional spring constant of flexure pivot (ranges from 0.30 – 0.45 N · m · rad^{-1}),
D = clamping distance (generally $9.50 - 9.85 \times 10^{-3}$ m),
W = sample width (m),
T = sample thickness (m), and
L = sample working length (m) (as opposed to actual sample length, L').

Note that, although f is *not* the sample frequency, the numerator of the modulus expression is related to the sample frequency via the differences of the squares of the system and natural free oscillation frequency, the latter being implicit in K.

From the decay of the amplitude envelope, the damping is displayed on a second channel of the recorder from which tan δ is computed from the relationship,

$$\tan \delta = \frac{VC}{f^2}, \quad (3)$$

where . . .

tan δ = ratio of energy dissipated to maximum potential energy stored per cycle,
V = system damping (mV), and
C = system constant (0.24 – 0.27 Hz^2 · mV^{-1} for an oscillation amplitude of 0.2 mm).

Since instrumental damping restricts the lower useful tan δ range ($\sim$0.008) and theoretical considerations progressively reduce the accuracy of the upper measurements, the manufacturer's optimum operating tan δ range is 0.01 – 0.3.

Prior to mounting the samples in the DMA apparatus, several constants were measured (1.61×10^{-3} kg · m^2, 0.38 N · m · rad^{-1}, and 9.93×10^{-3} m for J, K, and D, respectively) or assigned (C = 0.26 Hz^2 · mV^{-1}). Note that both J and K fell well within the range of typical instrument values reported, while D was slightly greater – a result of the similar mass but minor dimensional differences in the sample clamps that were specially designed for gripping more fragile materials. In addition the inherent tendency for the flexure pivots to self-damp, i.e., the quality factor (Q), was measured for the driven arm and judged acceptable at 300 (typically 300 – 700 where < 150 indicates a faulty pivot). The passive arm's pivot was also satisfactory, since a stable resonant frequency was observed ($f_0 \cong 2.4$) when both arms were linked together.

Samples with nominal dimensions, $L' \times W \times T$ = 25.4 mm × 3.3 mm × 2.4 mm were gripped with an effective working length, L = 12.7 mm. After setting the oscillation amplitude and the A/Z gain to 0.20 mm and 0.35, respectively, all scans were made at a heating rate of 10 °/min under $N_{2(g)}$ over the temperature range from −60 to +200°. Even though the clamping arrangement stressed the brittle samples more uniformly, a small amount of epoxy was used for specimens with a $\bar{M}_n < 6400$ to reduce the clamping pressure and to preclude any slippage). Similarly the oscillation amplitude was decreased first to 0.1 mm ($\bar{M}_n$ = 6400) and then to 0.075 mm ($\bar{M}_n$ = 2500) to reduce breakage. For all these acrylics no apparent error was introduced into f by varying the oscillation amplitudes, since the frequency response saturated out to a maximum value by 0.050 mm. Some uncertainty was probably introduced in tan δ, however, since C is a function of oscillation amplitude.

To account for temperature program and sample lag effects, a dynamic temperature calibration procedure was followed. By imbedding a chromel-alumel thermocouple into either the surface or the center of three PMMA specimens ($\bar{M}_n$ = 587 000), a simulated test resulted from which the actual sample *vs.* machine temperature relationship was generated. Such methodology was deemed more accurate than either the suggested Indium or PMMA calibration procedures, since the metal was judged to be too conductive to yield comparative data and the polymer was biased by the arbitrary assignment of the maximum damping peak to a T_α = 120°. By combining the temperature compensation with the continuous frequency and damping output, the modulus and tan δ versus temperature plots were computed (Wang 2200 PCS-II) at discrete 10° intervals.

Results and discussion

Results for four of the PMMA samples tested are illustrated in Figure 1. Over the wide range of $\bar{M}_n$ tested, these scans show that the modulus is rather invariant in the glassy region (ca 2×10^9 Pa), while the increasing number of chain ends

shifts the transition region to lower temperatures. This latter decrease corresponds to the intense spike observed on the tan δ versus temperature plot and represents the glass transition temperature, T_α. By amplifying the lower temperature region of these scans a second relaxation (T_β) was observed which, from ancillary experimental techniques, corresponds to the motion of the methoxy-carbonyl side group [11, 24, 25] (cf. other hypotheses, refs. 26–28). All of the PMMA results are summarized in Table 2.

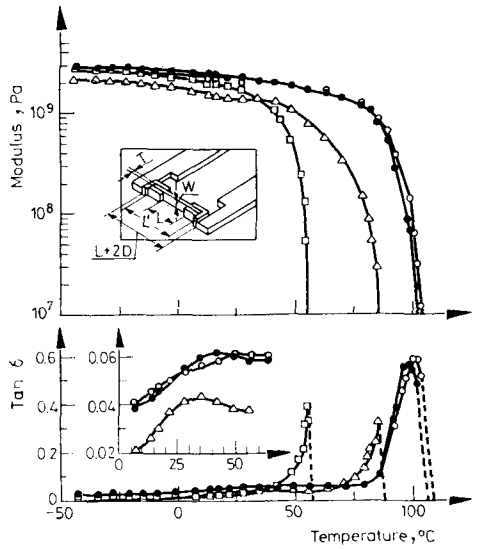

Fig. 1. Influence of molecular weight on the dynamic mechanical properties of poly(methyl methacrylate) (PMMA). ●, ○, △, and □ correspond to $\overline{M}_n$ of 587 000, 54 000, 6400, and 1600, respectively. Note the upper inset illustrating the geometry of the test apparatus and the lower inset detailing the β-transition (T_β)

Table 2

Summary of PMMA results

$\overline{M}_n \times 10^{-2}$	Modulus $\times 10^{-9}$, Pa	T_α, °C	T_β, °C
5870	2.3, 2.3	93, 98	48, 42
540	2.2	102	49
355	2.3	99	40
275	2.1	96	42
225	2.1	95	29
135	2.2	89	35
64	1.4	86	36
52	1.6	81	37
25	1.8	61	—[c]
16	1.8	56	—[c]

[c] No β-transition observed.

From the linear regression of the modulus data (•, Figure 2), a slight negative dependency is indicated over two-and-one-half orders of magnitude of $\overline{M}_n$. The present intercept of 2.1×10^9 Pa ($f \approx 20$ Hz at 25°) lays within the range observed

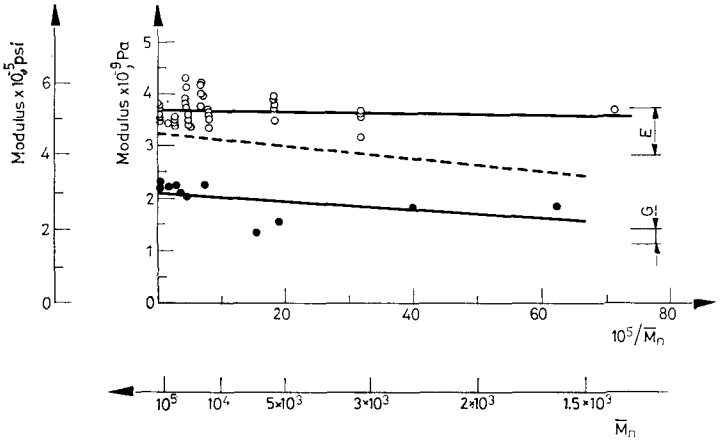

Fig. 2. Dependence of PMMA modulus of $\overline{M}_n$ as determined by DMA (•) and transverse rupture tests (o, cf ref. 1). Typical limits of Young's modulus (E) and the shear modulus (G) in tension and in transverse bending are shown at right (cf refs. 1 and 31). The dashed line results when the low L/T ratios of the DMA specimens are normalized with respect to the transverse bending data (cf. Figure 3)

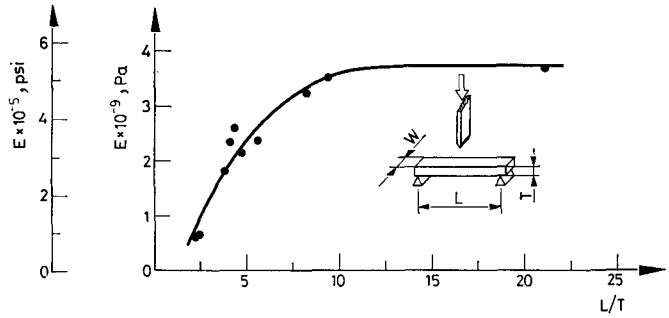

Fig. 3. Influence of sample geometry of transverse rupture test specimens on Young's modulus. Data points represent the mean of as many as 39 test bars (datum at $L/T = 21$), and span a molecular range similar to that outlined in Table 1

for the shear modulus ($1.4-3.0 \times 10^9$ Pa at $f = 1$ Hz) [11, 15, 29], but is less than that quoted either by Woodward and Sauer [16] ($E = 3.0 \times 10^9$ Pa at $f =$ $= 100-500$ Hz), Manson et al [14] ($E = 4.8 \times 10^9$ Pa at $f = 110$ Hz), or by the manufacturer [30] ($E \approx 5-10 \times 10^9$ Pa at $f \approx 15$ Hz, $L/T = 20$, and a heating rate $= 5°$/min). In contrast the same PMMA yielded E values of 2.8 and 3.7×10^9 Pa for tensile [31] and transverse bending tests [1], respectively, and computed

G values of $1.1-1.4\times10^9$ Pa based on a Poisson's ratio (ν) of 0.33 [9]. In the only other comprehensive study of PMMA modulus as a function of M_n^{-1}, a slight negative dependency was observed in transverse bending in which $E > 3.5\times10^9$ Pa for all $\bar{M}_n$ tested [1] (o, Figure 2).

Since the previous specimen configurations limited the maximum length of the present samples and the brittleness of the lower molecular weight tests bars restricted the minimum thickness attainable, the greatest L/T ratio which could be obtained was ~5. Accordingly, the calculated modulus was not truly the pure bending (equation 1, $L/T \geq 10$) nor the pure shear (equation 2, $L/T \approx 1$) case. Although the manner in which these dynamic tests departed from the optimum results computed via equation 1 was not known, some previously unpublished data might suggest a trend. Here Plexiglas G was fabricated into bars shown (Figure 3), typically of $L\times W = 25.4\times3.3$ mm, and L/T varied from 2.3 to 21. When flexed at 0.1 cm/min in three point bending using an Instron testing machine, an L/T dependence was noted for $L/T < 10$. From the ratio of the moduli at $L/T = 20$ and $L/T = 5$, a scaling factor (1.5) resulted. Since E *vs.* L/T was relatively independent of $\bar{M}_n$ in transverse bending, a constant factor of 1.5 was likewise applied to the DMA modulus data (cf. dashed line, Figure 2). For $\bar{M}_n > 5\times10^3$ this translated the obtained modulus values into the lower region of the reported E values.

Comparison of T_α and T_β (cf. Table 2) with several earlier investigations are shown in Figure 4 [4, 14, 21, 32]. In general the data separated into three broad bands that were discriminated primarily by the measurement technique, and, to a lesser extent, by the degree of stereoregularity. Although numerous values have been documented for T_α ranging from 78 – 125° (e.g., refs. 9, 13, 15, 16 and 32), the lowest detailed T_α determinations were observed both for the present DMA (●, heating rate = 10°/min., $f \approx 3$ Hz, and the syndiotactic fraction = 0.80), and for the Rheovibron measurements (□, $f = 110$ Hz) of Manson et al. [14]. While these latter investigators stated that materials with an $\bar{M}_n \lesssim 3.5\times10^4$ were too brittle to evaluate, nevertheless, they were able to obtain valuable data in the high molecular weight region. As the glass transitions of acrylics generally do, these dynamic mechanical properties data fitted Gibbs' theory [33] best – in this case when the fractional free volume at T_α, V_0, equals 0.025, and when the energy barrier to segmental rotation, ε, equals 0.96 kcal/mole segments ($T_\alpha^\infty = 111.0°$, cf inset of Figure 4). At the other extreme the DTA data of Thompson (△ and ▽) [21] and Kusy *et al.* (o) [4] were represented once again by the Gibbs function in which $V_0 = 0.025$ and $\varepsilon = 1.02$ kcal/mole segments ($T_\alpha^\infty = 121.5°$). Note that the latter authors' data (represented by the mean values of their previous multiple runs at 20°/min) fall between the other two series of data and correspond to a syndiotactic fraction of 0.80 (○) versus 0.75 (▽) and 0.82 (△). The refractometry data of Beevers and White (+) [32] fell within the envelope generated by the two Gibbs expressions.

When compared to T_α, the more diffuse nature of the β-relaxation phenomenon made T_β measurements more difficult to observe (cf. Figure 1 and Table 2). As

shown in Figure 4, however, results were obtained down to $\bar{M}_n = 5 \times 10^3$ and a regression line was drawn. Since at least two of the data show significant scatter, interpretation is limited to the observation that $T_\beta \approx 40\,^\circ$ ($f \approx 20$ Hz). In comparison, a transition map composed of data from over a half-dozen sources (cf.

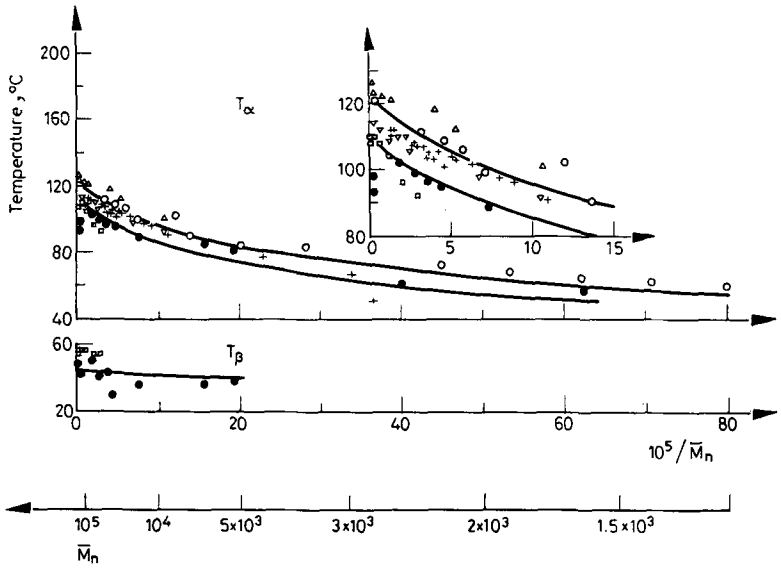

Fig. 4. Comparison of present T_α and T_β data (•) with previous results and with Gibbs' theory. △, ○, and ▽ were obtained via differential thermal analysis (refs. 4 and 21), while □ and + were determined via dynamic mechanical properties (ref. 14) and refractometry (ref. 32), respectively. For T_α, the upper curve corresponds to $V_0 = 0.025$ and $\varepsilon = 0.99$ Kcal/mole segments, while the lower curve corresponds to $V_0 = 0.025$ and $\varepsilon = 0.96$ Kcal/mole segments

Figure 4 of ref. 16), fixed $T_\beta = 24.44$, and $66 \pm 5°$ for $f = 1$, 10, and 100 Hz, respectively. These and other similar results [9, 11–13, 15] indicate that the current data and those of Manson et al. [14] were consistent within the context of the frequency shift factor.

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RÉSUMÉ — En se servant d'un nouvel appareil à rayons parallèles, on a déterminé les propriétés mécaniques dynamiques du poly(méthyl-méthacrylate) dans un large intervalle de poids moléculaires ($1500 < \overline{M}_n < 600\,000$). Les résultats on montré que le module (25°) ne dépend que peu de la longueur de la chaîne et est égal à 2.3×10^9 Pa pour le plus haut poids moléculaire étudié. L'acquisition simultanée des relaxations α et β a indiqué, en accord avec la relation de Gibbs, une diminution de T_α, tandis que T_β s'avere invariable. Les valeurs $T_\alpha^\infty = 111°$ et $T_\beta^\infty = 40°$ ont corroboré toutes deux des résultats antérieurs de diverses sources, y compris des mesures mécanique dynamiques. Un tel module ainsi que les données de la transition vitreuse sont essentiels pour calculer la résistance à la rupture, et pour déterminer les dommages par irradiation des matières acryliques.

ZUSAMMENFASSUNG — Unter Anwendung eines neuen Parallelstrahlgerätes wurden die dynamischen mechanischen Eigenschaften von Poly(methylmethacrylat) in einem weiten Molmassenbereich ($1500 < \overline{M}_n < 600\,000$) bestimmt. Die Ergebnisse zeigten, daß der Modul (25°)

nur wenig von der Kettenlänge abhängig und für die höchste erfaßte Molmasse gleich 2.3× $\times 10^9$ Pa war. Die gleichwertige Erfassung der α- und β-Relaxationen zeigte in Übereinstimmung mit der Gibbs-schen Abhängigkeit eine Abnahme von T_α, während T_β unverändert blieb. Sowohl $T_\alpha^\infty = 111°$ als auch $T_\beta^\infty = 40°$ bestätigten frühere Ergebnisse verschiedenen Ursprungs, dynamische mechanische Messungen mit inbegriffen. Solch ein Modul und Glas-Übergangsdaten sind zur Berechnung der Bruchfestigkeit bzw. zur Bestimmung der Bestrahlungsschäden in Acrylaten unerläßlich.

Резюме — Используя новую аппаратуру с параллельным балансиром, были определены динамические механические свойства полиметилметакрилата в широкой области молекулярных весов ($1500 < \overline{M}_n < 600\,000$). Результаты показали, что модуль (25°) только слегка зависил от длины цепи и был равным 2.3×10^9 Па для полимера с наибольшим молекулярным весом. Одновременное приобретение α- и β-релаксаций показало уменьшение T_α в соответствии с соотношением Гиббса, в то время как T_β не изменялось. Оба $T_\alpha^\infty = 111°$ и $T_\beta^\infty = 40°$ подтверждены предыдущими результатами из нескольких источников, включая динамические механические измерения. Такие модули и данные стеклообразного превращения ценны при вычислении разрыва вязкости и для оценки радиоактивного повреждения акрилоида.