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Characterization of the Glass Transition Using a Microindenter

by

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CHARACTERIZATION OF THE GLASS TRANSITION USING A MICROINDENTER

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ABSTRACT

The microindenter described here requires a very small sample (c. 10 mg), can be used with heating rates comparable to those in DSC (ie., 10°C/minute), and gives a large, clearly defined change at the glass transition. The essential features are a needle probe and a linear variable differential transformer (LVDT). By suitably controlling the force on the needle, the rate of heating, and the sample thickness, reproducible results can be obtained. The small sample size permits a relatively fast heating rate. Most mechanical tests (often using oscillating stress and strain) require large samples with a corresponding long time for temperature equilibration to take place (ASTM D 4065). Another indentation test, the Vicat Softening Temperature (ASTM 1525) also uses a thick (3 mm) sample. Like the Vicat test, the present procedure is best suited to amorphous polymers. The application to plasticized samples of poly(methyl methacrylate) illustrates the utility of the method. The simple, rugged, and inexpensive nature of the apparatus makes it suitable for an undergraduate experiment in a polymer laboratory course.

INTRODUCTION

The glass transition temperature, T_g, usually is defined in terms of the change in expansion coefficient as a polymer goes from the glassy to the rubbery state. Dilatometers for measuring the specific volume at various temperatures are not very convenient to use. When a confining fluid such as mercury is used, the expansion of the fluid can obscure the changes in the polymer, and air bubbles and leaks can be persistent and annoying. The most common test in use today to measure T_g is the Differential scanning calorimeter, DSC (ASTM D3418). However, when a broad transition range occurs, as in polymer blends and plasticized polymers, reproducibility is poor. Mechanical tests, usually using oscillating stress and strain, require larger samples with a corresponding longer time for temperature equilibration to take place (ASTM D 4065). Often the temperature is changed in 2 to 5°C steps with 2 to 5 minutes at each interval. An indentation test, the Vicat Softening Temperature (ASTM 1525) is used primarily with amorphous polymers. In the test, a flat-ended cylinder with a cross-sectional area of 1 mm^2 is loaded with a 1.0 kg mass. The softening temperature is that needed to achieve a penetration of 1 mm into a specimen which is at least 3 mm thick. The specimen is immersed in a non-interacting liquid and the fastest recommended heating rate is 2°C/minute. Schwartz has described the use of a thermomechanical analyzer to evaluate T_g by measuring either sample thermal expansion or probe penetration[1]. Testing was limited to thick samples (2 to 3 mm) and low heating rates (8°C/min or lower). More recently, Darlix et al[2] used a ball (1-mm D) indentation test with samples about 10 mm thick to characterize transitions in crystalline and amorphous polymers.

Characterization of polymers by thermomechanical and other tests has been reviewed by Shalaby[3]. The relationship between modulus and indentation hardness has been described by Arridge[4] and by Muhr and Thomas[5]. The transition temperatures measured by these various techniques will not necessarily agree with each other, even when the time scale is of the same magnitude.

Probably the most important practical aspect of T_g is that it represents for most amorphous polymers the upper limiting temperature for dimensional stability. Glassy polymers usually have a Deflection Temperature (still often called the "heat distortion" temperature) close to T_g (ASTM 648).

The microindenter described here requires a very small sample, can be used with heating rates comparable to those in DSC (ie., 10°C/minute), and gives a large, clearly defined change at the transition. By suitably controlling the force, time, and sample thickness, reproducible results can be obtained.

APPARATUS

The heart of the apparatus is a linear variable differential transformer (LVDT) and carrier-demodulator (Crescent-East, Inc.) (Fig. 1). When the carrier is energized with a 10 V AC current, the output is a DC signal of about 30 mV for a core movement of 1 mm. The coil is supported by a leg which rests on a metal coupon. The core is fitted with a needle (tip radius is 35 µm) which rests on the polymer sample. The needle can be loaded with various masses. With the output recorded on a 5 mv-full scale chart, core (needle) movements of 1 or 2 µm are seen easily.

Various means of ramping up the temperature of the sample can be used. Perhaps the simplest and least expensive is an aluminum block (Fig. 1) with a 100 W heater (rheostat controlled) and a thermocouple for temperature measurement. The rate of temperature increase is not quite linear, but decreases only by about 20 % over the range of room temperature up to 200°C. A programmable hot stage (Mettler) has been used, also. In any case, the essential feature is the recording of indentation versus temperature.

The sample (Fig. 2) is held in place on an aluminum coupon by the needle. We have used common sewing needles[6]. A polymer sample thickness between 50 and 100 µm is convenient. The area required is less than 1 cm^2 so that the total volume needed is less than 0.01 cm^3. This compares favorably with the amount used in DSC. Because of the small sample and the good conductivity of the aluminum support and block, the sample temperature is rather uniform.

PROCEDURE (with aluminum block heater)

The specimen is placed on the aluminum coupon. With the assembly in place on the cold aluminum block, the coil support and needle are placed on the bare coupon and on the specimen, respectively. The coil versus core position is adjusted so that the recorder does need to have a zero displacement. The heating is started (the block can be refrigerated before the experiment in order to extend the range of temperatures). A typical run (Fig. 3) shows some small rate of penetration until the vicinity of the glass transition is reached. The slope changes rapidly as the rubbery melt region is entered.

Several methods of interpreting the results can be utilized. With a standardized needle force (60 g), sample thickness (50 to 100 μm), and rate of heating (10 K/min), the temperature corresponding to a penetration of 10 μm appears to correlate well with the transition temperature measured by DSC.

RESULTS AND DISCUSSION

Films 50 to 100-μm thick were made by dissolving a polymer with or without a plasticizer in a suitable solvent, then casting the solution on a glass plate. After air drying, the films were baked at 140°C for 30 minutes. The same materials were evaluated in the microindenter and in a DSC (Perkin-Elmer Model II).

In a representative penetration trace (for poly(ethyl methacrylate), PEMA) (Fig. 3), the transition is easily seen in the microindenter plot. Several plasticizers were evaluated in poly(methyl methacrylate), PMMA, and in poly(styrene). One ester-type plasticizer, DBEP, di(butoxyethyl)phthalate[7], is compatible with both polymers and about equally effective at lowering T_g of both (Figs. 4 and 5). PMMA also is compatible (Fig. 6) with two polymeric plasticizers, PEO, poly(ethylene oxide)[8] with a M_w of $4x10^3$ and CO rubber, poly(epichlorohydrin)[9] with a M_w of $600x10^3$. In the range of concentrations tested, the lowering of T_g is approximately linear. The plasticizing efficiency in PMMA can be compared by examining the T_g at 20% (by weight) plasticizer. The lowering is greatest for PEO ($T_g = 63°$), less for DBEP ($T_g = 71°$) and least for CO rubber ($T_g = 82°$). The temperatures measured by both the microindenter and DSC for these amorphous polymers are in reasonable agreement

The effect of film thickness in the range of 50 to 100 µm is small but systematic (Fig. 7). The influence of heating rate on T_g was investigated in a preliminary manner. A particular sample of a commercial polystyrene 50-µm thick gave T_g's of 109 and 115°C at heating rates of 6 and 15°C/min, respectively.

Temperature Uniformity

The effect of thickness on uniformity of temperature can be estimated in a convenient fashion by using, as a very rough approximation, the time it takes for the center line of a polymer slab to approach the temperature of the surface. We assume that the center is initially at temperature t_o, and that the surface is at temperature T_o. The time, θ, for the center line temperature to reach a value of t is a function of a dimensionless group,

$$N = 4\kappa\theta/(c\rho\lambda^2) \qquad (1)$$

κ = thermal conductivity, say 3×10^{-4} cal/(s,cm,°C)
c = specific heat, say 0.3 cal/(g,°C)
ρ = density, say 1.2 g/cm^3
λ = slab thickness, cm

The time for $(T_o - t) = 0.01(T_o - t_o)$ is given[10] by N = 2. Thus, the "time scale" for good temperature control can be estimated (using the numbers for the various parameters given above) to be

$$\theta = 600\ \lambda^2 \qquad (2)$$

The "time scale" calculated in this manner, θ, is 150 sec for $\lambda = 5$ mm, 6 sec for $\lambda = 1$ mm, and 0.06 sec for $\lambda = 0.1$ mm (about 0.004-inch), which is the typical thickness used with the microindenter.

Modulus measurement by indentation

Various workers have attempted to correlate penetration of a probe with a modulus, as in many "hardness" measurements. According to Muhr and Thomas [5], the penetration distance, P, by a probe of radius R under a force F, is related to the shear modulus G by

$$P^3R = F^2(3/16G)^2 \qquad (3)$$

In the present work, $R = 35\times10^{-6}$ meter, and $F = 0.6$ newton, so that

$$G = 0.65\times10^{-3} \times P^{-3/2} \qquad (4)$$

For $P = 1\ \mu m$, the formula gives $G = 0.7$ MPa. The modulus of a polymer glass typically is on the order of 1000 MPa and the "zero-time" modulus of a rubbery melt is about 1 MPa. Since the microindenter does appear to distinguish the transition from glass to rubbery melt, one can conclude that the measurements are in qualitative agreement with the predictions of equation 3. That is, the needle should not penetrate into a glassy polymer to any significant degree, while it should penetrate a rubbery melt.

CONCLUSIONS

The microindenter test is rapid and easily carried out. Because it is essentially measuring a time-dependent modulus, it does not yield the detailed data on transitions available from a dynamic test. Also, it does not give the thermodynamic information one obtains from the DSC. However, when dealing with many amorphous polymer systems (including plasticized ones), the microindenter gives useful, unequivocal data with a minimum of investment of time and money. The simple, rugged, and inexpensive nature of the apparatus makes it suitable for an undergraduate experiment in a polymer laboratory course.

ACKNOWLEDGMENTS

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2. Darlix, B., B. Monasse and P. Montmitonnet, Polymer Testing, 6:107, 1986.

3. Shalaby, S. W., in "Thermal Characterization of Polymeric Materials," E. A. Turi (ed), Academic Press, New York, 1981, Chapter 3.

4. Arridge, R. G. C., "An Introduction to Polymer Mechanics," Taylor and Francis, Philadelphia, 1985, pp. 179-180.

5. Muhr, A. H., and A. G. Thomas, NR Tech., 20:27, 1989.

6. One suitable source is "Sharps", 40 to 50 mm-long sewing needles, William Prym, Inc., Dayville, CT (available at Jo-Ann Fabrics outlets).

7. Plasthall™ DBEP, C. P. Hall Co.

8. Carbowax™ 4000, Union Carbide Corp.

9. Hydrin™ 100, B. F. Goodrich Chemical Co.

10. Kern, D. Q., "Process Heat Transfer", McGraw-Hill, New York, 1950, p. 646.

Fig. 1 Microindenter

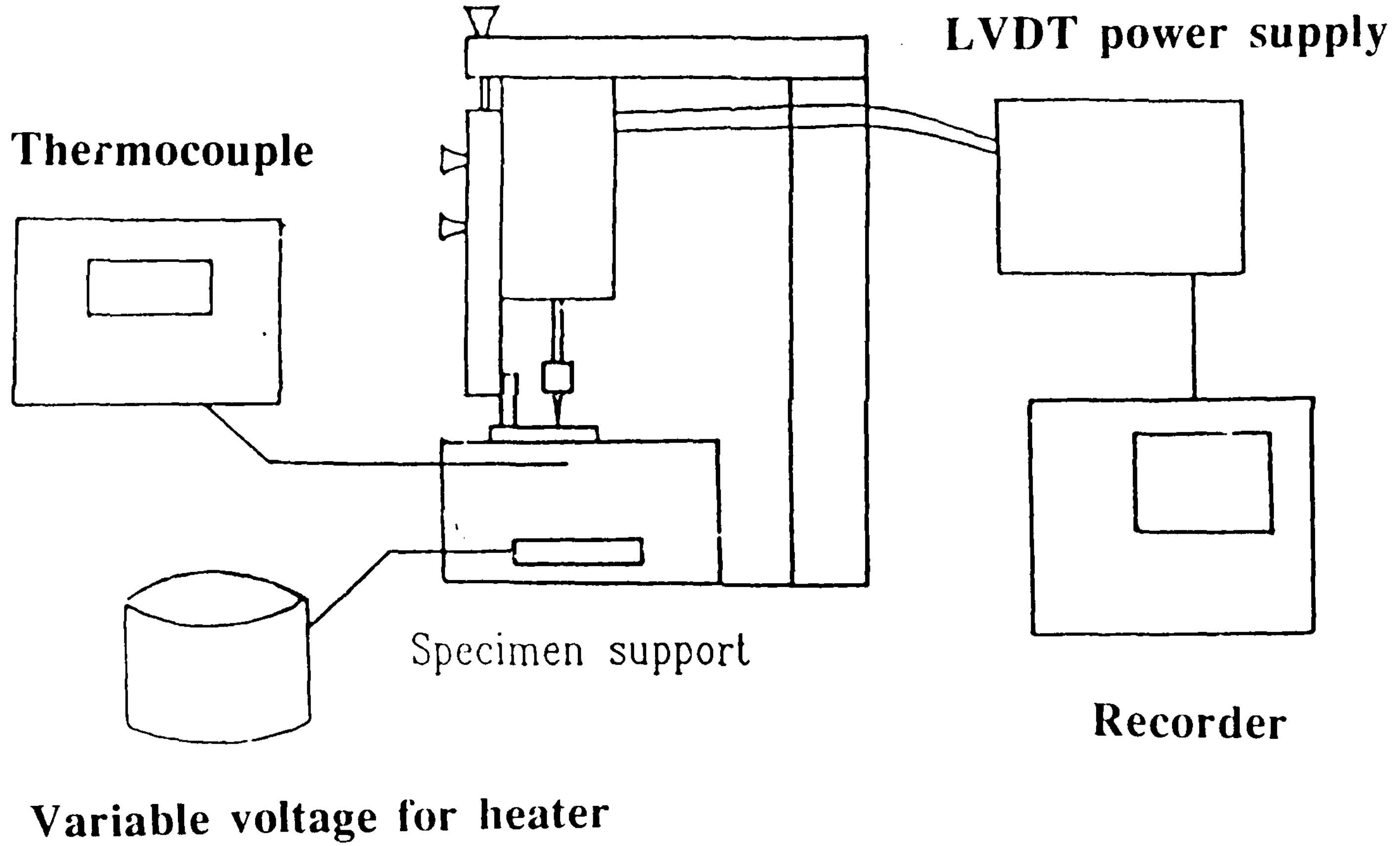


Fig. 2 Specimen details

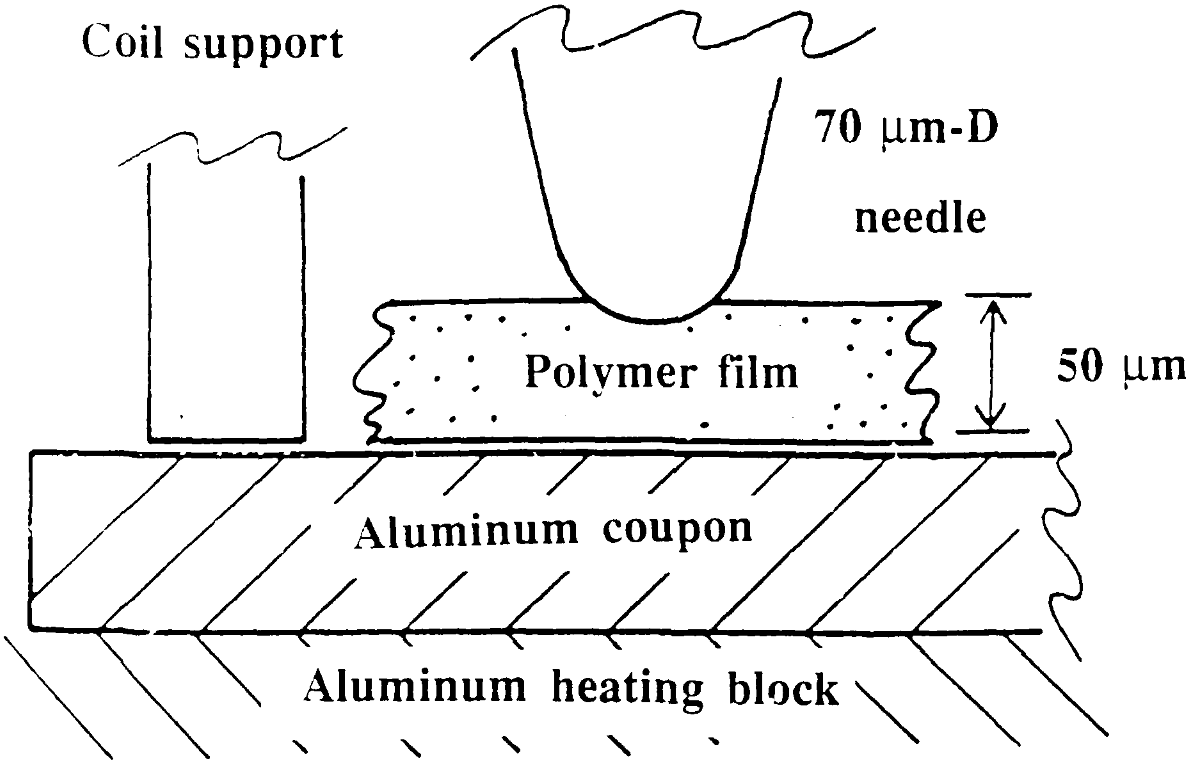


Fig. 3 Microindenter trace for Poly(ethyl methacrylate), (63 μm thick, 10K/min).

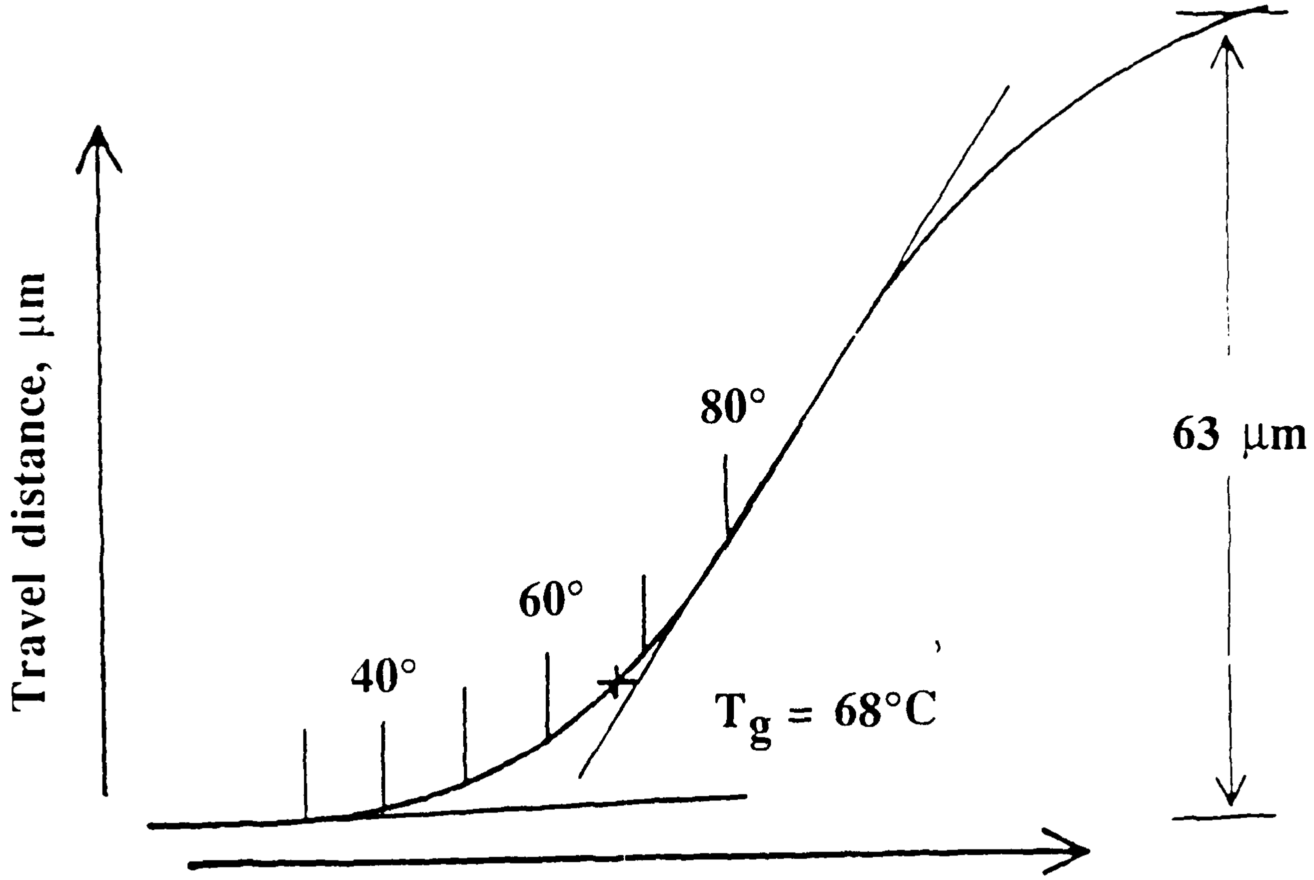


Fig. 4 PMMA (M_w = 950x10^3) plasticized by di(butoxyethyl) phthalate. Transition temperatures measured using (o) microindenter (at penetration of 10 μm, 10K/min), and (Δ) DSC (20K/min).

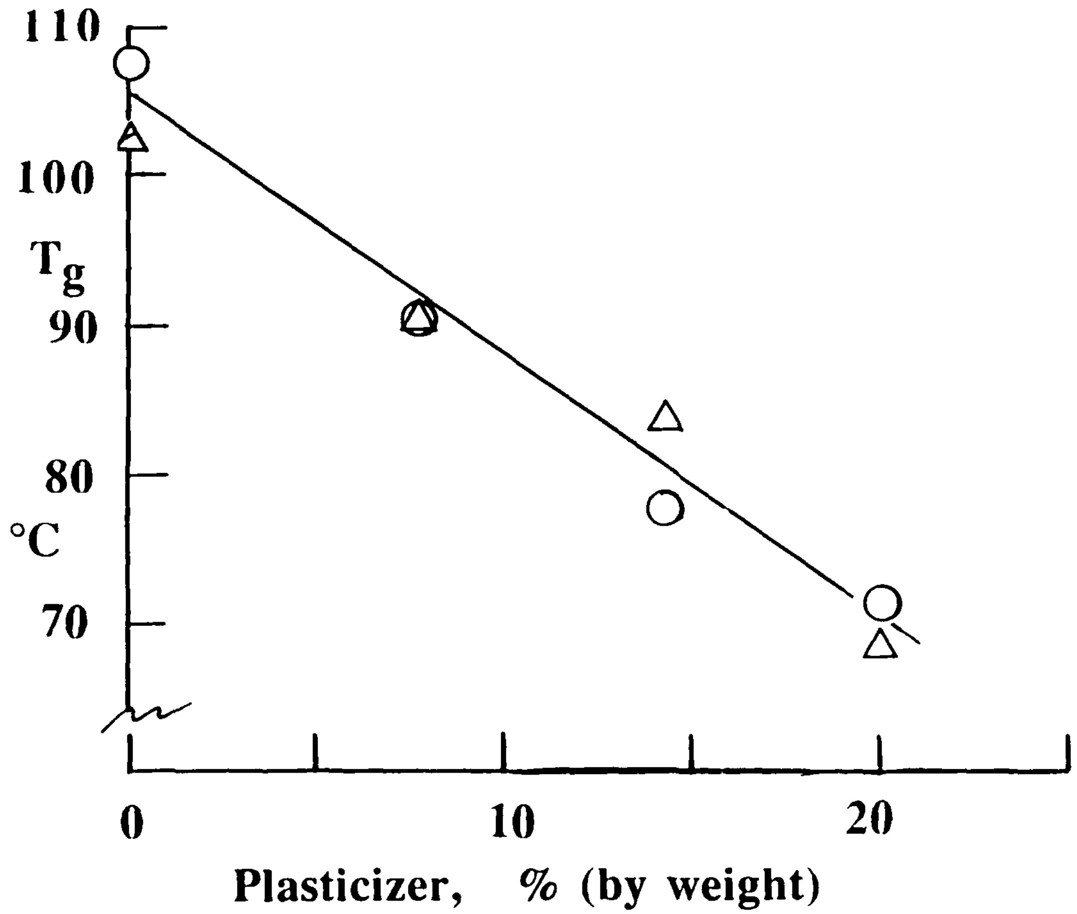
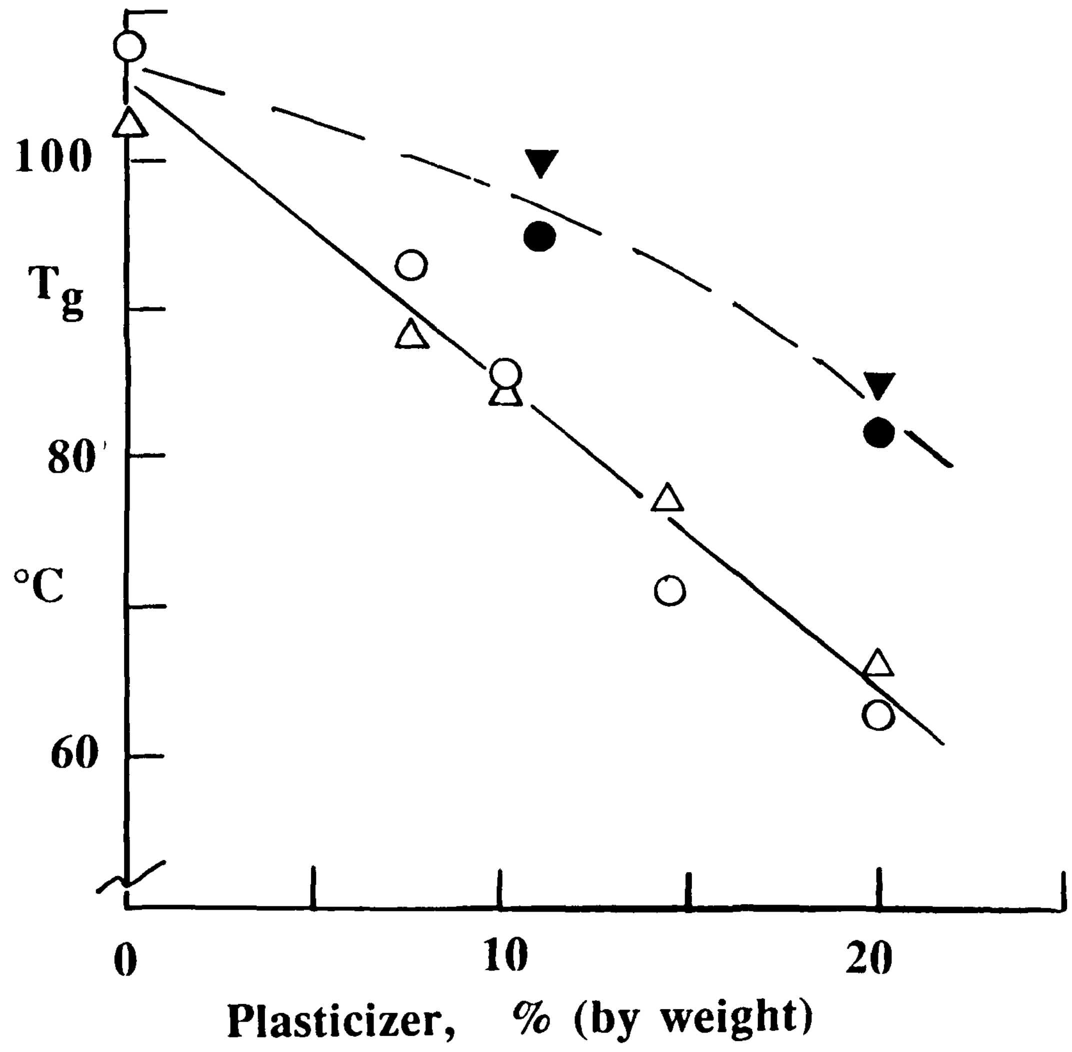


Fig. 5 PMMA (M_w = 950x10^3) plasticized by poly(ethyleneoxide), lower curve and by poly(epichlorohydrin), upper curve. Transition temperatures measured using (o, ●) microindenter (at penetration of 10 μm, 10K/min), and (Δ, ▼) DSC (20K/min).



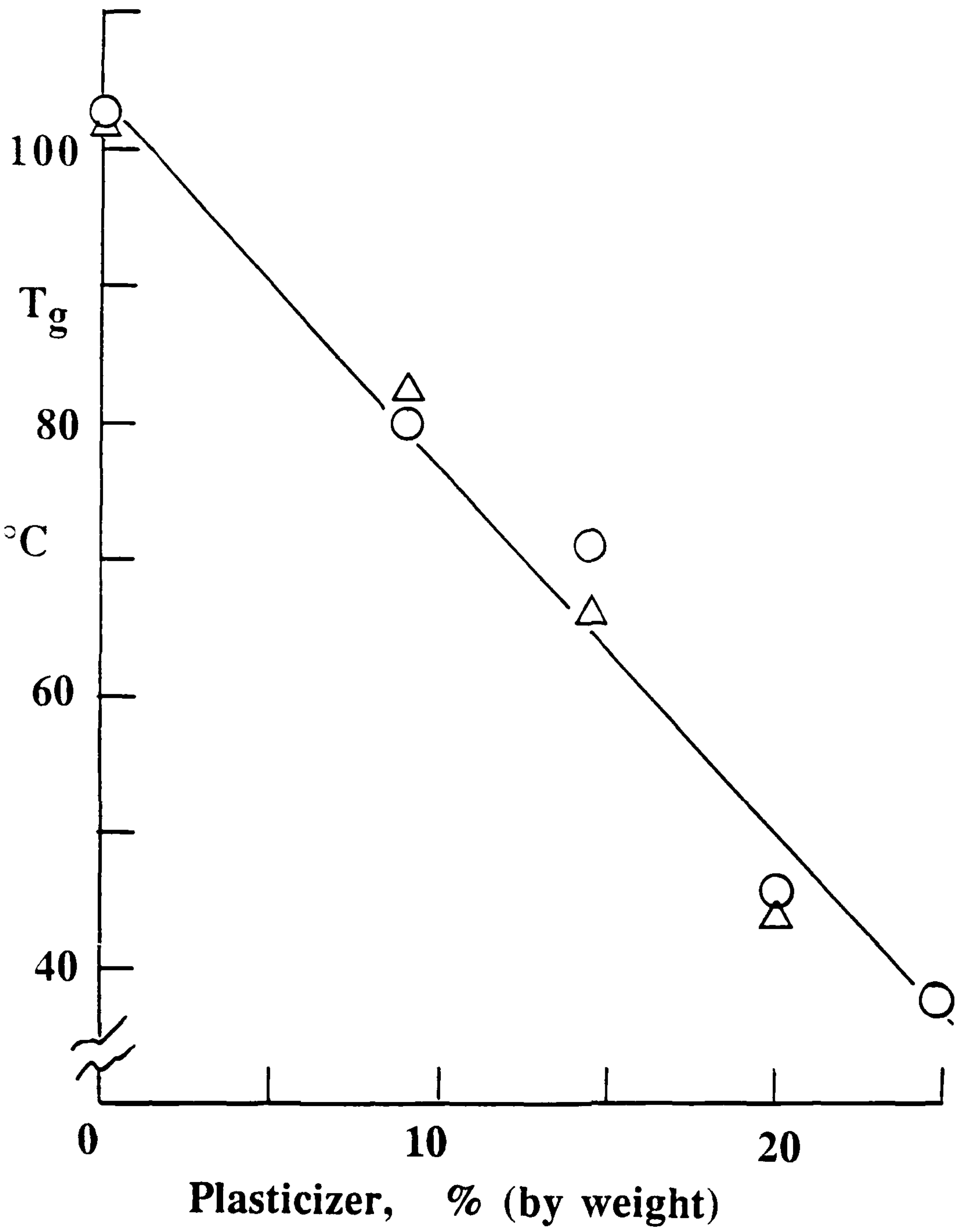
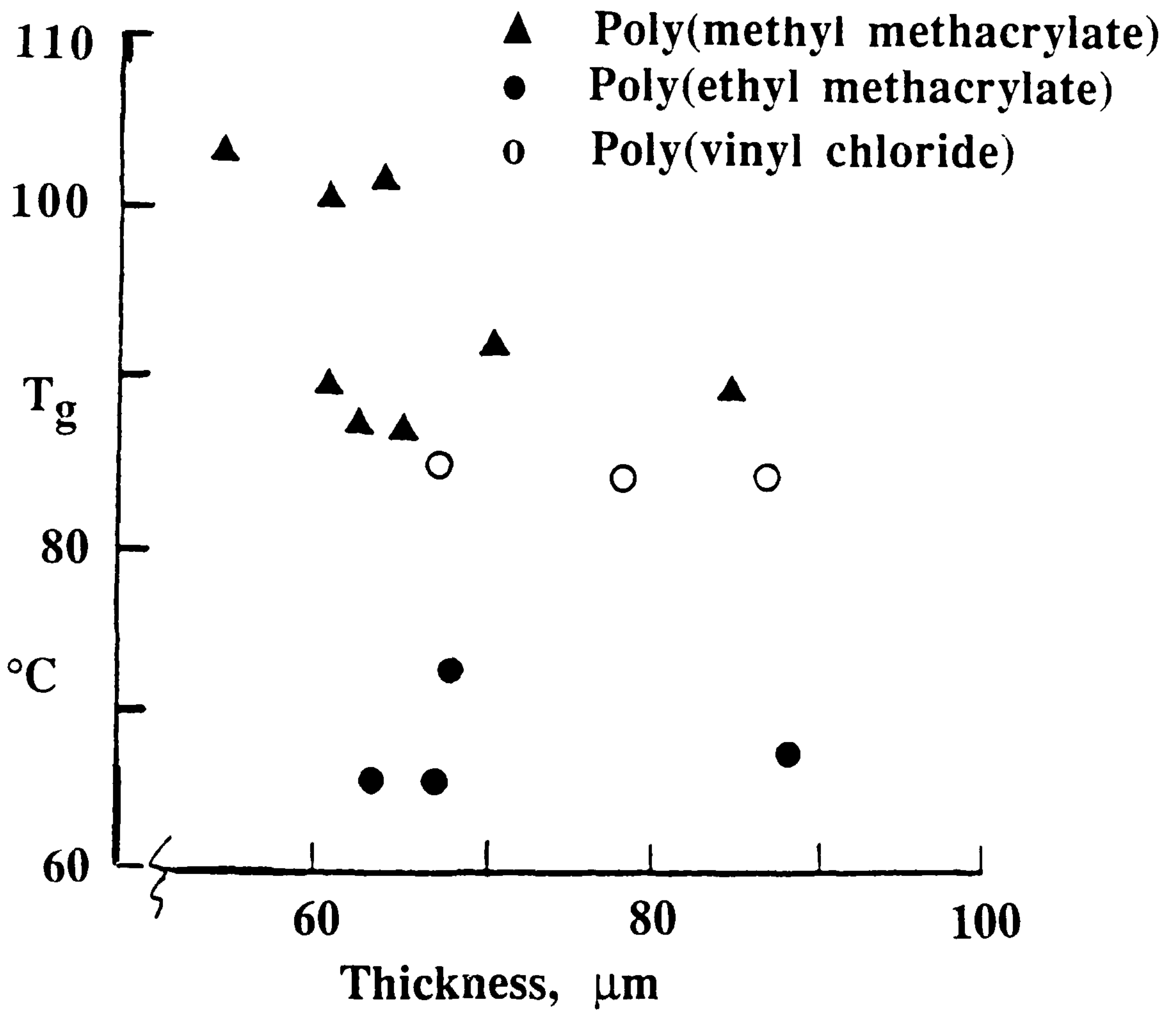


Fig. 6 Polystyrene (M_w = 261x10^3) plasticized by di(butoxyethyl) phthalate. Transition temperatures measured using (o) microindenter (at penetration of 10 μm, 10K/min), and (Δ) DSC (20K/min).

Fig. 7 Effect of thickness on T_g (MI) at a heating rate of 10K/min.



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