Effects of Composition and Irradiation on the Glass Transition Temperature of Methyl Methacrylate–Styrene Copolymers*

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Synopsis

The glass transition temperatures of polystyrene, poly(methyl methacrylate), and copolymers prepared from their respective monomers were determined by using a volume dilatometer. The glass transition temperatures of polystyrene and poly(methyl methacrylate) were found to be 82 and 104°C., respectively. The glass transition temperatures obtained for the copolymers were between the values determined for each of the homopolymers and were a monotonic function of the polymer composition. The experimental values agree with predictions in the literature based on interpolation formulae. The effects of changes in composition and radiation-induced crosslinking on the glass transition of the copolymer system are described.

Recent investigations[1-6] suggest that in many instances the physical properties of a polymer can be predicted from a knowledge of its glass transition temperature, T_g. In order to prepare a copolymer having specific physical properties, a convenient guide would be knowledge of its glass transition temperature and the relationship of the latter to the composition of the copolymer. Gordon and Taylor[7] derived an equation for such a relationship, and Wood[8] recently published a modification of the Gordon-Taylor equation.

In this study, our purpose was to test the applicability of Wood's equation to a copolymer system for which T_g and composition can be determined experimentally for all ranges of copolymer composition. The styrene–methyl methacrylate system was chosen because it fulfills these requirements.

In a copolymer system T_g is a function not only of the composition but also of crosslinking.[3,4] When crosslinking is introduced chemically, the composition is also changed. Hence it is difficult to separate the effects of these parameters on T_g, especially when the copolymer is composed of

markedly dissimilar monomers. It was suggested[4] that changes in T_g arising from changes in composition and crosslinking are independent and additive. This work also describes attempts to test the independence and additivity of these changes on one system, styrene–methyl methacrylate, in which crosslinking was introduced by high energy radiation rather than a chemical agent, thus keeping the composition invariant.

EXPERIMENTAL PROCEDURE

Materials

The inhibitor, hydroquinone, was removed from the methyl methacrylate and styrene monomers by distilling at 1 mm. Hg pressure and retaining only the center fraction. The purified monomers were transferred to Pyrex polymerization tubes containing 0.2 mole-% benzoyl peroxide initiator. The polymerization tubes were then attached to a vacuum line and the monomers were outgassed by repeatedly freezing and thawing them during evacuation. After outgassing, the tubes were sealed off in a vacuum. The polymerizations were carried out at 60°C. and taken to high conversions, approximately 95%. Residual monomers were removed by first dissolving the polymer in benzene and then adding the solution to methanol in a 1:4 ratio. The precipitated polymer was redissolved in benzene, freeze-dried, and then heated in a vacuum oven at 120°C. to remove the remaining volatile material.

Dilatometry

Volume temperature measurements were made with a volume dilatometer similar to that described by Flory, Mandelkern, and Hall.[9] The polymers were molded into blocks in a press at 150–160°C. Specimens were cut into cubes 1/4 in. on a side, weighed, and placed in the dilatometers. Mercury was used as the confining fluid in all the experiments. All measurements were made in a silicone oil bath with temperatures controlled to ±0.05°C. The specimens were heated at a rate of 0.5°C./min. and maintained at the desired temperature for 1 hr. before volume measurements were taken. The volume measurements were made at 10°C. intervals except in the region of the glass transition temperature, where measurements were made at 2°C. intervals.

After the volume expansion over the desired temperature range was examined, the weight of mercury contained in the dilatometer was determined. In order to convert the dilatometric readings to specific volumes an independent measurement of the densities of the polymer specimen was made at 25°C. The specific volume at this temperature v_{25} was obtained by the method of hydrostatic weighing described by Wood, Bekkedahl, and Roth.[10]

The copolymer compositions were determined by using a method devised by Meehan[11] and a method subsequently published by Tobolsky.[12]
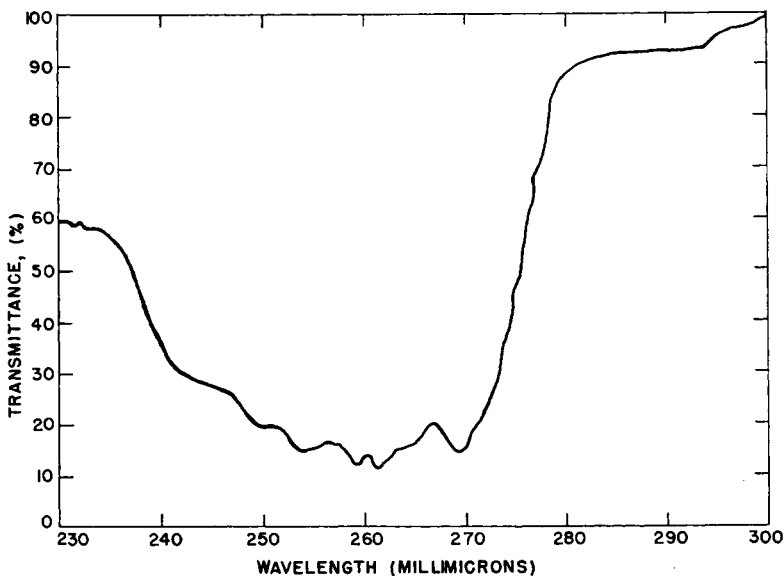
Fig. 1. Transmittance curve of polystyrene in chloroform for a concentration 3.2 × 10^{-4} g./cm.^{3} at 23°C. in a 1-cm. cell.
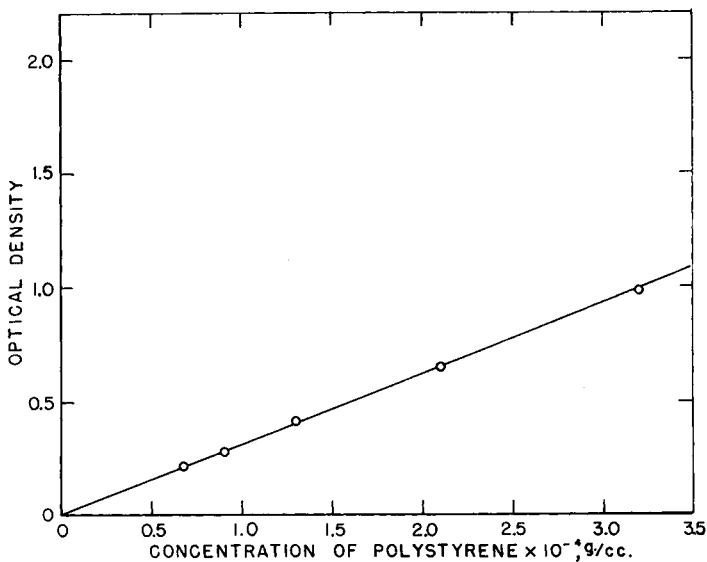

Fig. 2. Optical density at 262 mμ as a function of concentration of polystyrene in chloroform in a 1-cm. cell at 23.5°C.

Both of the methods are based on the determination of styrene content in methyl methacrylate–styrene copolymers by ultraviolet spectrophotometry. The benzene group in polystyrene and copolymers of polystyrene possesses a series of absorption bands in the ultraviolet region of 240–270

mμ as shown in Figure 1. The comonomer methyl methacrylate does not absorb in this region. A calibration curve of polystyrene content was constructed (see Fig. 2) by dissolving various concentrations of polystyrene in chloroform and determining the optical density at 262 mμ.

Irradiation Procedure

The 2,500-curie Co^{60} source at the National Bureau of Standards was used for all irradiations. This particular source (of the "swimming-pool" type) has been described by Bersch, Stromberg, and Achhammer.[13] The dose rate was approximately 0.3 Mrad/hr. Each specimen was irradiated in an evacuated Pyrex glass tube, 18 mm. in diameter and about 3 in. long.

RESULTS

If the volumes of two miscible liquids are additive upon mixing, then a plot of specific volume against weight fraction is linear, and the two partial specific volumes are constant. Gordon and Taylor[7] extended this principle to the monomeric units of a polymer and assumed that this linearity, reflecting volume additivity of the units, is common both to the rubbery and glassy states. Thus we have a simple law of essentially "ideal" copolymers corresponding to that of an ordinary ideal solution. The assumption of volume additivity is necessary in the derivation of the Gordon-Taylor equation relating T_g to copolymer composition. This will be discussed later.

To use the Gordon-Taylor equation, it was necessary to test first whether the copolymer system in this study obeyed the assumption of volume additivity. The specific volumes of the poly(styrene–methyl methacry-
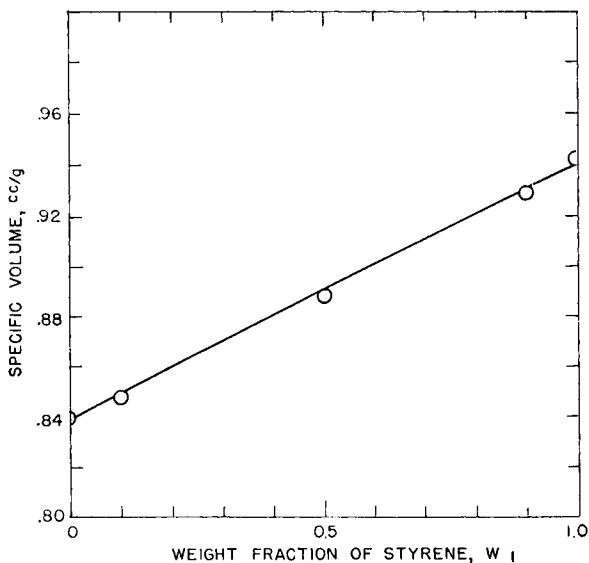

Fig. 3. Specific volumes of (methyl methacrylate–styrene) copolymers at 25°C.
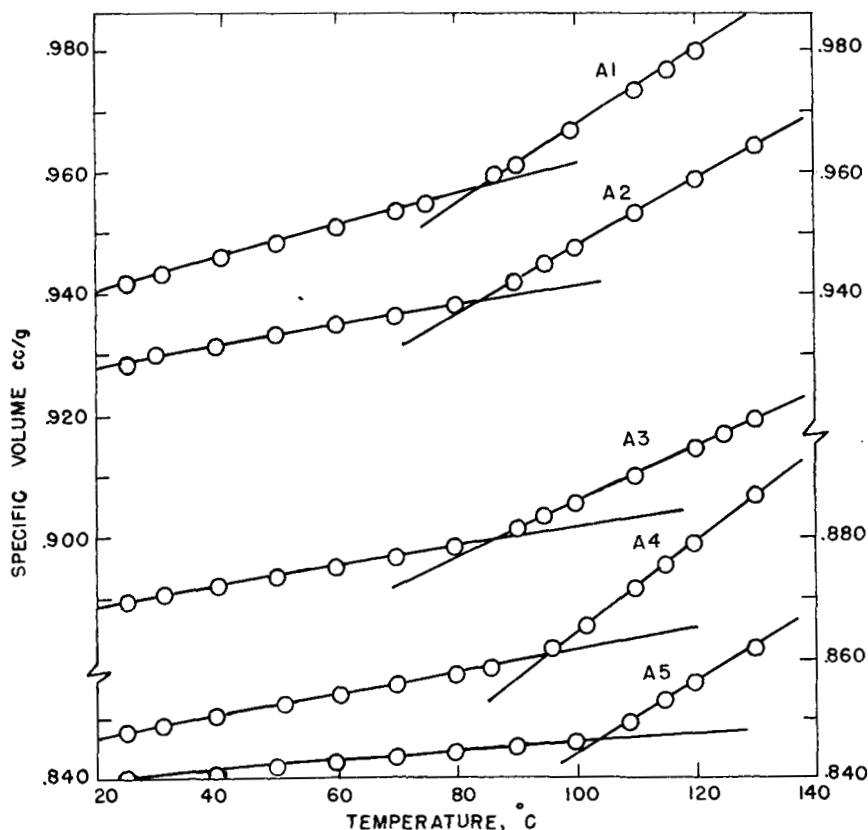
Fig. 4. Specific volume vs. temperature for styrene–methyl methacrylate copolymers.

late) copolymers, as determined by hydrostatic weighing, were plotted against copolymer composition at the reference temperature, 25°C. (see Fig. 3). The straight line represents the relationship between copolymer composition and specific volume for the system on the assumption that no volume contraction occurs as a result of copolymerization. The points on the curve represent the experimentally determined specific volumes. The agreement is within 2%.

The variations in specific volume with temperature for each copolymer composition were determined and the results are shown in Figure 4. The dilatometric measurements were taken over the temperature range from 25–130°C. on both heating and cooling cycles. The dilatometric results were reproducible to within 0.1% over the temperature range studied. The values reported in Table I were obtained from the results of the volume–temperature plots. While the volume–temperature coefficients were in good agreement with values reported in the literature,[1,2,14,15] the value of 82°C. reported here as the glass transition temperature for polystyrene is considerably lower than the value of 100°C. reported separately by Fox and

TABLE I
Dilatometric Data for Styrene–Methyl Methacrylate Copolymers

No.	Copolymer composition		Weight fraction of styrene in polymer w_1	Specific volume, ml./g.		T_g, °C.	Volume-temperature coefficients, ml./g./°C. $\times 10^4$	
				At 25°C. v_{25}	At glass transition temperature v_g		Liquid state $(dv/dt)_1$	Glassy state $(dv/dt)_2$
A-1	Polystyrene	125,000	1.0	0.9419	0.9561	82	5.9	2.7
A-2	Styrene–methyl methacrylate (0.9–0.1)	—	0.9	0.9291	0.9391	82.2	5.6	1.7
A-3	Styrene–methyl methacrylate (0.5–0.5)	—	0.5	0.8898	0.8997	84.6	4.6	1.6
A-4	Styrene–methyl methacrylate (0.1–0.9)	—	0.1	0.8481	0.8606	94.2	7.5	1.8
A-5	Poly(methyl methacrylate)	10^6	0.0	0.8404	0.8469	104	3.9	0.84

TABLE II
Molecular Weight–Glass Transition Temperature Data for Fractions of Polystyrene[a]

| Sample[b] | Polymerization data | | | | $[\eta]$, dl./g. | $\bar{M}_w \times 10^{-4}$ | $\bar{M}_n \times 10^{-4}$ | $\bar{M}_w/\bar{M}_n$ | T_g, °C. |
	Method	Time	Temp., °C.	Conversion, %					
H$_c$1	Bulk	4 days	60	>95	0.90	23.6	15.8	~1.5	88
H$_c$3	Bulk	4 days	60	95	0.46	9.3	7.1	1.3	86
M$_c$1	Bulk	17 hr.	60	34	0.94	25.1	—	—	91
M$_c$3	Bulk	17 hr.	60	34	0.53	11.4	10.0	1.2	90
L$_c$1	Bulk	6 hr.	60	12	0.58	12.7	10.5	1.2	95
L$_c$3	Bulk	6 hr.	60	12	0.26	4.3	—	—	95
U$_f$	Bulk	4 days	60	>95	0.57	12.7	3.7	3.4	82

[a] Made with 0.2 mole-% of benzoyl peroxide catalyst.
[b] H$_c$ = high conversion polystyrene; L$_c$ = low conversion polystyrene, U$_f$ = unfractionated polystyrene; M$_c$ = medium conversion polystyrene.
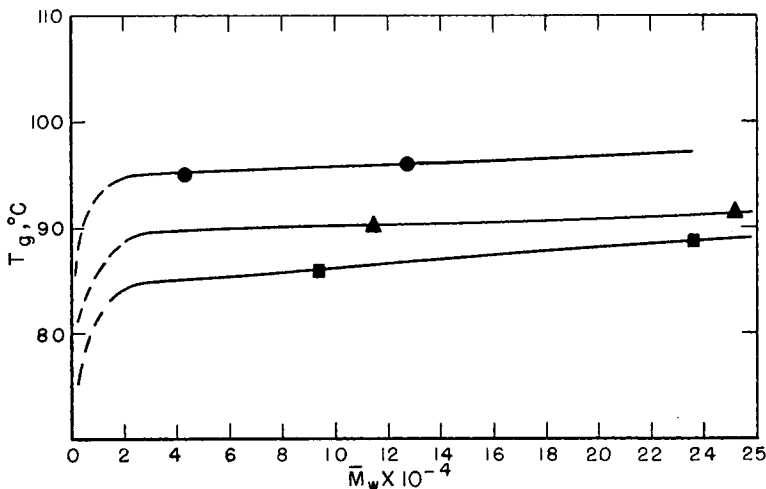
Fig. 5. Glass transition temperatures of polystyrene fractions of different degrees of conversion vs. molecular weight: (●) low conversion, (▲) medium conversion; (■) high conversion.

Flory[1] and Ueberreiter and Kanig.[2,14]   However, this disparity may arise from differences in molecular structure[16] because the polystyrene used in this study was polymerized to a high extent of conversion as opposed to the low conversions previously reported.[1,2,14,17]

Polystyrenes at low and medium conversions were also made in this laboratory using the identical procedure previously described for the high conversion polymer.   The polymers were fractionated and the T_g's of the high molecular weight fractions were measured; the results are shown in Figure 5.   These results are lower than the accepted value for polystyrene and are more in agreement with values reported for broad distribution polymers.   The ratios of weight-average to number-average molecular weights for the polystyrene fractions are given in Table II.   A value of 94°C. for T_g was obtained for the low conversion polymer, which is in good agreement with that reported by Fox and Flory[1] and Beevers[16] for polystyrene of a comparable degree of conversion.

DISCUSSION OF RESULTS

One criterion for glass formation was suggested by Williams, Landell, and Ferry,[17] who stated that glass formation occurs in glass-forming liquids when the ratio of the free volume to the specific volume reaches a critical constant value, that value being independent of the nature of the liquid. Utilizing this assumption, Fox[6] and Mandelkern[18] devised an equation relating the glass transition temperature, T_g, to copolymer composition:

$$\frac{1}{T_g} = \left[\frac{1}{(w_1 + Rw_2)}\right]\left(\frac{w_1}{T_{g1}} + \frac{Rw_2}{T_{g2}}\right) \tag{1}$$

where

$$R = [(\alpha_{L_2} - \alpha_2{}^* - k\,\alpha_{L_2})/(\alpha_{L_1} - \alpha_1{}^* - k\,\alpha_{L_1})]\,\frac{T_{g2}}{T_{g1}} \qquad (2)$$

In eqs. (1) and (2) T_g = glass transition temperature of the copolymer, T_{g1} and T_{g2} = glass transition temperatures of the homopolymers, w_1 and w_2 = weight fractions of the homopolymers, α_{L_1} and α_{L_2} = volume–temperature coefficients of the homopolymers in the liquid state, $\alpha_1{}^*$ and $\alpha_2{}^*$ = volume–temperature coefficients of the occupied volume of the homopolymers, k = ratio of free volume to the specific volume and, according to Williams et al.,[17] is equal to 0.025.

Mandelkern and co-workers[18] have suggested that because it is difficult to express α^* in terms of any of the measured volume-temperature coefficients, R might be best considered as an arbitrary parameter in eq. (1) above. Some experimental verification of this equation was obtained by Fox and Loshaek,[3] who determined T_g for a series of copolymers that covered a wide range of composition.

More recently, Wood[8] proposed a general equation relating the glass transition temperature of a multicomponent polymer to the properly weighted average of the T_g values of the homopolymers making up the copolymer. Thus, for a copolymer one can simply write:

$$A_1 w_1 (T_g - T_{g1}) + A_2 w_2 (T_g - T_{g2}) = 0 \qquad (3)$$

where A_1 and A_2 are defined as constants characteristic of the constituents in some unspecified manner and w_1 and w_2 are the weight fractions of the constituents. Then, by defining a constant K where

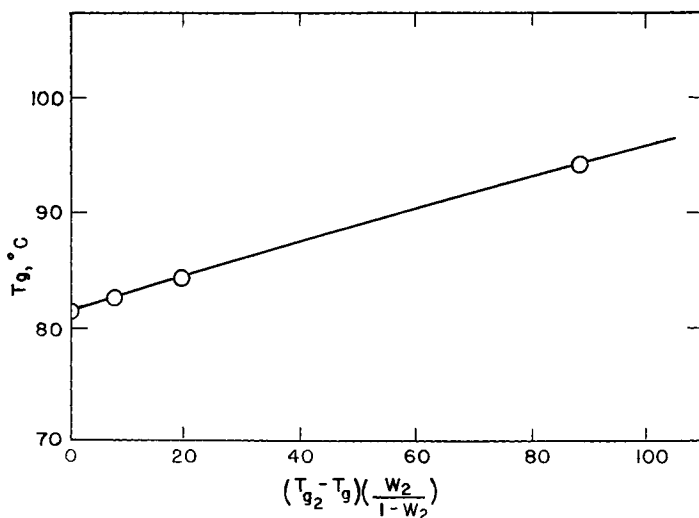$$K = A_2/A_1 \qquad (4)$$

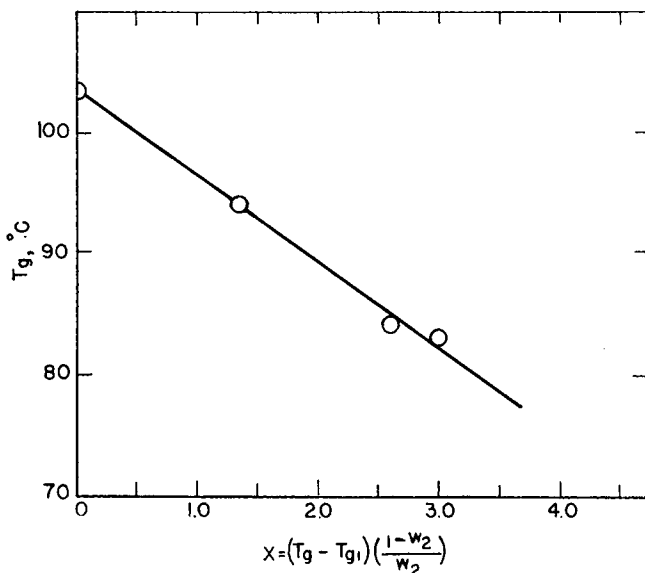Fig. 6. Plot of Wood's Equation, eq. (6), when only T_{g2} is known.

Fig. 7. Plot of Wood's equation, eq. (7), when only T_{g2} is known.

and assuming $T_{g2} > T_{g1}$, the basic equation can be rearranged:

$$T_g = [T_{g1} + (KT_{g2} - T_1)w_2]/[1 - (1 - K)w_2] \tag{5}$$

For plotting observed T_g as a function of copolymer composition in a two-component system, the most convenient form of eq. (5) is shown in eqs. (6) and (7):

$$T_g = K[(T_{g2} - T_g)(w_2)(1 - w_2)] + T_{g1} \tag{6}$$

$$T_g = -(1/K)[(T_g - T_{g1})(1 - w_2)/w_2] + T_{g2} \tag{7}$$

Equation (6) is suitable for use when T_{g2} is known and eq. (7) is suitable for use when T_{g1} is known. A plot of the quantity in brackets against observed T_g should be linear, barring complications that might arise from crystallinity or degradation.

Wood points out that since eqs. (6) and (7) contain three constants, experimental values for at least three compositions are necessary for a valid determination of the constants. The accuracy is also enhanced when the composition covers as wide a range as possible, as in the case for the copolymer system chosen for this study.

In Figure 6 the data obtained for the methyl methacrylate–styrene copolymer system are plotted according to eq. (6). The experimental points are represented by circles. An extrapolation gives a value of 82°C. for the T_g of polystyrene. This is in excellent agreement with the experimentally determined value. A similar plot was made utilizing eq. (7) and the results give an extrapolated value of 104°C. as the T_g for poly-(methyl methacrylate), which was also verified experimentally (see Fig. 7).
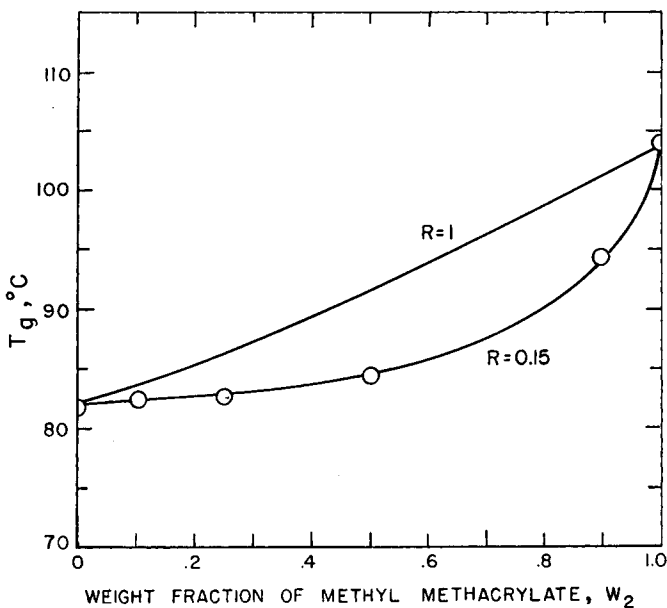
Fig. 8. Theoretical curves, eq. (1), for various values of R, of glass transition temperature vs. composition for styrene–methyl methacrylate copolymers: (O) experimental points.

It should be noted that the abscissa in Figure 7 is expanded as compared with that in Figure 6.

In Figure 8, the upper curve represents a theoretical plot based on eq. (1), in which R is arbitrarily assigned a value of unity. The lower curve represents a theoretical plot based on Wood's equation corresponding to a value of 0.15 for R. The experimental results obtained in this study are shown to fit this latter curve. When data from a large variety of copolymer systems are available, it should be possible to obtain numerical values for the constants in Wood's equation relating to each homopolymer. This would provide a reliable method for obtaining values of T_g for homopolymers whose T_g cannot readily be determined.

The glass transition temperature of copolymers of styrene and divinylbenzene was shown to increase linearly with increasing concentration of divinylbenzene.[19] Since the comonomers are so similar in structure, it was assumed that the changes in composition of the copolymers could be considered negligible. However, if the structures of the monomers are dissimilar, then one must also consider the effect of T_g arising from changes in composition, along with the crosslinking effects. Loshaek[4] demonstrated this in his treatment of copolymers of methyl methacrylate and glycol dimethacrylates. He assumes that the changes in T_g caused by changes in composition and by introduction of crosslinks are independent and additive, or simply:

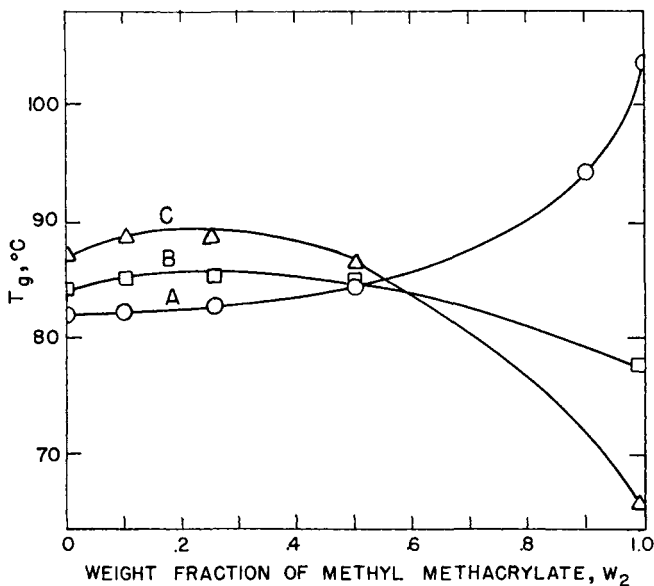$$\Delta T_g = \Delta_c T_g + \Delta_p T_g$$

Fig. 9. Effect of irradiation on T_g of styrene–methyl methacrylate copolymers: (O) unirradiated; (□) 50 Mrad, (△) 100 Mrad.

where ΔT_g is the total change in T_g from that of pure polymer, $\Delta_c T_g$ is the change in T_g caused by changes in composition, and $\Delta_p T_g$ is the change in T_g caused by introduction of crosslinks.

In this study attempts were made to investigate the applicability of this concept by using the styrene–methyl methacrylate system, in which the copolymer constituents are dissimilar in structure. Crosslinking was introduced by ionizing radiation rather than a chemical crosslinking agent which would affect the composition of the copolymer system. The use of ionizing radiation as the crosslinking agent introduces a complication of its own, namely degradation. This is reflected in the curves shown in Figure 9. Curve A represents changes in T_g as a function of composition only. Curves B and C represent changes in T_g as a function of both crosslinking and composition for total dosages of 50 and 100 Mrads, respectively; the higher dosages produce more crosslinks. Since changes in copolymer composition from 0 to 20% methyl methacrylate have essentially no effect on T_g, one can assume that in this region the observed changes in T'_g of the irradiated copolymers are due solely to crosslinking.

Poly(methyl methacrylate) degrades at a rate more rapid than that of polystyrene when exposed to high energy radiation. Curve B thus begins to drop with increasing methyl methacrylate concentration in the copolymer. Curve C, representing the higher radiation dosage, drops more sharply as expected because of more extensive degradation.

In summary, it appears to be possible to predict the glass transition temperatures for various compositions of a copolymer by using eqs. (6)

and (7).   It was shown that changes in T_g of styrene–methyl methacrylate copolymers can be affected by changes in the degree of crosslinking and composition.   It was also shown that the glass transition temperature of styrene–methyl methacrylate copolymers of low methyl methacrylate content is increased by radiation, reflecting an increase due to cross-linking.   For copolymers of high methyl methacrylate content, T_g is decreased by radiation, reflecting degradation of the methyl methacrylate.

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Résumé

On a déterminé au moyen d'un dilatomètre volumétrique la température de transition vitreuse du polystyrène, du polyméthacrylate de méthyl et des copolymères préparés à partir de leurs monomères respectifs. Les températures de transition du polystyrène et du polyméthacrylate de méthyl sont de l'ordre de 82°C et 104°C respectivement. Les températures de transition obtenues pour les copolymères sont intermédiaires entre les valeurs déterminées pour chacun des homopolymères et sont une fonction monotonique de la composition du polymère. Les valeurs expérimentales sont en accord avec les valeurs calculées au moyen de formules d'interpolation sur la base de données de la littérature. On a décrit les effets des changements de composition et du pontage induit par les radiations sur la transition vitreuse du système de copolymères.

Zusammenfassung

Die Glasumwandlungstemperatur von Polystyrol, Polymethylmethacrylat un von Copolymeren aus diesen Monomeren wurden mittels eines Volumsdilatometers bestimmt. Die Glasumwandlungstemperatur von Polystyrol und Polymethylmethacrylat lag bei 82°C bzw. 104°C. Die Glasumwandlungstemperatur der Copolymeren lag zwischen den für die Homopolymeren bestimmten Werten und bildete eine monotone Funktion der Zusammensetzung des Polymeren. Die experimentell erhaltenen Werte stimmen mit Literaturangaben auf Grundlage von Interpolationsformeln überein. Der Einfluss von Zusammensetzungsänderungen und strahlungs-induzierter Vernetzung auf die Glasumwandlung des Copolymersystems wird beschrieben.