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INFLUENCE OF HIGH ENERGY RADIATION ON THE GLASS TRANSITION OF POLY(METHYL METHACRYLATE)*

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ABSTRACT

Chemical changes produced by irradiation of crystalline polymers can be monitored quantitatively by DTA measurements of the melting point. The purpose of the present work is to investigate whether or not similar information can be obtained for a non-crystalline polymer by measurements of the glass transition temperature (T_g).

Atactic poly(methyl methacrylate) (PMMA) was exposed to ^{137}Cs γ-rays. After degassing and heat treatment, samples were scanned using a DuPont 990 Thermal Analyzer. By either the conventional or a tangent data analysis technique, T_g measurements not only agreed with previously reported data up to a dose of 75 Mrad but also were extended up to 500 Mrad. Moreover, the empirical plot of T_g vs. $\bar{M}_n^{-1}$ agreed with data obtained by free-radical polymerization and was judged to be a suitable calibration curve for estimating the radiation damage from DTA measurements. For samples of PMMA prepared both by irradiation and by free-radical polymerization, the dependence of T_g on molecular weight best fitted the theoretical expression of Gibbs. Using a reduced variables plot, the present results for irradiated PMMA compared well with synthesized vinyl polymers, substantiating the dominance of simple chain fracture.

INTRODUCTION

An understanding of the effect of radiation on polymers depends upon the manner in which irradiation affects molecular motion[1]. In this regard, a number of studies have been made on the influence of high energy radiations on melting transitions by the convenient technique of differential thermal analysis (DTA). Here, the depression of the melting temperature could be correlated quantitatively with the total chemical changes produced by irradiation[2]. This correlation is relatively simple because all chemical changes, such as fracture and crosslinking of the polymer

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molecules, uniformly cause a depression of the melting point. Such a reduction can be counted quantitatively by reference to a form of the Clapeyron equation.

In contrast, the influence of radiation on the glass transition temperature (T_g) is more complex, since T_g is not depressed by all chemical changes. For example, crosslinking elevates the temperature of this transition[3]. In order to minimize this complexity, poly(methyl methacrylate) (PMMA) was chosen for study because crosslinking has been demonstrated to be negligible, relative to fracture of the polymer molecules, for at least low doses of radiation[4, 5].

Previously, the depression of the T_g in PMMA after irradiation has been investigated using DTA by Thompson[6]. The study included stereoregular polymers, in addition to conventional atactic samples, up to a dose of 75 Mrad. More recently, Pratt followed the radiation-induced depression of T_g in a commercial atactic PMMA by means of a mechanical torsion pendulum[7]. Apart from the anomalous behaviour after low doses, attributed to the presence of residual monomer, the depression of T_g per unit dose was in agreement with the value reported by Thompson. These efforts were preceded by the detailed study of Beevers and White in which the temperature dependence of the refractive index was used to determine the T_g of PMMA[8]. Utilizing a wide range of molecular weights prepared by free-radical polymerization, these results conformed to the Fox–Flory relation (for $\overline{M}_n \gtrsim 10^4$) and to the Gibb's expression (in which $V_0 = 0.025$ and $\varepsilon = 0.98$ kcal/mole segments), overall.

The objective of the present work is to extend the scope of investigation on transitional changes to include the radiation-induced changes in T_g of PMMA down to the oligomer region and to compare these changes with those obtained by free-radical polymerization.

EXPERIMENTAL

A sheet of PMMA (Plexiglas G, Rohm and Haas Company, Philadelphia, PA, U.S.A.) of thickness 0.3 cm was cut into samples 0.75 cm × 1.5 cm. The samples were exposed in air to γ-rays from a ^{137}Cs source (dose rate = 0.8 Mrad/h; ambient temperature = 35°C). These samples were not immediately suitable for DTA runs because gas, which formed during irradiation, caused foaming on heating. To prevent either the thermocouple or the material from being expelled from the sample tube, the brittle irradiated samples were crushed into small pieces and packed into a standard DTA macro tube (27 mm long × 4 mm o.d.). Gas was removed, along with any other low molecular weight volatiles such as monomer, by heating at 150°C in vacuum ($< 10^{-3}$ torr) for 2 1/2 h.

After cooling overnight to room temperature, the 3 mm high cylinder of polymer was penetrated with a hot DTA thermocouple and immediately quenched in liquid nitrogen. Using glass beads as a reference material, DTA scans were made in a nitrogen atmosphere from −60 to +160°C at a heating rate of 20°C/min (DuPont 990 DTA). Although this heating rate resulted in somewhat higher T_g values than the true T_g, the shift was assumed to be independent of molecular weight (cf. T_g data of polystyrene[9]). After run 1, the DTA tube was quenched in liquid nitrogen and a second run made. Subsequent scans were in close agreement with run 2 and are not reported.

Preliminary evidence of any crosslinking resulting from prolonged irradiation was sought by ^{13}C Fourier transform NMR spectroscopy (Varian XL-100) with broad band proton decoupling. Using D-chloroform, isoviscosity solutions of PMMA were prepared in 10 mm o.d. tubes and scanned at 25.2 MHz.

Number average molecular weights of low molecular weight samples, resulting from high doses of radiation, were determined by vapour phase osmometry using chloroform at 35°C (Perkin Elmer Model 115 Molecular Weight Apparatus).

In order to determine any changes in tacticity due to irradiation, samples were dissolved in chloroform and deposited as films on a sodium chloride window. Ratios of absorbances at 9.45 μm and 7.25 μm were compared and the "percent syndiotactic" polymer calculated from the calibration of Baumann et al.[10] (Perkin Elmer Model 457 Grating Infra-red Spectrophotometer) (cf. ref. 11).

RESULTS AND DISCUSSION

The difference in appearance of DTA scans for slowly cooled (run 1) and

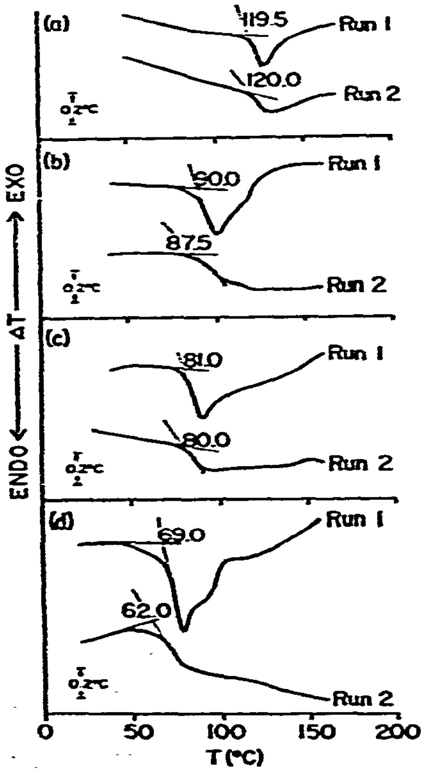


Fig. 1. The glass transition of radiation degraded PMMA (conventional method). (a) 0 Mrad; (b) 77 Mrad; (c) 158 Mrad; (d) 252 Mrad.

TABLE 1

SUMMARY OF T_g DATA FOR IRRADIATED PMMA AS DETERMINED BY CONVENTIONAL METHOD (cf. Fig. 1)

Dose (Mrad)	*Calculated* $\bar{M}_n$	T_g *(°C)*	
		Run 1	*Run 2*
0	5.9×10^5	122.0	121.0
0	5.9×10^5	119.0	122.5
17	3.1×10^4	108.5	110.0
25	2.2×10^4	108.0	108.0
32	1.7×10^4	106.0	103.0
38	1.4×10^4	92.0	92.0
40	1.4×10^4	105.0	97.5
67	8.3×10^3	100.0	99.0
67	8.3×10^3	97.0	98.0
77	7.2×10^3	90.0	87.5
77	7.2×10^3	85.0	85.0
112	5.0×10^3	83.5	79.0
158	3.6×10^3	81.0	80.0
252	2.2×10^3	69.0	66.0
252	2.2×10^3	65.0	65.0
252	2.2×10^3	69.0	62.0
256	2.2×10^3	74.0	69.5
300	1.9×10^3	59.0	55.0
300	1.9×10^3	63.0	59.0
300	1.9×10^3	63.0	62.0
350	1.6×10^3	59.0	49.5
350	1.6×10^3	60.0	51.5
350	1.6×10^3	60.0	56.0
400	1.4×10^3	48.0	48.0
400	1.4×10^3	59.0	56.5
400	1.4×10^3	56.0	55.0
450	1.3×10^3	48.0	55.0
450	1.3×10^3	53.0	52.5
450	1.3×10^3	49.0	54.0
500	1.2×10^3	63.0	56.0
500	1.2×10^3	61.0	54.5
500	1.2×10^3	54.5	46.0

rapidly quenched (run 2) samples is typical for polymers and has been interpreted in various ways[12, 13]. However, for present purposes only, a decision concerning the definition of a value of T_g must be made. Following a convention set by Keavney and Eberlin in an early application of DTA to determine T_g of polymers[14], a preliminary choice could be to take the intersection of lines drawn through the baseline and the descending trace as shown in Fig. 1. The additional decision of choosing between runs 1 and 2 (or subsequent runs) is not critical at high values of molecular weight, but as the molecular weight decreases, the difference is sometimes considerable (Table 1). Since a preference for either run 1 or run 2 could not be justified, the decision was made to take the mean of scans 1 and 2. These values are shown plotted against the reciprocal of molecular weight in Fig. 2(a) (solid circles).

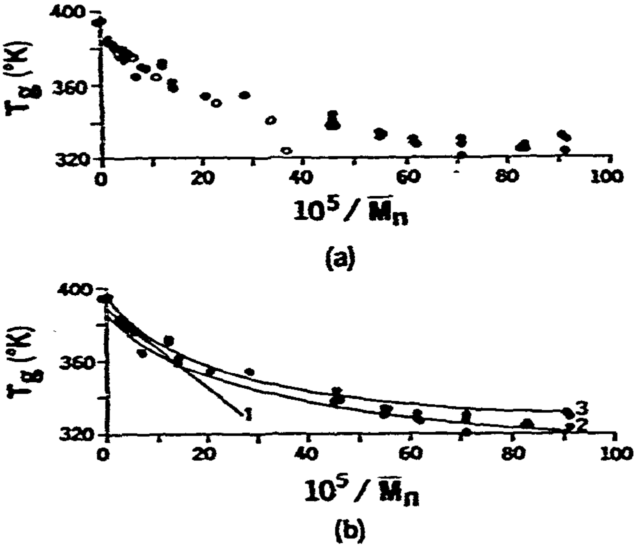


Fig. 2. Influence of $\bar{M}_n^{-1}$ on the T_g of PMMA (conventional method). (a) Comparison of present data (●) prepared by radiation degradation with previous data [Beevers and White[8] (○)] prepared by free-radical polymerization. (b) Comparison of present data (cf. Table 1) with theory. Curve 1, eqn. (1) with $T_{g\infty} = 387$ K and $K = 2.1 \times 10^5$; curve 2, eqn. (2) with $V_0 = 0.025$ and $\varepsilon = 0.97$ kcal/mole segments; curve 3, eqn. (2) with $V_0 = 0.025$ and $\varepsilon = 1.0$ kcal/mole segments.

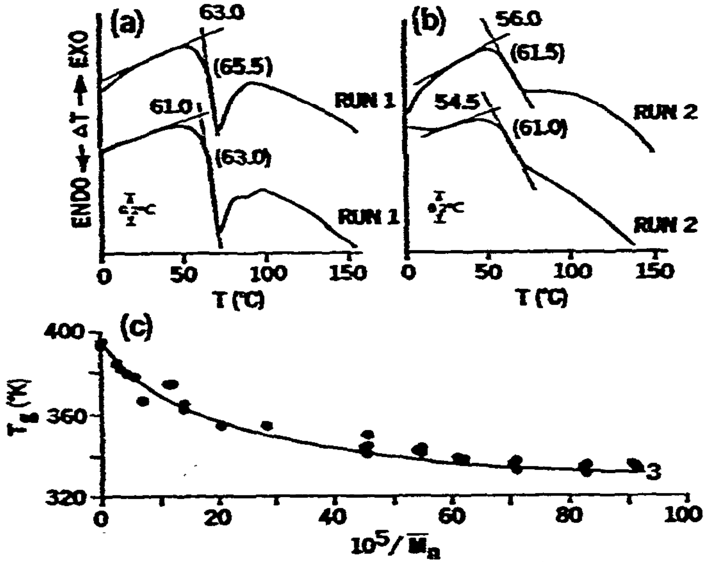


Fig. 3. Analysis of the T_g for irradiated PMMA by the tangent method. (a) and (b) Comparison of T_g results obtained by conventional versus tangent method (in parentheses) for two specimens after 500 Mrad. (c) Comparison of tangent method data (cf. Table 2) with curve 3 [cf. Fig. 2(b)].

To some extent, the scatter of T_g values in Fig. 2(a) was attributable to the difficulty of choosing a baseline because of the rapidly changing curvature prior to the endotherm of the DTA trace. Similar difficulties have been encountered previously in DTA work on other polymers. For example, an alternative approach was presented by

TABLE 2

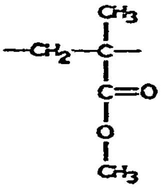
SUMMARY OF T_g DATA FOR IRRADIATED PMMA AS DETERMINED BY TANGENT METHOD (cf. Fig. 3)

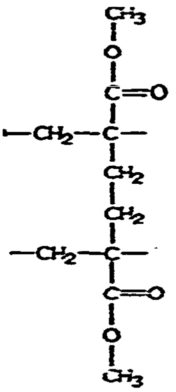
Dose	*Calculated* $\bar{M}_n$	T_g *(°C)*	
(Mrad)		*Run 1*	*Run 2*
0	5.9×10^5	122.0	122.5
0	5.9×10^5	119.0	122.5
17	3.1×10^4	110.0	112.0
25	2.2×10^4	109.0	109.0
32	1.7×10^4	106.5	106.5
38	1.4×10^4	93.0	93.5
40	1.4×10^4	108.0	102.0
67	8.3×10^3	102.5	102.5
67	8.3×10^3	101.0	101.5
77	7.2×10^3	93.0	92.5
77	7.2×10^3	87.0	90.0
112	5.0×10^3	87.0	80.0
158	3.6×10^3	83.5	82.5
252	2.2×10^3	71.5	71.0
252	2.2×10^3	69.0	70.0
252	2.2×10^3	72.0	70.0
256	2.2×10^3	79.5	76.0
300	1.9×10^3	66.5	66.0
300	1.9×10^3	68.5	69.0
300	1.9×10^3	68.5	71.0
350	1.6×10^3	64.0	67.0
350	1.6×10^3	65.5	65.0
350	1.6×10^3	64.0	66.0
400	1.4×10^3	59.0	61.5
400	1.4×10^3	64.0	64.0
400	1.4×10^3	61.0	66.0
450	1.3×10^3	59.0	63.0
450	1.3×10^3	59.5	61.0
450	1.3×10^3	52.0	63.0
500	1.2×10^3	65.5	61.5
500	1.2×10^3	63.0	61.0
500	1.2×10^3	62.0	60.0

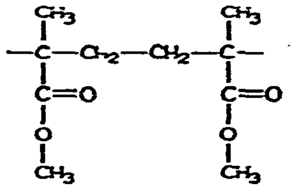
Rudin and Burgin[9] in related studies on the influence of molecular weight of polystyrenes on T_g. There, the T_g was designated by the temperature at which the longest straight line segments of the peak sides intersected. In the present work, the modification chosen differs only slightly from conventional practice. Here, T_g is taken as the lower temperature at which the trace separates from a line drawn through the descending slope of the endotherm. Results obtained by this "tangent" method are shown in parentheses in Figs. 3(a) and 3(b), along with values obtained by the conventional method. These comparisons are illustrated for traces which allow reasonable definition by either method. However, since in many cases the conventional method gave more equivocal results, the tangent method was preferred (Table 2 and Fig. 3).

The values of molecular weight in Tables 1 and 2 were calculated on the following assumptions. First, that crosslinking is negligible; second, that the polymer molecules are fractured randomly along their length by irradiation (in a reaction involving simultaneous formation of gas); and third, that the yield of fractures is directly proportional to dose — or, more specifically, that 1.7 fractures occur per 100 eV of absorbed energy (1 Mrad = 6×10^{19} eV/g). Previously[4], these assumptions were rigorously shown to be good approximations up to a dose of 10 Mrad. More recently[5], further evidence has been obtained that these assumptions are valid in estimating the number average molecular weights up to a dose of at least 40 Mrad. In the present work, the dose range has been extended ten-fold, re-opening the question of validity of these three assumptions.

Preliminary evidence for the occurrence of crosslinking was sought by an examination of the NMR spectra. Results for unirradiated PMMA were similar to those reported previously by Johnson et al.[15]. Against a background of line broadening, the spectra of irradiated samples provided no evidence of additional structures which increased in intensity with dose and which were consistent with the formation of groups of the general type $-CH_2-CH_2-$. Conceivably, such groups could be formed from the repeat unit of PMMA (I) by elimination of hydrogen gas and yield a variety of crosslinked structures such as II. However, this would not constitute unequivocal evidence of crosslinking because such groups might also be formed by the recombination of free radicals after main chain fracture (III). Since a laborious program of work with model compounds would be required to distinguish between structures as closely related as II and III, this line of investigation was suspended in favour of another discriminating technique, vapour phase osmometry.


(I)


(II)


(III)

Vapour phase osmometry (VPO) provides direct measurements of number average molecular weight. In Table 3, results show that these measurements are comparable with the values calculated on the assumptions stated earlier. Thus even after such enormous doses, crosslinking is very small in comparison with chain fracture. If from the data in Table 3 the ratio of crosslinks to fractures is calculated, a ratio of only 0.1 to 0.2 is obtained even after doses as high as 450 to 500 Mrad. For doses less than 10 Mrad, Shultz previously calculated a ratio of less than 0.1 from a comparison of solution viscosity and light scattering data[4].

TABLE 3

CHANGES, OTHER THAN RANDOM FRACTURE, DUE TO IRRADIATION OF PMMA

Dose (Mrad)	*Tacticity, % syndiotactic*	*–CH_2–CH_2– groups*	*$\bar{M}_n$ Calculated*	*VPO*
0	82	None		
80		None evident		
137	77			
252	80			
327		None evident		
450			1,270	1,630
500			1,160	1,310

In addition to the explicit assumptions concerning changes in molecular weight, there are also implicit assumptions that no other changes occur which would affect T_g. The most important of these is tacticity, since the glass transition of isotactic PMMA is known to occur at a much lower temperature (ca. 45°C)[11] than the syndiotactic polymer (ca. 160°C)[6]. While there is NMR evidence that the isotactic polymer is racemized by irradiation[16], the present infrared data on the atactic polymer (which is predominantly syndiotactic) indicates that tacticity is little influenced by irradiation (Table 3).

In summary, the experimental results show that the dependence of T_g on the molecular weight of PMMA can be studied using irradiated samples up to very high doses. At the highest doses studied, crosslinking may result in slightly higher values for T_g than would normally be observed for a completely linear polymer.

COMPARISON WITH THEORIES

A number of theories have been proposed to account for the dependence of T_g on molecular weight and have been discussed in relation to PMMA by Beevers and White[8]. According to the "free volume" theory of Fox and Flory, the relationship is given by eqn. (1). There, $T_{g\infty}$ is the glass transition temperature of a polymer of infinite number average molecular weight, T_g is the value for a polymer of molecular weight M, and K is a constant[17, 18].

$$T_g = T_{g\infty} - \frac{K}{M} \qquad (1)$$

In Fig. 2(a), the experimental data of Beevers and White (open circles) is compared with the present data (solid circles). For their data, a straight line was drawn with a slope of 2.1 ± 0.2 × 10^5 and an intercept of 387 ± 1, as shown in Fig. 2(b). Both Thompson[6] and Pratt[7], working with specimens having a higher range of molecular weights, assigned comparable values. A similar initial slope could have been assigned on the basis of the present work, but in view of the much greater range of molecular weights covered, a more general expression was sought.

Beevers and White also considered that their data better fitted other theoretical equations, namely those derived from statistical mechanics. These equations are unwieldy but as they were misstated they are detailed as follows.

$$\frac{2\beta \exp \beta}{1 + 2 \exp \beta} - \ln [1 + 2 \exp \beta] = -\frac{P}{P-2}\left[\frac{V_0 \ln V_0}{1 - V_0} - \frac{\ln 2P}{P-2} + \frac{P-1}{P-2}\right] \tag{2}$$

$$\frac{2\beta \exp \beta}{1 + 2 \exp \beta} - \ln [1 + 2 \exp \beta] = \tag{3}$$

$$= -\frac{x}{x-3}\left[\frac{1}{1-V_0}\left\{\ln V_0 + (1 + V_0) \ln \left[\frac{(x+1)}{2x}\frac{1-V_0}{V_0} + 1\right]\right\} + \frac{\ln 3(x+1)}{x}\right]$$

Equation (2) was derived by Gibbs[19] on the assumption that the glass transition occurs when the temperature becomes low enough so that the rotation of segments of the backbone chain ceases, i.e. when the configurational entropy becomes zero. This energy barrier to segmental rotation, ε, is contained in the terms $\beta = -\varepsilon/kT_g$ in which k is Boltzmann's constant. As for the other terms, V_0 is the fractional free volume at T_g, while P is the degree of polymerization ($\bar{M}_n/100$ for PMMA). Equation (3) is a refinement of eqn. (2) derived by Gibbs and Di Marzio[20] in which $x = 2P$.

Following Gibb's suggestion, Beevers and White assumed $V_0 = 0.025$ and obtained $\varepsilon = 1.66$ kcal/mole segments using the Gibbs–Di Marzio equation ($T_{g\infty} =$ 385 K). However, a better fit to their data was obtained from the original Gibbs equation using $V_0 = 0.025$ and $\varepsilon = 0.98$ kcal/mole segments ($T_{g\infty} = 390$ K). Using eqn. (2), the present, more extensive data yields $\varepsilon = 0.97$ kcal/mole segments ($T_{g\infty} =$ 385 K) when T_g is defined by the "conventional" DTA method [curve 2, Fig. 2(b)] and $\varepsilon = 1.0$ kcal/mole segments ($T_{g\infty} = 395$ K) when T_g is defined by the "tangent" method [Fig. 3(c)]. In view of more recent perspectives on the applicability of eqns. (2) and (3) to the glass transition and to questions about the choice of an appropriate value for the free volume fraction, further refinement is unwarranted[3]. Instead, emphasis is placed on the good agreement with the previous data of Beevers and White in which samples were prepared from polymers synthesized under a variety of conditions. That agreement is consistent with the opinion that factors other than number average molecular weight, e.g. tacticity and molecular weight distribution, can be neglected.

PERSPECTIVE

The present work shows that radiation-induced changes in PMMA can be monitored over an extremely wide range of doses by measurements of T_g. As anticipated from previous but more limited work, the behavior of PMMA is especially simple because radiation-induced crosslinking is negligible in comparison with chain

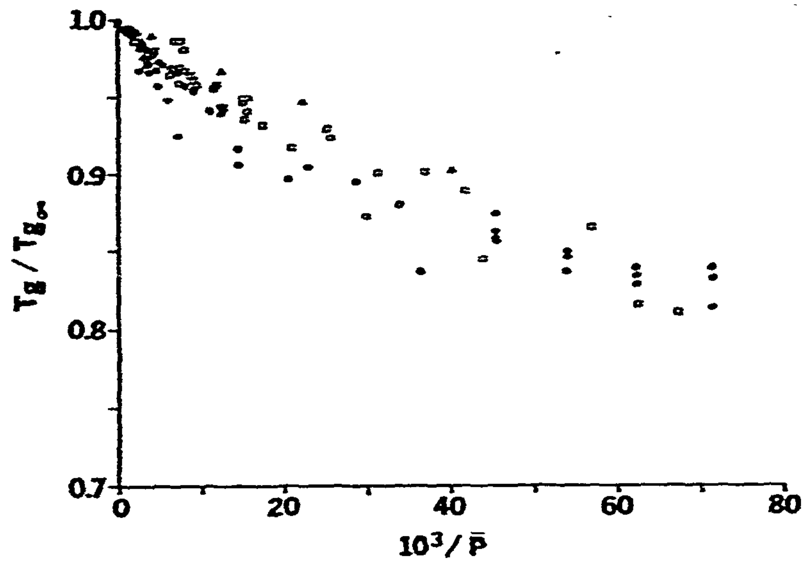


Fig. 4. Influence of the mean reciprocal degree of polymerization ($\bar{P}^{-1}$) on the reduced parameters ($T_g/T_{g\infty}$) for glassy polymers when $\bar{M}_n \gtrsim 1$–2×10^3. ●, Present data on PMMA ($T_{g\infty} = 395$ K) (conventional method); ○, Beevers and White[8] on PMMA ($T_{g\infty} = 387$ K); △, Ueberreiter and Kanig[21] on PS ($T_{g\infty} = 373$ K); □, Pezzin et al.[22] on PVC ($T_{g\infty} = 352$ K).

fracture. This simplicity may be shown by comparing the current data with earlier results for linear polymers. Using a plot of the reduced variables, $T_g/T_{g\infty}$, versus the mean reciprocal degree of polymerization, Fig. 4 shows that the synthesized PMMA[8], polystyrene[21], and polyvinyl chloride[22] share a common relationship with the irradiated PMMA down to $\bar{M}_n \sim 2 \times 10^3$. Below this molecular weight, departures occur on the reduced variable plot for the three vinyl polymers, presumably a result of the ever increasing role which their different side and end groups play in segmental motion. It would be interesting to find how other irradiated polymers differ with respect to Fig. 4. In this regard, both polystyrene[23] and polyvinyl chloride[24, 25] are known to have a more complex radiation chemistry than PMMA, including a high ratio of crosslinks to fracture.

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