Glass transition elevation of polystyrene by crosslinks

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Analysis of data by Ueberreiter and Kanig on the influence of crosslinking on the elevation of the glass transition temperature (ΔT) of polystyrene gives a plot which departs from a straight line in a way which is suggestive of an entanglement effect. Therefore this work was reinvestigated by differential scanning calorimetric studies of networks prepared by copolymerization of styrene and *p*-divinyl benzene (DVB). ΔT was found to be simply proportional to the feed of DVB. A case is made that the earlier results differ because of an artifact caused by residual monomer and it is concluded that in crosslinked polystyrene, there is no evidence that entanglements contribute to an elevation of T_g. Similar conclusions are drawn from previously reported data on natural rubber and polymethyl methacrylate.

INTRODUCTION

Ueberreiter and Kanig were first to report a case in which the glass transition temperature of a polymer, T_g, is elevated by crosslinking[1]. More specifically, they reported that for crosslinked networks formed from mixtures of divinyl benzene (DVB) (mol fraction $=n$) and styrene the elevation of the glass transition temperature, ΔT, is given by equation (1):

$$\Delta T = T_g(n) - T_g(n=0) = 586\,n \qquad (1)$$

Values of T_g were obtained from plots of volume (V) *versus* temperature (T) using Tammann's criterion for a second order transition at a maximum in d^2V/dT^2, which was chosen mainly from experience with inorganic glasses. However, subsequent experience with organic polymeric glasses has shown that a preferred criterion is that 'The glass transition, T_g, is taken at the point of intersection of two straight lines which represent the volume–temperature coefficient in the liquid and in the glassy state'[2]. When the results of Ueberreiter and Kanig are analysed on this latter criterion it is possible to define values of T_g until, above $n=0.13$, the transition range becomes too broad (c.f. ref 1: *Figure 3*). When values obtained in this way are plotted against concentration of crosslinks, calculated on the provisional assumption that one molecule of divinyl benzene yields one crosslink, then although a straight line may be drawn it does not pass through the origin as required by equation 1 (*Figure 1a*). Some additional data of Boyer and Spencer[3] have been included but are too limited to check the trend indicated in *Figure 1a*. The data of Ueberreiter and Kanig were plotted previously by Fox and Loshaek. The scatter of data was greater than in *Figure 1a* and high values of T_g at low feeds of DVB were neglected in favour of a straight line interpretation passing through the origin of coordinates (c.f. ref. 4: *Figure 5*).

The present work was undertaken to ascertain whether the trend in *Figure 1a* is a reproducible property of crosslinked polystyrene. Such a trend is suggestive of a contribution by entanglements to an elevation of T_g. Previously an effect of this kind has been suggested, to account for the dependence of T_g on molecular weight, for various linear polymers, including polystyrene[5]. In the case of a crosslinked network the region in which such an effect would be expected can be predicted by analogy with the way in which entanglements contribute to the density of elastically effective chains. To this end, data by Wesslau are cited for a polystyrene network prepared by copolymerization of styrene with methacrylic anhydride (*Figure 1b*)[6]. A usual[7], the entanglement contribution is initially considerable but then declines rapidly as the concentration of chemical crosslinks preponderates (*Figure 1b*: inset). This initial trend seems comparable to the T_g data and this similarity serves to emphasize the need for further experimental investigation.

EXPERIMENTAL

Styrene (Aldrich, Milwaukee, Wisconsin) was vacuum distilled and the middle fraction stored under nitrogen in a freezer; purity was ascertained by ^{13}C n.m.r. spectroscopy. *p*-Divinyl benzene (DVB) was isolated from a commercial product, which includes isomers of divinyl benzene (c.f. ref. 8), by the bromination–debromination reaction sequence detailed by Storey[9]. Recrystallized *p*-divinyl benzene had a melting point of 25°C in agreement with Storey's value of 25°–26°C (a value of 31°C is given in ref. 10). Benzoyl peroxide (Aldrich) was taken directly from a newly opened bottle.

Monomeric reactants with dissolved benzoyl peroxide (0.1 wt %) were rigorously degassed and heated in vacuum as follows: 2 days at 40°C, plus 2 days at 60°C, and finally 2 days at 80°C. Although the polymeric products appeared to be completely polymerized they were, nevertheless, exposed to γ-rays (16 Mrad at 0.8 Mrad/h; ambient temperature $=35$°C) to ensure reaction of any residual monomer. Irradiation would also result in a small, but

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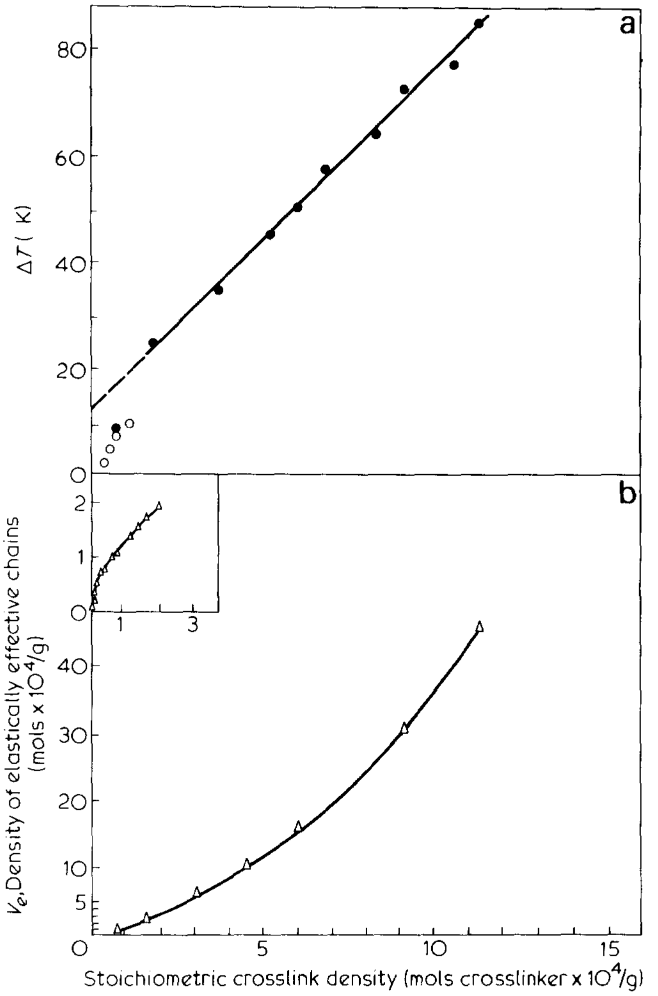

Figure 1 Elevation of T_g and density of elastically effective crosslinks *versus* crosslink density. The concentration of crosslinks was calculated on the assumption that the efficiency of DVB is unity (ϵ = 1.0). (a): ●, Ueberreiter and Kanig; ○, Boyer and Spencer. (b) (lower): Wesslau; styrene: methacrylic anhydride (ϵ = 1.0)

negligible, amount of crosslinking (c.f. ref. 11). Single fragments (30–50 mg) were cut from the polymer and scanned, from room temperature to $T_g + \sim 30°C$, in the differential scanning calorimetry (d.s.c.) mode of a DuPont 990 Thermal Analyzer. Samples were promptly cooled to room temperature using a 'quench cooling can', provided with the instrument, before proceeding to second and third runs. In preliminary experiments a variety of quenching procedures had been tried but, in agreement with previous reports on linear polystyrene, were found to be without influence on values of T_g as determined in second and subsequent runs. In contrast, d.s.c. traces in first runs could be influenced by prolonged annealing as reported previously for linear polystyrene[12,13], at least for samples with lower degrees of crosslinking.

RESULTS AND DISCUSSION

Detailed studies of linear polystyrene by the d.s.c. method have been reported previously[14] and it will suffice to limit documentation to results for crosslinked networks. A first run on a lightly crosslinked network gave an endothermal peak which was no longer evident after quenching (runs 2 and 3; *Figure 2*). The peak could be restored, partially, by slowly cooling the sample overnight from 200°C to room temperature (run 4). With increasing degrees of crosslinking the peak decreased in prominence (*Figure 3*) and eventually could not be detected. An endothermal peak with similar characteristics was reported previously for linear polystyrene by Wunderlich *et al.* They attributed the phenomenon to macromolecular relaxations controlled by the rates of trapping and release

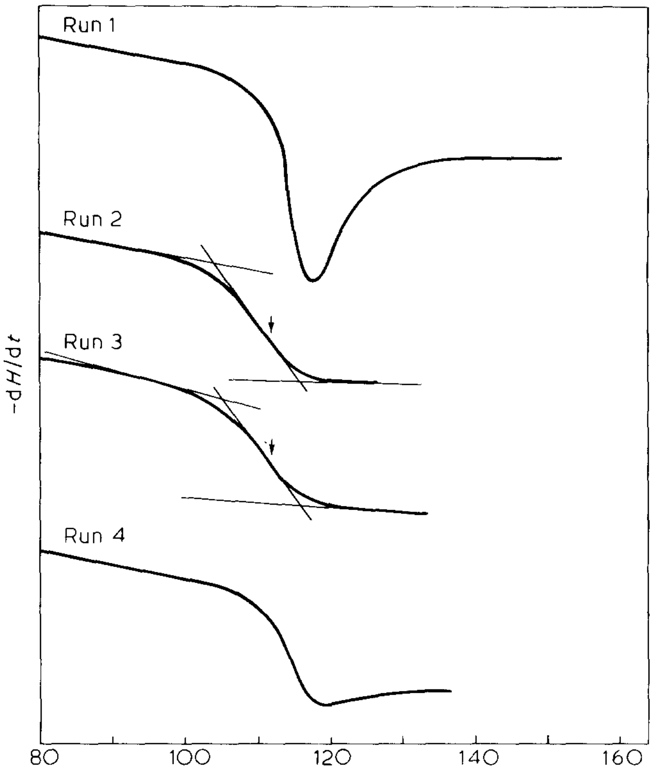

Figure 2 D.s.c. traces for lightly crosslinked polystyrene. 0.44 mol% DVB; scan rate = 10°C/min

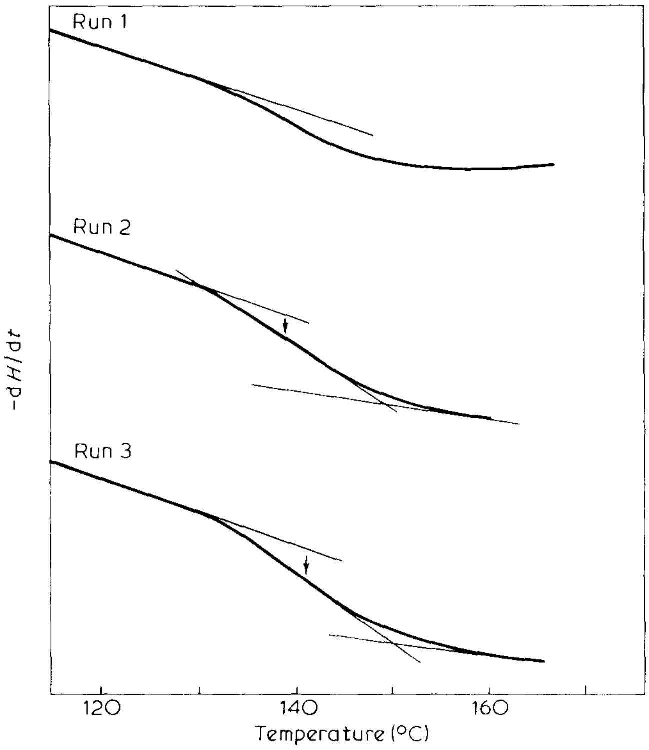

Figure 3 D.s.c. traces for more highly crosslinked polystyrene. 7.47 mol% DVB; scan rate = 10°C/min

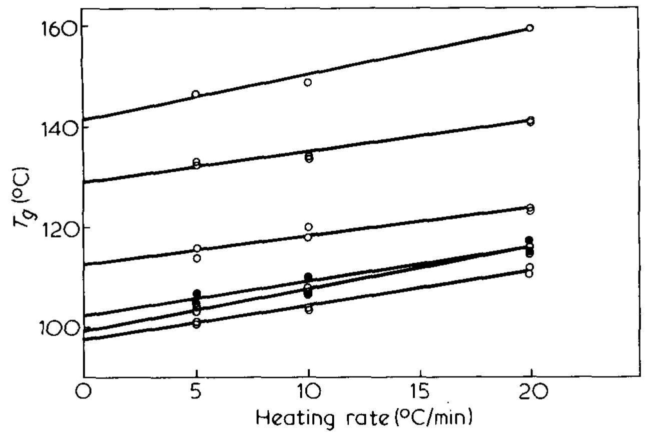

Figure 4 Extrapolation of d.s.c. data to zero scan rate. Various feeds of DVB; to avoid overcrowding, some data were omitted. One set is distinguished by filled circles

of holes of the type invoked by Eyring in his theory of liquids[12]. More recently an additional phenomenon was distinguished by Hentze for the case of macromolecules capable of crystallization, such as polyethylene terephthalate and polycarbonate. He suggested that such macromolecules are capable of close packing, short of crystallization, resulting in the possibility of an 'amorphous–amorphous two-phase' transition[13]. In this regard, the present results are of interest in showing that endothermal peaks are still observed in networks in which macromolecular packing may be presumed to be limited by crosslinks. This observation seems consistent with Hentze's view that an amorphous–amorphous transition need not be invoked in order to account for glass transition phenomena in atactic polystyrene.

A value for T_g may be deduced from a d.s.c. run which includes an endothermal component[15]. However, the more usual procedure[13,14,18,19] was followed of using the simpler type of scan observed in run 2. Upper and lower values of T_g were estimated from the method of intersecting tangents, as illustrated in *Figure 2*. Unless otherwise stated, the values reported in the present work are the arithmetic mean of these upper and lower bounds. Values of T_g were reproducible in the third and subsequent runs using the quenching procedure described in the experimental section. Results obtained at heating rates in the range allowing best precision (c.f. ref. 14), from 20°C/min to 5°C/min, were extrapolated to zero rate (*Figure 4*). Under such conditions results reproducible to ±2°C were obtained in separately synthesized copolymers throughout the range studied, up to a feed of 11 mol% DVB. At higher feeds definition of T_g was inadequate and, in this respect, the d.s.c. data are somewhat more restricted than the previous dilatometric data which allowed definition up to 13 mol% DVB (c.f. *Figure 1*).

The present results differ from the data of Ueberreiter and Kanig in that plots of ΔT *versus* feed of crosslinker extrapolate close to the origin of coordinates. This is true by reference either to upper and lower bound estimates of T_g or to mean values (*Figure 5*). A possible reason for the intercept indicated by the earlier work may be traced to the unusually low value of T_g obtained for the linear polymer; 82°C according to Ueberreiter and Kanig or 78°C according to the present analysis of their data. In contrast the value obtained from *Figure 4*, by extrapolation to zero heating rate, is 97°C. The value obtained by interpolation to a heating rate of 8°C/min., of $T_g = 103$°C, is in satisfactory agreement with the mean value of 102.3°C reported by Griffiths and Maisey[14]. The low value obtained in the early work is presumably due to failure to remove residual monomer as was mentioned subsequently in related work by Ueberreiter[20] although without re-evaluation of the experimental basis of equation 1. Presumably residual monomer would be less of a problem in reactions including a crosslinking comonomer because of acceleration of the rate of polymerization by the gel effect (c.f. ref. 9 for rate measurements on mixtures of styrene and *p*-divinyl benzene). Therefore, the intercept (of ~13°C) should be regarded as including an artifact caused by the depression of T_g of the linear polymer by residual monomer. Consequently, it is concluded that there is no reliable evidence for a contribution by entanglements to an elevation of T_g in polystyrene networks. This conclusion is drawn despite the fact that crosslinking efficiency is expected to decrease with increasing feed of DVB. The basis of this judgement is that it seems unlikely that crosslinking efficiency would drop so rapidly in the range of 0 to 2 wt% DVB as to compensate for the pronounced entanglement effect which is to be inferred from the inset in *Figure 1b*.

In broader perspective, it is worth inquiring whether an entanglement contribution can be discerned from data reported for other crosslinked networks. Most information is available for natural rubber but much of this is complex inasmuch as networks prepared with high concentrations of sulphur involve extensive side reactions, apart from crosslinking, which also affect the value of T_g[21]. The least objectionable data, in limitation of side reactions, has been obtained by crosslinking purified natural rubber by means of di-tertbutyl peroxide. Mason's tabulation[22] of dilatometric estimates of T_g for such networks was used to derive the graphical display in *Figure 6*. The solid line indicates the rather limited range in which analytical estimates of chemical crosslinks can be compared reliably with measurements of elastic modulus. Within this range, entanglements have been shown to exalt values of the modulus markedly up to a crosslink density approaching 10^{-4} mols/g[23,24]. Yet within this

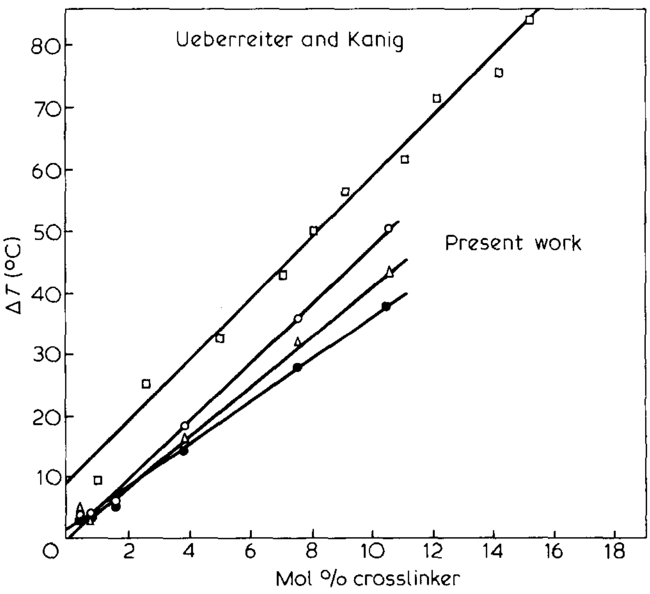

Figure 5 ΔT ***versus*** crosslinking density ($\epsilon = 1$)

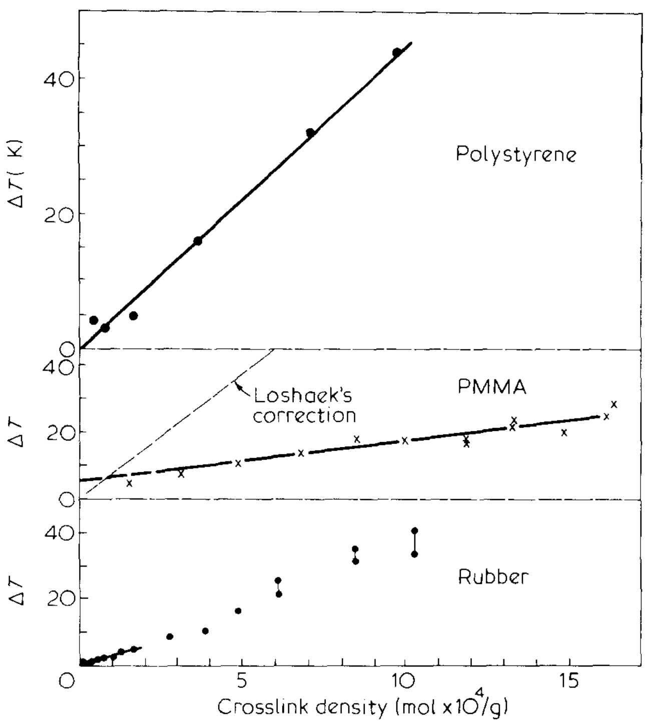

Figure 6 **Δ*T versus* crosslinking density for various polymers. Natural rubber from Mason (ref. 22: *Table 2*). Polymethyl methacrylate (PMMA) from Loshaek (ref. 25: *Table 2* and *Figure 4*); $\epsilon = 0.3$. Polystyrene (ϵ = 1.0)**

same range no exaltation of T_g is apparent. Therefore it is concluded that, in Mason's experiments, entanglements have little or no influence on T_g.

Loshaek prepared crosslinked networks by copolymerization of methyl methacrylate with various dimethacrylates. The maximum crosslink density would be attained if each dimethacrylate molecule formed one intermolecular crosslink but actually the efficiency, ε, in such reactions is always less than unity. The value[25,26] of $\varepsilon = 0.3$ has been adopted in *Figure 6* but from the present point of view the choice of a particular value is less critical than the question of its constancy with variations in composition of the monomeric reaction mixture. In fact Hwa has made a detailed study of copolymers of methyl methacrylate and methylene glycol dimethacrylate which suggests that the value of ε does vary in the very range in which entanglement phenomena are expected to be important[27]. Accordingly Loshaek's data for copolymers of methyl methacrylate and ethylene glycol dimethacrylate must also be regarded with caution. With this reservation, it is to be seen that there is little or no evidence for exaltation of T_g by entanglements, either by reference to primary data or to Loshaek's correction for a 'copolymer effect' (*Figure 6*).

In summary, no evidence has been found to support the idea that entanglements can exalt T_g in a chemically crosslinked network. Apparently their potential in this respect, as realized in some linear polymers including polystyrene and PMMA[5], is not enhanced by chemical crosslinking. This absence of an effect is in contrast to an enhanced contribution of entanglements to values of modulus of elasticity on account of 'trapping' by crosslinking[28].

A final comment should be made on the pertinence of the present data to the evaluation of theories which relate T_g to crosslink density[29-31]. For example, DiMarzio's theory predicts an increasing slope in plots of T_g *versus* crosslink density which appears to be contradicted by results for the polystyrene networks. However, it should be emphasized that none of the experimental data for crosslinked networks prepared by copolymerization of mixtures of olefins and diolefins is immediately suitable for comparison with theory. This is because the provisional assumption of a constant crosslinking efficiency, despite changes in feed of the diene, is an oversimplification. It is widely recognized that more detailed analyses are needed to take account of complicating factors such as cyclization reactions and the 'shielding' from reaction of pendant double bonds[8,32-35].

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