

The Glass Transition Temperature of Star-Shaped Polystyrenes

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Synopsis

The glass transition temperatures of linear and four- and six-branched regular star polystyrenes are measured by penetration, differential scanning calorimetry, and a density gradient technique. The results of the three methods show that the glass transition temperature depends on the concentration of chain ends in the polymer sample. An attempt is made to assess the influence of the presence of the branch point on the glass transition temperature using a series of four-branched polystyrenes containing varying amounts of isoprene near the branch point. However, any effect of the central branch point on the glass transition temperature is obscured by plastification of polystyrene by polyisoprene.

INTRODUCTION

Twenty years ago, Fox and Flory¹ observed that, for a homologous series of fractionated linear polystyrenes, the glass transition temperature depends linearly on the inverse of the number-average molecular weight of the polymer, in other words, on the concentration of the endgroups in the sample:

$$T_g = T_{g\infty} - \frac{K}{M_n}$$

Considering a polymer as a copolymer of internal units and endgroups, Ueberreiter and Kanig² derived that the inverse of the glass transition temperature is a function of the inverse of the number-average molecular weight in agreement with their experimental results which included the dimer:

$$\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{K'}{M_n}$$

They showed that K' depends on the nature of the endgroups in the polymer. The Fox-Flory relation is an approximation limited to higher molecular weight polymers for which the weight fraction of the endgroups is small. These relations, first formulated for polystyrene,^{1,2} were later confirmed by studies on other linear polymers including poly(methyl methacrylate),^{3,4} polyacrylonitrile,^{5,6} polypropylene,⁷ and poly(α -methyl-

styrene),⁸ poly(vinyl chloride),⁹ poly(ethylene adipate),¹⁰ and poly(dimethylsiloxane).¹¹ Recently, a number of regular four- and six-branched star polystyrenes became available.^{12,13} It was thought of interest to test the relation between the glass transition temperature and the endgroup concentration with polymers containing more than two ends per molecule. The effect of the presence of the central branch point was also investigated.

EXPERIMENTAL

All narrow molecular weight-distribution linear polystyrenes were prepared by anionic polymerization initiated with *sec*-butyllithium in benzene at 30°C.¹⁴ The four-branched polystyrenes were prepared by coupling of the living poly(styryllithium) with 1,2-bis(methyldichlorosilyl)ethane.¹² The six-branched polystyrene could not be obtained unless the poly(styryllithium) was converted first to isoprenyllithium ends before coupling with 1,2-bis(trichlorosilyl)ethane.^{12,13} Details of the preparation, fractionation, determination of the molecular weight, and the degree of branching of the star polymers are given in the original papers.^{12,13} The data of interest to this study are collected in Table I. Some four-branched star polymers of constant polystyrene molecular weight but with varying amounts of isoprene next to the central branch point were synthesized. The structure of such polymers can be represented by (S-I)₄.¹⁵ For further comparison, a series of styrene-isoprene diblock copolymers with constant polystyrene molecular weight was also prepared. The characteristics of those polymers are shown in Table II.

TABLE I
Glass Transition Temperature of Linear, Four-, and Six-Branched Star Polystyrenes

Sample	$10^{-3} M_n$	D.B. ^a	Isoprene, %	Pen.	T_g , °C (DSC)	Dens. grad.
L 1	1240 ^b			104.0	102.5	97.5
L 2	58			102.5		
L 3	21.8			98.0		
L 4	11.6				96.6	88.5
L 5	11.1			93.5		
L 6	4.7			81.7	85.0	
L 7	2.8 ₅				68.5	
S181A	1027 ^b	(4.12)		103.5	104.4	
S121A	88.5	3.92		102.0	100.8	
S131A	45.5	3.92		100.5	99.5	91.5
S23A1	20.3	4.06		95.0	93.1	86
HS051A	1090 ^b	(5.63)	0.0 ₆	103.5		
HS061A	107	5.83	0.8	101.0		
HS071A	64.4	5.90	1.1	99.5	99.0	92.5
HS131	29.6	5.93	1.8	94.7	93.6	86

^a Degree of branching equals $M_{n \text{ star}}/M_{n \text{ precursor}}$. Values in parentheses $M_w \text{ star}/M_n \text{ precursor}$.

^b M_w from light scattering.

TABLE II
Influence of Isoprene on the T_g of Four-Branched Star Polystyrene and of
Styrene-Isoprene Diblock Copolymers

Sample	M_n Polystyrene	Isoprene, wt-%	T_g , °C ^a	ΔT^b
Star Polymer				
S23A1	5000	—	97.0	
S23C1		1.8	92.7	4.3
S24A1	5200	—	97.3	—
S24B1		3.0 ₅	90.7	6.6
S24C1		7.0	78.6	18.7
S24D1		13.7	59.0	38.3
Diblock				
25A	5200	—	88.9	—
25B		2.0	85.8	3.1
25C		7.1	68.6	20.3
25D		13.8	48.9	40.0

^a Glass transition temperature by differential scanning calorimetry at 10°C/min heating rate.

^b $T_g - T_{g \text{ polystyrene}}$.

The glass transition temperatures of the polymers were determined by three methods. Pressure-molded and annealed polymer pellets, 2 mm thick, were heated at 1.25°C/min on a Perkin-Elmer thermomechanical analyzer (TMS-1) equipped with a penetration probe that was loaded with 15 g. The experimental conditions could be varied by a factor of 2 without affecting the results. When the movement of the probe was recorded in the differential mode, a sharp deflection point corresponding to a small penetration was observed. The average of three determinations which agreed within 1°C was taken.

Glass transition temperatures were measured also on a Perkin-Elmer differential scanning calorimeter (DSC-1B). The temperature scale of the instrument was calibrated as described by Wunderlich.¹⁶ The 15-mg samples were run in triplicate at 2.5°, 5°, 10°, 20°, and 40°C/min heating rates. When the glass transition temperature was obtained as the intersection of the baseline and the sloping part of the curve, extrapolation to 0°/min heating rate was best performed linearly, the glass transition temperature increasing by 2.5° ± 0.3°C per 10°C/min heating rate. The glass transition temperature was also evaluated as the temperature where the heat capacity of the polymer reaches the mean of that of the glassy and rubber-like states. In that case, the extrapolation to 0°/min heating rate had to be performed by smooth curves. The glass transition temperature at 0°C/min heating rate is consistently 4.5° ± 0.5°C lower than at the most reproducible 10°C/min heating rate. The 0°C/min glass transition temperatures obtained by the latter method were 1° ± 0.5°C higher than the

corresponding values evaluated by the former method. Results from the latter method are quoted below.

Finally, the glass transition temperatures for a number of polymers were determined from specific volume–temperature curves obtained by means of a density gradient technique.¹⁷ The density gradient was produced by the partial mixing of two layers of aqueous caesium chloride of approximately 1.015 and 1.10 g/cm³. The 1-mg samples were annealed at 150°C for a few hours. The densities were measured at 10°C intervals in one cooling and one heating mode. Each density measurement took from 60 to 90 min. The precision with which the glass transition temperature can be determined is limited by the slight curvature in the specific volume–temperature plot above the glass transition temperature and amounts to between 1° and 2°C.

RESULTS AND DISCUSSION

Some examples of specific volume–temperature data are shown in Figure 1. The thermal expansion coefficients of the polymers derived from such plots yield $\alpha_G = (2.2 \pm 0.1) \times 10^{-4} \text{ cm}^3/\text{°C}$ and $\alpha_L = (6.3 \pm 0.2) \times 10^{-4} \text{ cm}^3/\text{°C}$ below and above the glass transition temperature, respectively. Both coefficients are independent of the polymer structure and in fair agreement with published values for linear polystyrene in the same temperature ranges.^{1,2,17}

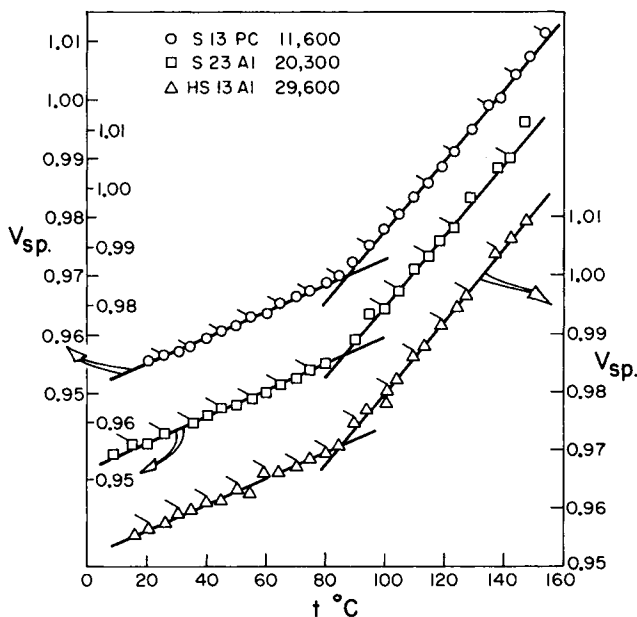


Fig. 1. Specific volume–temperature plots for linear (O), four-branched (□), and six-branched (Δ) star polystyrene. Vertical axis is shifted to avoid overlapping of the curves.

The glass transition temperatures obtained by the three methods are collected in Table I. Results of the different measuring techniques are not directly comparable and have to be treated independently. This is especially true for the results obtained by the penetration method which measures a softening point, this being a temperature at which the viscosity of the sample reaches a certain value. When, as has been observed,¹ the viscosity at the glass transition temperature varies with the molecular weight and presumably with the architecture of the polymer, it follows that the softening temperature and glass transition temperature do not necessarily run parallel. However, the very high apparent activation energy of flow at the glass transition temperature ($E_{T_g} > 100$ kcal/mole) and the shallow minimum observed for the viscosity at the glass transition temperature for linear polystyrene of $M_n \approx 15,000$ ¹ should minimize any systematic deviation between the softening temperature and the glass transition temperature. The large difference between the glass transition temperature obtained by the DSC and density gradient methods can not be rationalized easily. The time scales of those two methods may be quite different despite the extrapolation to 0°C/min heating rate of DSC data.

The dependence of the experimental glass transition temperature on the heating rate has been discussed¹⁸ and was applied to differential scanning calorimetry.¹⁰ It should be pointed out that a low glass transition temperature for polystyrene was also observed by Gordon and McNab with the density gradient method. Although they ascribed this to the presence of impurities in the polymer samples, it cannot be excluded that polymer-confining liquid interactions occur.

Fox-Flory plots of the results from each method reveal that the glass transition temperature is independent of the structure for the highest molecular weight samples. The glass transition temperatures of the linear polymers follow the molecular weight dependence observed by Fox and Flory.¹ The slopes in the Fox-Flory plots for the four- and six-branched star polymers have values respectively about two and three times the slope for the linear polymers. Therefore, in Figure 2, the glass transition temperature is plotted against the number of endgroups per molecule divided by the number-average molecular weight, i.e., proportional to the volume concentration of endgroups in the polymer. The number of ends per molecule is taken as 2, 4, and 6 for the linear, four-, and six-branched polymers, respectively. From Figure 2, it can be seen that within the experimental accuracy the glass transition temperatures of the star polymers follow the endgroup concentration dependence established for linear polymers.

It could be argued that if data of greater accuracy or extending to lower molecular weights were available, minor differences in the glass transition temperature chain end concentration relation of the various polymer architectures should become distinguishable. As pointed out by Meares,¹⁹ such minor differences would have to be ascribed to the presence of the central branch point and would be expected to have an effect opposite that of the endgroups. Unfortunately, the various techniques used could not

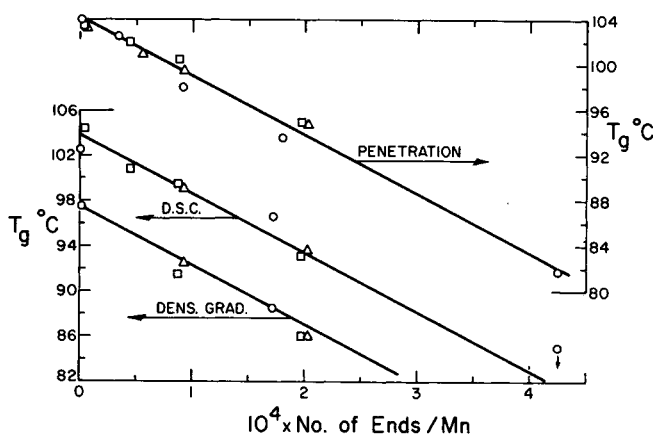


Fig. 2. Dependence of glass transition temperature on the number of endgroups per molecule divided by the molecular weight of the polymer, i.e., the endgroup concentration in the sample: (O) linear; (□) four-branched star; (Δ) six-branched star polymers.

be refined further in our hands, nor can the molecular weight range be extended downward without making the endgroups a sizable weight fraction of the polymers.

An indirect way to assess the importance of the presence of the branch point was sought when preparing four-branched star polymers with a constant molecular weight of the polystyrene but varying amounts of isoprene next to the branch point. The glass transition temperatures of these polymers were determined by the DSC method at $10^\circ\text{C}/\text{min}$ heating rate. The results are given in Table II. The presence of isoprene decreases the glass transition temperature of polystyrene rapidly below the glass transition temperature of the isolated polystyrene branch. Obviously, the small amounts of polyisoprene plasticize the polystyrene, thereby obscuring any effect that the chain loosening at the branch point may have on the glass transition temperature. The decrease of the glass transition temperature with the presence of isoprene is not specific to the star structure of the polymers. From Table II it can be seen that the glass transition temperature of styrene-isoprene diblock copolymers in which the polystyrene has the same molecular weight as in the branches of the star polymers is lower by identical amounts depending on the fraction of polyisoprene in the copolymer. No glass transition characteristic of pure isoprene could be found in a large sample of 25D under experimental conditions for which it was established that 5% of isolated polyisoprene would have been detected. The implications of the observed mixing of polystyrene and polyisoprene blocks on the domain formation in block copolymers is under further investigation.

The results of the lowering of the glass transition temperature on addition of small amounts of isoprene can be applied to the six-branched polymers. In the case of polymers HS061A and HS071A, which contain 0.8

and 1.1 wt-% isoprene, respectively, the measured glass transition temperatures are, within experimental error, those of the pure polymers. Polymer HS131, however, contains 1.8% isoprene. This may have caused a lowering of the glass transition temperature of between 2° and 4°C. It cannot be excluded, therefore, that six-branched polymers with a tighter central branch point would have glass transition temperatures higher than calculated solely from their endgroup concentration. Increases of the glass transition temperatures due to the presence of many interchain linkages are well established for crosslinked polymers.^{20,21}

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