

# Glass Transitions of Styrene/ $\alpha$ -Methylstyrene Statistical Copolymers and of Their Blends with PPO<sup>®</sup> Resin

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## Synopsis

The glass transition temperatures ( $T_g$ ) and specific heat increments ( $\Delta C_p$ ) at  $T_g$  of S/AMS statistical copolymers having weight fractions AMS of 0.00, 0.09, 0.17, 0.26, 0.36, and 0.44 are (by DSC) 380.0 (0.280), 384.2 (0.275), 388.8 (0.284), 391.5 (0.275), 398.3 (0.272), and 405.9 (0.27) °K (J·g<sup>-1</sup>·deg<sup>-1</sup>), respectively. The  $T_g$  ( $\Delta C_p$ ) for the PPO resin are 492.2 (0.221). The glass transitions of P(S/AMS) (1) + PPO resin (2) blends having  $w_2 = 0.25, 0.50,$  and  $0.75$  were also measured. Examination of the copolymer and blend  $T_g$  vs. composition data indicates that a relation recently proposed by Couchman gives a somewhat better approximation than the simple Fox relation. However, the nonadjustable  $k = \Delta C_{p2}/\Delta C_{p1}$  constant in the Couchman relation must be replaced by a smaller empirical  $k$  to give a true match of calculated to observed  $T_g$ .

## INTRODUCTION

PPO<sup>®</sup> resin [General Electric Co. trademark for poly(2,6-dimethyl-1,4-phenylene oxide)] has been reported to be miscible with poly( $\alpha$ -methylstyrene) (PAMS) and with poly(styrene-co- $\alpha$ -methylstyrene) (P(S/AMS)).<sup>1-3</sup> Also PPO resin and the A-B block copolymer poly(styrene-bl- $\alpha$ -methylstyrene) have been found miscible.<sup>4</sup> The heat distortion temperatures of PPO resin/P(S/AMS) statistical copolymer blends display a simple monotonic increase with increasing AMS content.<sup>2</sup> Rapid emulsion copolymerization of styrene with  $\alpha$ -methylstyrene to yield high molecular weight statistical copolymers has been achieved.<sup>5</sup> The glass transition temperatures  $T_g$  of these copolymers and of their blends with PPO resin are here reported.

## EXPERIMENTAL

### Materials

The PPO resin designated PR5255, has an intrinsic viscosity at 30°C in chloroform of 0.49 dL/g,  $M_n = 18,500$  by osmometry, and  $M_w = 37,200$  by light scattering. The examinations [by DSC and/or thermo-optical analysis (TOA)] of the glass transitions of its blends with polystyrene,<sup>6</sup> poly(styrene-co-*p*-chlorostyrene),<sup>7</sup> poly(styrene-bl-butadiene-bl-styrene),<sup>8</sup> poly(2-methyl-6-benzyl-1,4-phenylene oxide),<sup>9</sup> and poly(2-methyl-6-phenyl-1,4-phenylene oxide)<sup>10</sup> have been previously reported.

TABLE I  
 Styrene- $\alpha$ -methylstyrene Statistical Copolymers<sup>5</sup>

Code <sup>a</sup>	Weight fraction styrene		% conversion	$10^{-5} \times M_n^c$	$[\eta]^c$
	Feed	Copolymer <sup>b</sup>			
2C	0.90	0.91	93	2.8	1.87
3A	0.80	0.83	70	3.9	4.74
4A	0.70	0.74	60	2.4	2.58
5C	0.60	0.64	87	—	0.95
6C	0.50	0.56	79	1.3	0.69

<sup>a</sup> Ref. 5 designations.

<sup>b</sup> Calculated with  $r_1 = 1.124$ ,  $r_2 = 0.627$ .

<sup>c</sup> Ref. 7:  $M_n$  by osmometry; intrinsic viscosity (dL/g) at 25°C in toluene.

An anionically polymerized polystyrene (PS 13a, Pressure Chemical Co.) having a reported  $M_w = 67,000$  and  $M_w/M_n = 1.15$  was studied.

The high-conversion styrene/ $\alpha$ -methylstyrene statistical copolymers P(S/AMS) used in the present study were supplied by Rudin and Samanta.<sup>5</sup> They were prepared by free radical polymerization in emulsions. These copolymers are identified and some pertinent data are listed in Table I. Since for styrene<sup>1</sup> and  $\alpha$ -methylstyrene<sup>2</sup> copolymerizations the relative reactivity ratios have been found to be<sup>11</sup>  $r_1 = 1.124$ ,  $r_2 = 0.627$ , the weight fractions of styrene in the copolymers are slightly greater than its weight fractions in the feeds.

The as-received copolymers were here dissolved in toluene (10 g copolymer/100 mL toluene ratio), precipitated into methanol in a Waring blender, filtered, steeped in 40°C methanol with stirring (two decants), filtered, and dried in a vacuum oven 15 h at 100°C with slight nitrogen bleed. The copolymers were finely divided, fibrous powders after this treatment. Blends were prepared by weighing 2 g total polymer into 40 mL toluene, stirring, precipitating into methanol in a Waring blender, filtering, and drying in a vacuum oven 15 h at 100°C with slight nitrogen bleed. Low bulk density, fibrous blends resulted.

### Glass Transition Measurements

Glass transitions were determined in a Perkin-Elmer Model DSC-2C Differential Scanning Calorimeter on 10 mg samples compacted into disks and crimped in standard aluminum containers. Temperature was calibrated by indium and potassium chromate fusion; differential power calibration was effected using an indium enthalpy of 28.4 J·g<sup>-1</sup>. Two heatings were conducted at 20°/min from 283 K to 453 K for the copolymers and 283–553 K for the blends with a -40°/min cooling between heats. As expected from previous TGA data,<sup>11</sup> little weight loss was detected in the samples after the DSC runs. Since some  $T_g$  lowering was noted for the pure copolymers in preliminary DSC runs to 553°K, runs to only 453 K were made to obtain more accurate  $T_g$  data for them. Nitrogen flow was maintained in the DSC sample chamber. Analog plots and digital data were taken during the heating scans. The midpoint temperatures ( $T_g$ ) in the specific heat transitions and the specific heat increments ( $\Delta C_p$ ) at these temperatures are reported from interactive microcomputer processing of the second heat data. Choice of tangent placements on the CRT-displayed curves allows definite subjective bias which introduces approximately  $\pm 0.5^\circ$

uncertainty in  $T_g$  and approximately  $\pm 0.02 \text{ J g}^{-1} \cdot \text{deg}^{-1}$  uncertainty in  $\Delta C_p$  (for 10 mg samples). A trend toward underestimation of  $\Delta C_p$  is noted as the breadth of the transition region increases in the blends. The  $\Delta C_p$  of the 20 mg samples of single polymers are considered accurate to approximately  $\pm 0.005 \text{ J} \cdot \text{g}^{-1} \cdot \text{deg}^{-1}$ .

## RESULTS AND DISCUSSION

Figure 1 presents the DSC heating curve for the polystyrene (PS 13a, Pressure Chemical Co.) sample. The markings of  $T_g$  and of  $\Delta C_p$ , the specific heat increment at  $T_g$ , are indicated. The glass transition temperatures and specific heat increments for this sample, P(S/AMS) samples, the PPO resin, and the P(S/AMS) (1) + PPO resin (2) blends are given in Table II.

The glass transition temperatures of PAMS as a function of molecular weight and tacticity has been rather extensively examined by DTA<sup>12,13</sup> and DSC.<sup>13,14</sup> At  $5^\circ/\text{min}$  heating rate, using the intersection of the initial baseline with the tangent to the DTA curve in the transition region, a  $T_g = 446 \text{ K}$  was reported for high molecular weight PAMS.<sup>12</sup> Similar treatment of DTA ( $5^\circ/\text{min}$ ) and DSC ( $10\text{--}20^\circ/\text{min}$ ) data yielded  $T_g$  values in the range  $445\text{--}455^\circ\text{K}$  for HMW PAMS samples of differing tacticities.<sup>13</sup> Transition midpoint  $T_g$  determined by DSC with extrapolation to  $1^\circ/\text{min}$  heating rate gave  $T_g = 453 - 3.1 \times 10^{-5}/M_n$  for a series of ar ionically polymerized PAMS.<sup>14</sup> Rather large heating rate effects on observed  $T_g$  were reported. We cannot tell from the experimental description whether temperatures were calibrated by metal fusion standards at each heating rate or if the major rate effect on observed  $T_g$  is due to response time and heat transfer rates. Apparent melting temperatures of indium in the DSC-2C (nitrogen purge) decrease by about  $2^\circ$  in going from  $20^\circ/\text{min}$  to  $1.25^\circ/\text{min}$  heating rate. Further DTA and DSC studies on PAMS and on di- and triblock styrene/ $\alpha$ -methylstyrene copolymers and blends<sup>15-17</sup> indicate consistently that  $T_g = 453 \text{ K}$  is a valid assignment for high molecular weight PAMS or  $\alpha$ -methyl-

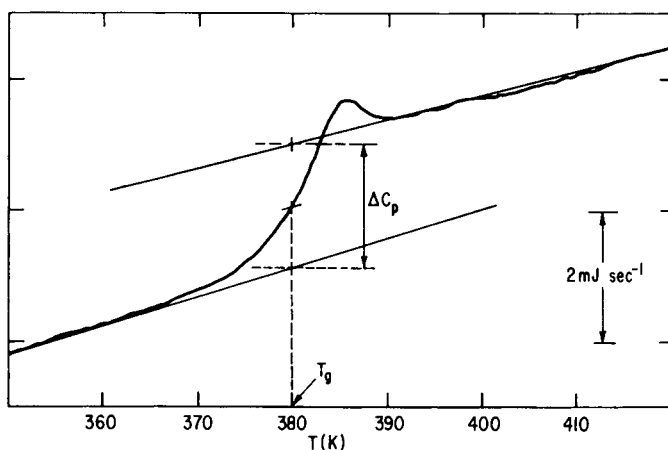


Fig. 1. DSC specific heat vs. temperature curve for polystyrene PS13a.  $20^\circ/\text{min}$  heating after  $-40^\circ/\text{min}$  from  $483\text{--}283 \text{ K}$ .

TABLE II  
P(S/AMS) + PPO Resin Blends: Glass Transition Temperatures ( $T_g$ ) and Specific Heat  
Increments ( $\Delta C_p$ ) at  $T_g$ . Second Heating Scans (20°/min)

Blend <sup>a</sup>	$T_g$ (K)	$\Delta C_p$ (J·g <sup>-1</sup> ·K <sup>-1</sup> )
1.00/0.00 (0.00)	380.0	0.280
0.91/0.09 (0.00)	384.2	0.275
0.83/0.17 (0.00)	388.8	0.284
0.74/0.26 (0.00)	391.5	0.275
0.64/0.36 (0.00)	398.3	0.272
0.56/0.44 (0.00)	405.9	0.27
0.00/1.00 (0.00)	453 <sup>b</sup>	—
0.91/0.09 (0.25)	402.3	0.28
0.83/0.17 (0.25)	408.1	0.28
0.74/0.26 (0.25)	410.0	0.26
0.64/0.36 (0.25)	413.4	0.23
0.56/0.44 (0.25)	418.5	0.22
0.91/0.09 (0.50)	424.4	0.24
0.83/0.17 (0.50)	427.9	0.25
0.74/0.26 (0.50)	429.1	0.23
0.64/0.36 (0.50)	431.4	0.21
0.56/0.44 (0.50)	434.9	0.22
0.91/0.09 (0.75)	452.3	0.23
0.83/0.17 (0.75)	453.6	0.23
0.74/0.26 (0.75)	453.4	0.23
0.64/0.36 (0.75)	455.3	0.20
0.56/0.44 (0.75)	460.5	0.21
(1.00)	492.2	0.221

<sup>a</sup> Blend designation is weight ratio S/AMS in the copolymer and (weight fraction PPO resin in the blend); S/AMS( $w_{PPO}$ ).

<sup>b</sup> Selected literature value.

styrene blocks. In view of the existing literature<sup>12-17</sup> we will accept 453 K as the provisional  $T_g$  of PAMS. This value is included in Table II.

The  $\Delta C_p$  of 0.280 and 0.221 J·g<sup>-1</sup>·deg<sup>-1</sup> found for PS and PPO resin, respectively (cf. Table II), are the same as those found by Fried.<sup>19,20</sup> This must be somewhat fortuitous since his data were not taken on these same samples, and the  $\Delta C_p$  marking method appears slightly different. Somewhat higher values of  $\Delta C_p$  for PS have been measured by other investigators: 0.296,<sup>21</sup> 0.282,<sup>22</sup> 0.31,<sup>23</sup> 0.295,<sup>24</sup> and 0.288<sup>25</sup> J·g<sup>-1</sup>·deg<sup>-1</sup>.

The glass transition temperature as a function of weight fraction comonomer in copolymers and as a function of weight fraction PPO resin in the blends can be examined within the framework of several semiempirical equations.<sup>18,26-28</sup> The Couchman equation for polymer blends will be used as a unifying expression.<sup>18</sup> This may be written as

$$\ln T_g = \frac{\ln T_{g1} + (kw_2/w_1) \ln T_{g2}}{1 + (kw_2/w_1)} \quad (1)$$

where  $T_{g1}$ ,  $T_{g2}$  and  $w_1$ ,  $w_2$  are the glass transition temperatures and weight fractions of the respective polymers, and  $k = \Delta C_{p2}/\Delta C_{p1}$  is the ratio of the specific heat increments of the polymers at their glass transition temperatures.

With  $T_{g1}/T_{g2} \sim 1$  and the empirical relation<sup>29</sup>  $\Delta C_{pi} \times T_{gi} = \text{const}$ , eq. (1) reduces to the Fox relation<sup>26</sup>

TABLE III  
Apparent  $\Delta C_{p2}/\Delta C_{p1}$  Ratios for Poly(styrene(1)-co- $\alpha$ -Methylstyrene(2))<sup>a</sup>

Copolymer	$w_2$	$k$ eq. (1')	$k'$ eq. (3')
2C	0.09	0.67	0.62
3A	0.17	0.73	0.67
4A	0.26	0.58	0.53
5C	0.36	0.65	0.59
6C	0.44	0.76	0.70
		Avg = 0.68	avg = 0.62

<sup>a</sup>  $T_{g1} = 380$  K,  $T_{g2} = 453$  K.

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{2}$$

Extending eq. (1) by analogy to copolymers, with the  $T_{g1}$ ,  $T_{g2}$  and  $w_1, w_2$  representing the homopolymer glass transition temperatures and comonomer weight fractions in the copolymers, one obtains<sup>18</sup> for  $T_{g1}/T_{g2} \sim 1$  the Wood equation<sup>27</sup>

$$T_g = \frac{T_{g1} + (k'w_2/w_1)T_{g2}}{1 + (k'w_2/w_1)} \tag{3}$$

where  $k' = \Delta C_{p2}/\Delta C_{p1}$  is now the ratio of the specific heat increments of the respective homopolymers at their glass transition temperatures.

Rearrangements of eqs. (1) and (3) permit point-by-point calculations of  $k$  and  $k'$  from the copolymer  $w_2, T_g$  data [styrene (1)- $\alpha$ -methylstyrene(2) in

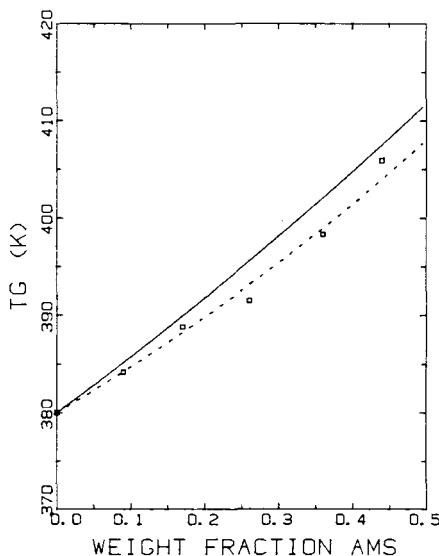


Fig. 2. Glass transition temperatures of P(S/AMS) statistical copolymers as a function of weight fraction AMS. ( $\square$ ) exptl  $T_g$ ; (---) calcd  $T_g$  [eq. (1)] with empirical  $k = 0.68$ ; (—) calcd  $T_g$  [eq. (1)] with  $k = 380/453$ .

TABLE IV  
Composition Dependence of  $T_g$  for P(S/AMS) (1)-PPO Resin (2) Blends. Application on Eqs. (1) and (2)

Copolymer	$w_2$	$k^a$	$T_g$ (K)			Fox <sup>d</sup>
			Obsd	Couchman <sup>b</sup>	Couchman <sup>c</sup>	
2C	0.25	0.69	402.3	402.0	404.9	406.5
	0.50	0.67	424.4	424.4	428.2	431.5
	0.75	0.64	452.3	453.3	457.7	459.9
3A	0.25	0.78	408.1	406.1	408.1	410.4
	0.50	0.68	427.9	427.7	431.1	434.4
	0.75	0.63	453.6	455.4	458.6	461.5
4A	0.25	0.76	410.0	408.2	410.9	412.6
	0.50	0.67	429.1	429.1	433.6	436.1
	0.75	0.60	453.4	456.2	460.3	462.5
5C	0.25	0.64	413.4	412.8	416.7	418.2
	0.50	0.61	431.4	431.5	438.0	440.3
	0.75	0.57	455.3	456.7	462.8	464.8
6C	0.25	0.57	418.5	418.4	423.0	424.5
	0.50	0.56	434.9	435.0	442.7	444.9
	0.75	0.63	460.5	458.0	465.5	467.4

<sup>a</sup> Calculated by eq. (1a).

<sup>b</sup> Calculated by eq. (1) using  $k$  value from  $w_2 = 0.50$ .

<sup>c</sup> Calculated by eq. (1) using  $k = \Delta C_{p2}/\Delta C_{p1}$ .

<sup>d</sup> Calculated by eq. (2).

P(S/AMS) copolymers]:

$$k = \ln(T_g/T_{g1})/[(w_2/w_1) \ln(T_{g2}/T_g)] \quad (1')$$

$$k' = (T_g - T_{g1})/[(w_2/w_1)(T_{g2} - T_g)] \quad (3')$$

The results of these calculations are presented in Table III. There is considerable scatter, but no observable trend with composition, in the point-by-point  $k$  and  $k'$  values. The unweighted averages are  $k = 0.68$  and  $k' = 0.62$ .

The experimental  $T_g$  for the copolymers and the  $T_g$  (---) calculated according to eq. (1) with  $k = 0.68$  are plotted in Figure 2 against weight fraction AMS.  $T_g$  (obsd) -  $T_g$  (calcd) for the five data points are  $0.0^\circ$ ,  $+0.5^\circ$ ,  $-1.6^\circ$ ,  $-0.6^\circ$ , and  $+2.0^\circ$ . This is a rather good fit, but the empirical  $k = 0.68$  assures this. The very slight downward trend in  $\Delta C_p$  with increasing AMS content in the copolymers (cf. Table II) indicates the ratio  $\Delta C_p$  (PAMS)/ $\Delta C_p$  (PS) is certainly not as low as 0.68. The  $\Delta C_p \times T_g$  products for the PS13a and the P(S/AMS) series are reasonably constant (106, 106, 110, 108, 108, and 110 J·g<sup>-1</sup>), but they possibly increase slightly with increasing AMS content. If the product were absolutely constant one would expect  $k = \Delta C_p$  (PAMS)/ $\Delta C_p$  (PS) = 380/453 = 0.84. The theoretical relation [eq. (1)] for the copolymer  $T_g$  using  $k = 0.84$  is represented as a solid curve in Figure 2. Table IV lists for the P(S/AMS) (1) + PPO resin (2) blends the observed  $T_g$ ,  $T_g$  calculated by eq. (1) using the empirical  $k$  ( $w_2 = 0.50$ ) and  $k = \Delta C_{p2}/\Delta C_{p1}$  and  $T_g$  calculated by eq. (2). Figure 3 presents the data and the calculated curves. As in the treatment of the P(S/AMS)  $T_g$  as a function of comonomer weight fractions, the empirical  $k$  values (0.68–0.56) required to best fit the P(S/AMS) (1) + PPO resin (2) data are considerably lower

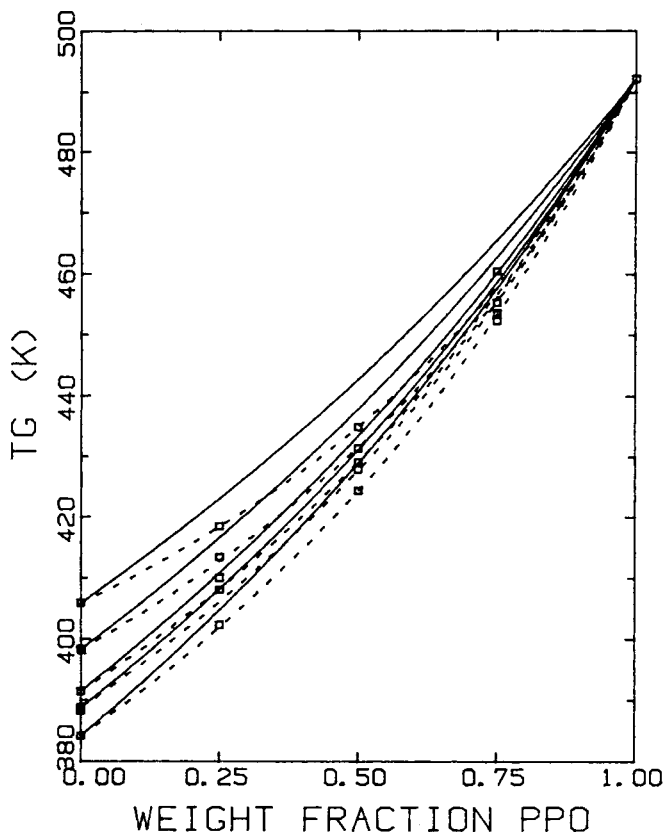


Fig. 3. Glass transition temperatures of P(S/AMS) (1) + PPO resin (2) blends as a function of weight fraction PPO resin. ( $\square$ ) exptl  $T_g$ ; (---) calcd  $T_g$  [eq. (1)] with empirical  $k$  evaluated at  $w_2 = 0.50$ ; (—) calcd  $T_g$  [eq. (1)] with  $k = \Delta C_{p2}/\Delta C_{p1}$ .

than the  $k = \Delta C_{p2}/\Delta C_{p1}$  (0.78–0.82) calculated from the measured specific heat increments. This finding is in accord with the finding of Couchman<sup>18</sup> for poly(styrene-co-4-chlorostyrene) (1) + PPO resin (2) blends<sup>19,20</sup> in which a lower, empirical  $k$  value would be necessary to best fit the  $T_g$  vs. weight fraction composition data. Although a better fit was found for polystyrene (1) + PPO resin (2) blends, the deviation was still in the direction of  $k = \Delta C_{p2}/\Delta C_{p1}$  not being small enough to match the data.

In conclusion, glass transition temperatures and specific heat increments at  $T_g$  have been determined for poly(styrene-co- $\alpha$ -methylstyrene) statistical copolymers for  $\alpha$ -methylstyrene weight fractions  $0 < w(\text{AMS}) < 0.44$ . Treatment of the copolymer  $T_g$ /composition data by the Couchman relation [eq. (1)] containing the nonadjustable parameter  $k = \Delta C_{p2}/\Delta C_{p1}$  yields a better fit than does the Fox relation [eq. (2)]. An empirical value for  $k$ , lower than that indicated by the small decrease in  $\Delta C_p$  P(S/AMS) with increasing AMS content, would be needed to fit these data more accurately. Glass transition temperature data for PPO resin and P(S/AMS) (1) + PPO resin (2) blends show a similar pattern in which the experimental  $k = \Delta C_{p2}/\Delta C_{p1}$  values give  $T_g$  fits [by application of eq. (1)] somewhat better than those given by the Fox relation [eq. (2)].

However, lower, empirical  $k$  values are needed for good correspondence of calculated and observed  $T_g$  values.

### References

1. E. P. Cizek (assigned to General Electric Co.), U.S. Pat. 3,383,435 (1968).
2. Ichiro Saito, Takashi Sakauchi, and Shojiro Yoda (assigned to Kanegafuchi Chemical Industry Co., Ltd.), Jpn. Pat. JP-74109446 (1974).
3. Assigned to Kanegafuchi Kagaku, Jpn. Pat. JP-127624 (1982).
4. L. M. Robeson, M. Matzner, L. J. Fetters, and J. E. McGrath, *Polym. Prepr.*, **14**(2), 1063 (1973).
5. A. Rudin and M. C. Samanta, *J. Appl. Polym. Sci.*, **24**, 1665 (1979).
6. A. R. Shultz and B. M. Gendron, *J. Appl. Polym. Sci.*, **16**, 461 (1972).
7. A. R. Shultz and B. M. Beach, *Macromolecules*, **7**, 902 (1974).
8. A. R. Shultz and B. M. Beach, *J. Appl. Polym. Sci.*, **21**, 2305 (1977).
9. A. R. Shultz and B. M. Gendron, *J. Polym. Sci., Symp.*, **43**, 89 (1973).
10. A. R. Shultz and B. M. Gendron, *J. Macromol. Sci. Chem.*, **A8**(1), 175 (1974).
11. A. Rudin and M. C. Samanta, *J. Appl. Polym. Sci.*, **24**, 1899 (1979).
12. J. M. G. Cowie and P. M. Toporowski, *Eur. Polym. J.*, **4**, 621 (1968).
13. J. M. G. Cowie and P. M. Toporowski, *J. Macromol. Sci. Phys.*, **B3**, 81 (1969).
14. S. L. Malhotra, Ly Minh, and L. P. Blanchard, *J. Macromol. Sci. Chem.*, **A12**, 167 (1978).
15. D. J. Dunn and S. Krause, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 591 (1974).
16. S. Krause, D. J. Dunn, A. Seyed-Mozzaffari, and A. M. Biswas, *Macromolecules*, **10**, 786 (1977).
17. S. Krause and A. M. Biswas, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 2033 (1977).
18. P. R. Couchman, *Macromolecules*, **11**, 1156 (1978).
19. J. R. Fried, Ph.D. dissertation, Polymer Science and Engineering, University of Massachusetts, 1976.
20. J. R. Fried, F. E. Karasz, and W. J. McKnight, *Macromolecules*, **11**, 150 (1978).
21. F. E. Karasz, H. E. Bair, and J. M. O'Reilly, *J. Phys. Chem.*, **69**, 2657 (1965).
22. H. E. Bair, *Polym. Eng. Sci.*, **10**, 247 (1970).
23. B. Morese-Seguella, M. St. Jacques, J. M. Renaud, and J. Prudhomme, *Macromolecules*, **13**, 100 (1980).
24. U. Gaur and B. Wunderlich, *Macromolecules*, **13**, 1618 (1980).
25. S. Krause, M. Iskandar, and M. Iqbal, *Macromolecules*, **15**, 105 (1982).
26. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
27. L. A. Wood, *J. Polym. Sci.*, **28**, 319 (1958).
28. P. R. Couchman, *Phys. Lett.*, **70A**, 155 (1979).
29. R. F. Boyer, *J. Macromol. Sci., Phys.*, **7**, 487 (1973).

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