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Glass Transition Temperature of Poly-p-isopropyl-α-methylstyrene by Differential Scanning Calorimetry

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ABSTRACT

Glass transition temperature (T_g) studies on poly-p-isopropyl-α-methylstyrene having $\overline{M}_n$ values ranging from 5×10^3 to 1.53×10^5 were carried out with the DSC-2 differential scanning calorimeter. The variation of T_{g_e} (at q = 1°K/min) with $\overline{M}_n$ obeys the relation, $T_{g_e}(°K) = 422 - 3.6 \times 10^5/\overline{M}_n$. A comparison of T_{g_∞} values for polystyrene (379°K), poly-α-methylstyrene (453°K), and poly-p-isopropyl-α-methylstyrene (422°K) reveals that although the addition of an α-methyl group in polystyrene increases its T_{g_∞} from 379 to 453°K due to steric hindrance, the addition of the p-isopropyl group in poly-α-methylstyrene lowers it from 453 to 422°K due to reduced chain stiffness and smaller interchain steric hindrance. Poly-p-isopropyl-α-methylstyrene samples having similar $\overline{M}_n$ but different T_g values are shown to possess different structures. The effect of polydispersity on T_g is also stressed.

INTRODUCTION

Studies carried out in this laboratory on the glass transition temperature T_g of polystyrene [1] and of poly-α-methylstyrene [2] were reported on earlier. On replacing the methine proton of polystyrene with a methyl group in the α-position, the value of $T_{g\infty}$ (the glass transition temperature when the molecular weight goes to infinity) was found to increase. These results agree well with those reported by another group of workers [3]. The presence of substituents, such as halogens [4-6] and dimethyl- and diethylamines [7, 8], in the aromatic ring has also been shown to affect T_g values.

The presence of a halogen substituent in the ortho or para position increased T_g while in the meta position it decreased T_g [6]. Furthermore, the addition of a bulkier substituent such as tert-butyl in polystyrene showed a considerable increase in its T_g. The presence of dimethyl- and diethylamines [7, 8] in the para position of the polystyrene aromatic rings yielded interesting results. While p-dimethylaminostyrene samples showed an increase in their T_g values compared to that of their polystyrene counterpart, the diethylaminostyrene samples showed no significant changes.

With a view to studying the combined effects of other substituents both in the ring as well as on the side chain of polystyrene, glass transition measurements were made on poly-p-isopropyl-α-methylstyrene (PPIPαMS) samples of differing molecular weights. The principal results of these studies are given in the present paper.

EXPERIMENTAL

Materials

Anionically prepared [9-11] PPIPαMS samples showing unimodal gel permeation chromatographic (GPC) molecular weight distributions [9] and having number-average molecular weights $\overline{M}_n$ ranging from 5×10^3 to 1.53×10^5 were used in the present study. PPIPαMS samples of series S were prepared in bulk at -25°C with a butyllithium-tetramethylethylenediamine (BuLi-TMEDA) complex, whereas those of series F were the different fractions of the PPIPαMS sample K-1 polymerized at 25°C with an Na-K alloy [9]. The calibration of the GPC instrument was performed with PPIPαMS samples of low polydispersity, P_d ($\overline{M}_w/\overline{M}_n$), whose $\overline{M}_w$ and $\overline{M}_n$ values were calculated from their light scattering and membrane osmometry data respectively [10]. The structure and tacticity of the polymers were calculated from their nuclear magnetic resonance (NMR) spectra recorded in o-dichlorobenzene at 100°C [11] as well as in CCl_4 at 75°C with tetramethylsilane as the internal standard in both cases.

T_g Measurements

T_g values were measured [2] with a Perkin-Elmer DSC-2 differential scanning calorimeter. For each T_g measurement 10 mg of polymer sample was used. In order to have a homogeneous polymer sample, the sample was heated for a few seconds to a temperature 30°K above T_g (estimated from a preliminary run), after which it was quenched through the glass transition region at a rate of 320°K/min as suggested in the literature [12]. After quenching, T_g was determined by heating the sample at different heating rates.

RESULTS AND DISCUSSION

In Fig. 1 are shown typical DSC-2 thermograms of unannealed PPIPαMS (sample F-7) obtained in the glass transition region at different heating rates q. The values of T_g measured at $\Delta C_p/2$ [12],

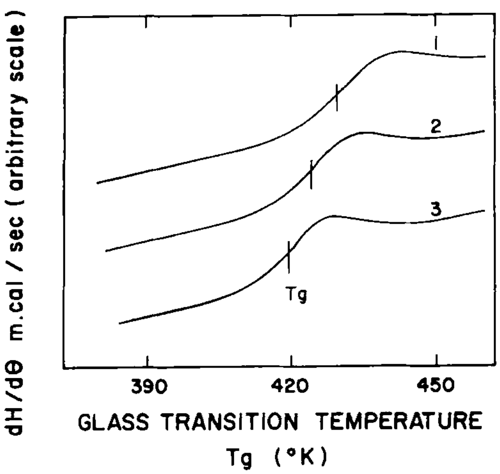

FIG. 1. Typical DSC-2 thermograms of unannealed poly-p-isopropyl-α-methylstyrene (sample F-7) obtained in the glass transition region at various heating rates: (1) 40°K/min; (2) 20°K/min; (3) 10°K/min.

TABLE 1. Influence of Heating Rate q and $\overline{M}_n$ on the T_g of Poly-p-isopropyl-α-methylstyrene

			T_g (°K)			T_{g_e} (°K)
Sample	$\overline{M}_n \times 10^{-3}$	$\overline{P}_d = \overline{M}_w/\overline{M}_n$	q = 40°K/min	q = 20°K/min	q = 10°K/min	at q = 1°K/min[a]
S-4	5	3.0	364	362	360	353
S-14	6	1.3	379	375	373	363
S-13	6.5	1.6	375	371	370	361
S-2	9	1.6	410	403	401	386
S-21	9	1.4	397	392	390	378
S-11	10.5	3.2	375	372	371	364
S-10	10.5	1.1	406	403	402	395
S-8	12	1.2	409	406	404	396
F-8	16	2.1	409	404	403	393
S-20	18	1.3	420	414	411	396
S-22	19	1.4	413	407	404	388
S-5	22	1.8	429	424	422	411
S-16	22	2.2	418	413	408	392
S-18	22	2.1	423	419	417	407
S-9	24	1.6	420	416	414	404
S-23	24	1.8	398	394	390	377
F-7	30	2.2	427	422	420	408

S-27	32	2.4	410	408	406	399
S-17	40	2.3	412	408	406	395
S-1	47	4.1	426	421	419	408
F-6	47	3.3	429	425	423	414
S-15	68	4.0	429	425	422	410
F-5	70	3.9	431	428	426	418
S-25	130	3.3	436	433	431	423
S-19	153	3.8	428	426	425	420

[a] Extrapolated values by using the equation: $\log q = a - b/T_g$ [1].

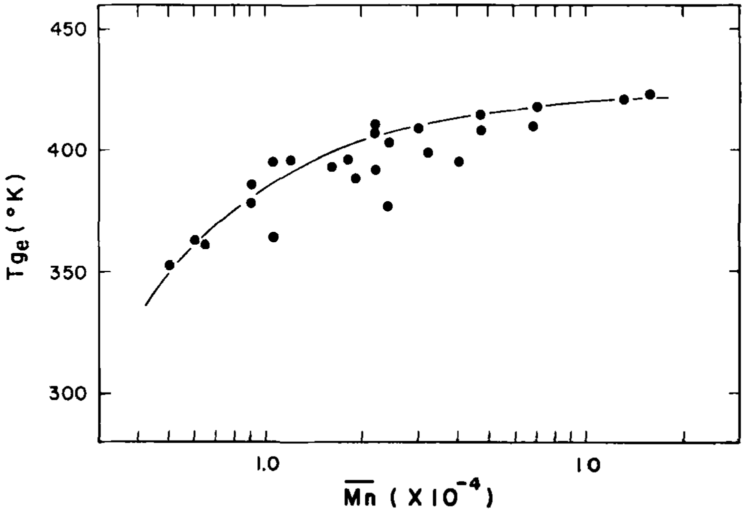

FIG. 2. Extrapolated T_g values (to q = 1) as a function of $\overline{M}_n$. See Table 1 for other data.

were found to increase with increasing heating rate. To compare the DSC data with that obtained for other substituted styrenes, a standard procedure was adopted whereby T_g values measured at different q rates were extrapolated to a q value of 1°K/min by using a plot of log q versus $1/T_g$. The principal results on the T_g of PPIPαMS are summarized in Table 1. The values of T_{g_e} were found to increase with increasing $\overline{M}_n$.

In Fig. 2 is shown a plot of T_{g_e} as a function of $\overline{M}_n$. T_{g_e} increases up to a point beyond which it remains essentially constant (T_{g_∞}). The critical value of the molecular weight is in the vicinity of 1.0×10^5.

In Fig. 3 is shown a plot of T_{g_e} as a function of $1/\overline{M}_n$ which yielded a straight line corresponding to Eq. (1).

$$T_{g_e}(°K) = 422 - 3.6 \times 10^5/\overline{M}_n \qquad (1)$$

In earlier work from this laboratory [1, 2], T_{g_e} of polystyrene (PS) [Eq. (2)] and poly-α-methylstyrene (PαMS) [Eq. (3)] were related to $\overline{M}_n$ respectively as follows:

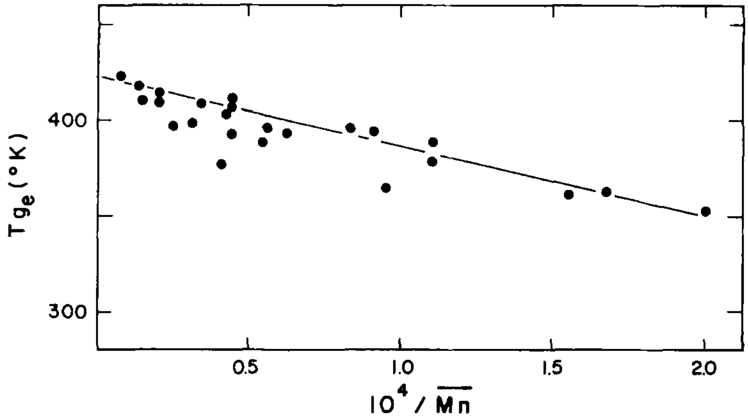

FIG. 3. Extrapolated T_g values (to q = 1) as a function of $1/M_n$. See Table 1 for other data.

$$T_{g_e}(°K) = 379 - 2.1 \times 10^5/\overline{M}_n \tag{2}$$

and

$$T_{g_e}(°K) = 453 - 3.1 \times 10^5/\overline{M}_n \tag{3}$$

The addition of a methyl substituent in the α position increased the value of T_{g_∞} from 379°K (for PS) to 453°K (for PαMS); however, the further addition of an isopropyl substituent in the paraposition decreased the value of T_g from 453°K (for PαMS) to 422°K (for PPIPαMS). Normally one would have expected PPIPαMS to have had a higher T_{g_∞} value than that of PαMS, because of the presence of the bulkier p-substituent in the former polymer. Similar results are reported on the T_{g_∞} of N,N-dimethylaminostyrene [7] and N,N-diethylaminostyrene [8], where the T_g of the latter polymer, in spite of the presence of a bulkier p-substituent than present on the former, has a relatively lower value.

These authors [7, 8] reported that the T_{g_∞} of N,N-dimethylaminostyrene is about 50° higher than that of polystyrene because of the presence of (a) the dipolar interactions between the substituted phenyl groups on the same and adjacent chains resulting in an overall chain stiffness and (b) increased interchain steric hindrance. Replacing the methyl groups of the N,N-dimethylaminostyrene by ethyl groups increases the bulkiness and flexibility of the N,N-dialkyl substituent thereby reducing the interchain steric hindrance as well as the chain stiffness and consequently reducing the value of T_{g_∞}.

The prime reason for ascribing these variations in T_{g_∞} to the improved flexibility of chains and reduced steric hindrances due to the bulk size of the substituents, rather than the free volume (θ) contribution of each chain end (θ), arises out of the fact that θ (calculated from Bueche's [13] equation relating the slope K in the plot of T_{g_e} as a function of $1/\overline{M}_n$, the polymer density ρ, and the difference $\Delta\alpha$ in the expansion coefficients in the liquid and the glass states) increases regularly from 80 Å^3 to 108 Å^3 to 134 Å^3 on changing from polystyrene to poly-N,N-dimethylaminostyrene and finally to poly-N,N-diethylaminostyrene but the T_{g_∞} yielded values of ~100°C, ~150°C and ~100°C, respectively. It would appear that the effect of the changes in the free volume of the polymer chain ends, due to increasing molecular weights, is small when compared to the swept free volume [8] associated with the bulkier para substituent.

The free volume θ in the case of PPIPαMS obtained from the K value of 3.6×10^5 and $\rho = 0.89$ (calculated from the molar volume data of the polymer [14] is about 100 Å^3. The θ values of PS and PαMS are 80 Å^3 [13] and 85 Å^3 [3]. The T_{g_∞} values of these three polymers, viz., PS, PαMS, and PPIPαMS, however, do not follow the increasing θ trend but show values of 379°K [1], 453°K [2], and 422°K, respectively. This indicates that, like the other study on the T_{g_∞} of poly-N,N-diethylaminostyrene [8], the presence of a bulkier substituent in PPIPαMS increases the flexibility of chains, thus causing better chain packing, less steric hindrance, and consequently lower T_{g_∞}.

Structure of PPIPαMS and Its Relation with T_g

Structure Determination. In an earlier study related to the polymerization of PIPαMS with BuLi-TMEDA [9, 11] it was reported that the ratios of the various types of protons (as calculated from the NMR spectra recorded in o-dichlorobenzene) in the polymers did not necessarily correspond to those observed in the monomer. For instance, in p-isopropyl-α-methylstyrene (PIPαMS) the ten proton-proton ratios, viz., iso-CH_3/H_B, iso-CH_3/α-CH_3, iso-CH_3/β-CH_2, iso-CH_3/CH, H_B/α-CH_3, H_B/β-CH_2, H_B/CH, α-CH_3/β-CH_2,

α-CH_3/CH and β-CH_2/CH are 1.5, 2, 3, 6, 1.3, 2, 4, 1.5, 3, 2, respectively. In a high molecular weight polymer, S-25, prepared with BuLi-TMEDA, these ratios were found to be 1.5, 1.6, 2.4, 5.8, 1.0, 1.5, 3.8, 1.5, 3.6, and 2.4, respectively. On the basis of these studies it was reported that the irregular structures in S-25 may have their origin from two possible reactions: isomerization involving the methine protons of the isopropyl group [15] and substitution or metalation in the benzene ring.

Keeping this in mind, the structures of most of the polymers used in the present study were carefully investigated so that a relatión between Tg_e and the molecular weight $\overline{M}_n$ might be established using only the data of polymers having similar proportions of the various protons. The approach used, however, was slightly different in the present case where, instead of calculating the ten proton-proton ratios, the number of different types of protons per monomer unit were calculated for all polymers and compared with those in the regular polymer of infinite molecular weight (4 H_B, 1 CH, 2 β-CH_2, 6 iso-CH_3 and 3 α-CH_3). The highlights of the NMR spectra recorded in o-dichlorobenzene at 100°C and in CCl_4 at 75°C are presented in Table 2. In o-dichlorobenzene, the zones where the resonances of different protons appear, are better defined than for the case when CCl_4 is the solvent where the contribution due to β-methylenes, isomethyls, and α-methyls is sometimes difficult to separate. Furthermore, in CCl_4, a part of the resonance due to rr triads is merged with that due to the internal standard TMS.

Based on these assignments, in Tables 3 and 4 are presented the structure analyses of the polymers from series S and F used in this study. The analyses presented in Table 3 (in o-dichlorobenzene) were carried out by adding the integrals of all of the protons situated between 7.0 and 10.0 τ and dividing the sum by 12 (1 $C\underline{H}$, 2 $C\underline{H_2}$, 6 iso-CH_3, 3 α-CH_3) which yielded a value corresponding to one proton and consequently the number of protons per monomer unit for different types of protons. The data listed in Table 4 were calculated for the region between 3 to 10 τ and by dividing the sum integral of this zone by 16 (4 H_B, 1 CH, 2 CH_2, 6 iso-CH_3, 3 α-CH_3). This gave a value for one proton which was used in analyzing different types of protons.

The structure analyses for all the polymers in Table 3 reveal the following information: (a) the number of CH protons remains constant at 1.0; (b) the number of β-methylenes increases and varies between 2.1 and 2.45; (c) the number of iso-CH_3 decreases and varies between 5.1 and 5.8; (d) the α-CH_3 protons show an increase, except in a few cases where these decrease (S-13 and S-9) or remain constant (S-20 and F-7); and (e) the propagation step for most polymers does not deviate much from Bernoullian statistics $P_{m/r} + P_{r/m} \lessapprox 1$ [16].

TABLE 2. NMR Parameters for Poly-p-isopropyl-α-methylstyrene in o-Dichlorobenzene and Carbon Tetrachloride.

	τ	
Type of proton	o-Dichlorobenzene [11]	Carbon tetrachloride
Benzene ($\underline{H}_B$)	-	3.0-4.1
Methine ($-\overset{\vert}{\underset{\vert}{C}}\underline{H}$)	7.05-7.4	7.0-7.5
Methylene ($-C\underline{H}_2-$)	7.9-8.6	7.8-8.7
Methyls of isopropyl $\left\{ \begin{array}{c} -CH \\ / \quad \backslash \\ \underline{H}_3C \quad C\underline{H}_3 \end{array} \right.$	8.7-9.9	8.7-9.0
Methyl (α) ($-C\underline{H}_3$)	9.0-9.9 9.06 (mm), 9.4 (mr), 9.7 (rr)	9.0-10.0 9.23 (mm), 9.57 (mr), 9.88 (rr)

TABLE 3. NMR Characterization of Poly-p-isopropyl-α-methylstyrene[a]

Sample	Structure of polymer per monomer unit				Intensity of triads due to α-methyl			Propagation statistics	
	$-\underline{C}H$	$-\underline{CH_2}-$	CH / \ $\underline{H_3C}$ CH_3	CH / \ $\underline{H_3C}$ CH_2- + α-CH_3	mm	mr	rr	$P_{m/r}$	$P_{r/m}$
S-4	1.0	2.3	5.3	3.5	0.25	0.43	0.32	0.46	0.40
S-13	1.0	2.3	5.8	2.9	0.21	0.47	0.32	0.53	0.42
S-2	1.0	2.5	5.1	3.4	0.17	0.43	0.40	0.56	0.35
S-10	1.0	2.1	5.4	3.4	0.20	0.44	0.36	0.57	0.38
S-11	1.0	2.5	5.3	3.2	0.25	0.44	0.31	0.47	0.41
S-8	1.0	2.3	5.4	3.2	0.19	0.45	0.36	0.54	0.38
S-20	1.0	2.3	5.7	3.0	0.18	0.45	0.37	0.56	0.38
S-22	1.0	2.2	5.6	3.2	0.20	0.43	0.37	0.52	0.37
S-9	1.0	2.3	5.8	2.8	0.17	0.46	0.37	0.57	0.38
S-5	1.0	2.2	5.7	3.1	0.20	0.46	0.34	0.53	0.40
S-16	1.0	2.3	5.4	3.3	0.21	0.44	0.35	0.51	0.39
S-18	1.0	2.3	5.1	3.6	0.16	0.41	0.43	0.56	0.32
S-23	1.0	2.3	5.4	3.2	0.21	0.43	0.36	0.51	0.37
F-7	1.0	2.3	5.7	3.0	0.16	0.39	0.45	0.55	0.30
S-27	1.0	2.4	5.3	3.3	0.19	0.39	0.42	0.51	0.32

(continued)

TABLE 3 (continued)

Sample	Structure of polymer per monomer unit				Intensity of triads due to α-methyl			Propagation statistics	
	$-\underline{CH}-$	$-C\underline{H}_2-$	CH / \\ $\underline{H_3}C$ $C\underline{H_3}$	CH / \\ $\underline{H_3}C$ CH_2- $+ \alpha$-$C\underline{H_3}$	mm	mr	rr	$P_{m/r}$	$P_{r/m}$
S-17	1.0	2.4	5.5	3.1	0.17	0.44	0.39	0.56	0.36
F-6	1.0	2.3	5.7	3.1	0.15	0.40	0.45	0.57	0.31
S-15	1.0	2.25	5.35	3.35	0.18	0.41	0.41	0.53	0.33
F-5	1.0	2.45	5.15	3.35	0.17	0.38	0.45	0.57	0.31
S-25	1.0	2.25	5.4	3.4	0.19	0.48	0.33	0.49	0.37

[a] Data of Léonard and Malhotra [11]. Spectra were recorded in o-dichlorobenzene at 100°C.

TABLE 4. NMR Characterization of Poly-p-isopropyl-α-methylstyrene[a]

	Structure of polymer per monomer unit					Intensity of triads due to α-methyl			Propagation statistics	
Sample	C_6H_4	$-\underline{CH}-$	$-C\underline{H_2}-$	CH / \ $\underline{H_3}$C C$\underline{H_3}$	CH / \ $\underline{H_3}$C C$\underline{H}_2$– + α-C$\underline{H_3}$	mm	mr	rr	$P_{m/r}$	$P_{r/m}$
S-4	3.7	1.0	2.8	5.6	0.5 + 2.3	0.15	0.45	0.40	0.60	0.36
S-14	3.8	0.9	2.05	6.15	0.35 + 2.7	0.17	0.47	0.36	0.58	0.39
S-13	3.8	0.95	2.35	6.0	0.25 + 2.65	0.20	0.47	0.33	0.54	0.41
S-2	4.0	1.05	2.1	6.05	2.85	0.17	0.45	0.38	0.57	0.37
S-21	3.7	0.9	1.9	6.15	0.4 + 2.9	0.17	0.47	0.36	0.58	0.39
S-11	4.0	1.0	2.2	5.8	3.0	0.25	0.43	0.32	0.46	0.40
S-8	3.9	0.95	2.0	6.0	0.2 + 3.0	0.17	0.45	0.38	0.57	0.37
S-20	3.9	1.0	2.0	6.05	3.05	0.21	0.43	0.36	0.50	0.37
S-22	3.8	0.9	2.2	6.1	3.0	0.18	0.45	0.37	0.55	0.38
S-9	3.8	0.85	1.9	6.2	3.2	0.22	0.44	0.34	0.50	0.39
S-5	3.95	1.0	2.0	5.85	0.2 + 3.0	0.18	0.46	0.36	0.56	0.39
S-16	3.7	0.85	2.7	5.75	3.0	0.22	0.44	0.34	0.50	0.39
S-18	4.0	0.8	2.4	5.3	0.3 + 3.2	0.17	0.47	0.36	0.58	0.39
S-23	3.8	1.0	2.4	6.0	2.7	0.18	0.45	0.37	0.55	0.38
S-27	3.8	1.0	2.3	6.0	2.8	0.17	0.40	0.43	0.54	0.32

(continued)

TABLE 4 (continued)

	Structure of polymer per monomer unit					Intensity of triads due to α-methyl			Propagation statistics	
Sample	C_6H_4	$-\overset{\vert}{\underset{\vert}{C}}\underline{H}$	$-C\underline{H_2}-$	CH / \\ $\underline{H_3}C\quad C\underline{H_3}$	CH / \\ $\underline{H_3}C\quad C\underline{H_2}-$ $+\ \alpha\text{-}C\underline{H_3}$	mm	mr	rr	$P_{m/r}$	$P_{r/m}$
S-17	3.9	0.9	2.2	6.0	2.9	0.19	0.44	0.37	0.54	0.37
S-1	4.0	1.0	2.4	5.9	2.6	0.17	0.44	0.39	0.56	0.36
S-15	4.0	0.95	2.05	6.1	2.95	0.13	0.45	0.42	0.63	0.35
S-19	4.0	0.85	2.0	5.7	3.4	0.21	0.44	0.35	0.51	0.39

[a] Spectra were recorded in CCl_4 at 75°C.

On the other hand, the analyses presented in Table 4 show a slightly different picture. Most of the polymers listed in Table 4 (with the exception of S-4, S-16, S-18, and S-19 where the β-methylenes increase and iso-CH_3 decrease) appear to be regular or very close to being regular products. The propagation step analyses, however, agree well with those obtained from the spectra in o-dichlorobenzene and show little deviation from Bernoullian statistics.

As it is difficult to distinguish which of these analyses is the more accurate, both have been retained for the present study.

Effect of Structural Differences on T_g. In Table 5 is presented a comparison (in the form of increase or decrease) of the number of different protons in the various PPIPαMS samples with those in the regular polymer. An increase in the number of a given type of protons is represented by (→), a decrease by (←), and a no change by (=). An examination of the results in Table 5 reveals that polymers with the same $\overline{M}_n$ and more or less the same $\overline{P}_d$ (S-2, S-21), (S-15, F-5), and (S-5, S-16, S-18) but exhibiting different T_{g_e} values have different structures. Although it is difficult to establish the exact contribution of each proton type towards T_{g_e} a general pattern may be established. It would appear that in polymers with identical $\overline{M}_n$ and $\overline{P}_d$ values, the one exhibiting the lower T_{g_e} has the following characteristics: a smaller number of benzene protons (S-21, S-16 and S-23) due to some substitution or the initiation of new chains in the ring (aromatic groups have been shown to contribute more towards T_g than aliphatic groups [17]); a lesser number of isopropyl groups converted to $-CH(CH_3)CH_2-$ (S-15), which appear to elevate T_g (F-5) (this finds support from earlier results which show that the addition of isopropyl groups at the para position in PαMS lowers its T_{g_∞} from 453°K to 422°K); a lesser number of α-CH_3 groups (S-23) which increase T_{g_e} (S-18) (T_{g_∞} of PS = 379°K and of PαMS = 453°K).

Polymers having the same $\overline{M}_n$ and similar structures may also have different T_{g_e} values if their polydispersity ratios are different (S-1, F-6), (S-15, F-5). It would appear that the shorter chain segments in the polydispersed polymers initiate and bring about the transition at a lower temperature.

Although most of the polymers studied agree well with the general trends of structure and polydispersity effects, samples S-23 and S-11 are the exceptions. Polymer S-23 has the same $\overline{M}_n$, slightly different structure, and a higher $\overline{P}_d$ as compared to that of S-9 but shows a T_{g_e} value which is 27°K lower than that of S-9. On the other hand, polymer

TABLE 5. Effect of Structural Differences (Data of Tables 3 and 4) and $\overline{P}_d$ on T_g

				Changes in proton content of PPIPαMS					
			T_{g_e} at $q = 1$				$-CH$ / \		
Sample	$\overline{M}_n \times 10^{-3}$	$\overline{P}_d$	(°K)	C_6H_4	$-C\underline{H}$	$-C\underline{H}_2-$	$\underline{H}_3C$ $C\underline{H}_3$	α - $C\underline{H}_3$	Comments
S-2	9	1.6	386	=	→	→	→	←	Table 4
S-21	9	1.4	378	←	←	←	→	→	
S-20	18	1.3	396	=	=	=	=	=	
S-22	19	1.4	388	←	←	→	←	=	
S-5	22	1.8	411	=	=	=	←	→	
S-16	22	2.2	392	←	←	→	←	=	
S-18	22	2.1	407	=	←	→	←	→	
S-9	24	1.6	404	←	←	←	→	→	
S-23	24	1.8	377	←	=	→	=	←	
S-15	68	4.0	410	-	=	→	←	→	Table 3
F-5	70	3.9	418	-	=	⇉	⇇	→	
S-11	10.5	3.2	364	-	=	→	←	→	Table 3
S-10	10.5	1.1	395	-	=	→	←	→	
S-1	47	4.1	408	-	=	→	←	←	Table 3
F-6	47	3.3	414	-	=	→	←	→	Table 4

S-11 has same $\overline{M}_n$ but a higher $\overline{P}_d$ as compared to that of S-10; yet the T_g of the former is 30°K lower than that of the latter. A difference of this magnitude in T_g cannot be ascribed solely to the high polydispersity index of S-11. These results show that besides $\overline{M}_n$, $\overline{P}_d$, and structural and configurational differences there are other parameters which must control T_g.

Further work on the effects of other substituents on T_g is in progress and the results of these studies will be reported on in due course.

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