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Polymerization of α -Methylstyrene with Potassium as Initiator. VIII. Glass Transition Temperature Study of Reaction Products

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ABSTRACT

A glass transition temperature (T_g) study on poly- α -methylstyrene samples having bimodal molecular weight distributions composed of components D + A and B + C, was carried out with a DSC-2 differential scanning calorimeter. T_g data were also collected on binary blends of poly- α -methylstyrene samples prepared from narrowly dispersed low and high molecular weight polymers. Extrapolated T_{g_e} (at $q = 1^\circ\text{K}/\text{min}$) data of the bimodal polymers showed that the percent proportion, the molecular weight \overline{M}_n , and the steric configuration of component D + A play an important role in determining their overall glass transition temperatures, these being lower than those recorded for a unimodal polymer of the same \overline{M}_n . In binary blends of poly- α -methylstyrene, the overall glass transition is not affected by the presence of the low molecular weight component

either because its steric structure differs with that of D + A or because of the fact that in binary blends the chain-end segments of the two components are not well packed.

INTRODUCTION

Gel permeation chromatographic (GPC) molecular weight distributions of poly- α -methylstyrene prepared from reactions initiated with potassium in tetrahydrofuran (THF) [1, 2], in p-dioxane [3], and in cyclohexane [4] were reported on earlier. It was shown that irrespective of the solvent used, the polymers prepared at temperatures above 298°K with high "living-end" concentrations [LE] have bimodal and sometimes even multimodal molecular weight distributions.

Nuclear magnetic resonance (NMR) studies [5, 6] of these polymers showed that the propagation reactions responsible for the formation of low D + A and high B + C molecular weight components obeyed Bernoullian statistics, the P_m value being somewhat higher for the former component. Based on these studies [5, 6] it was postulated that the reaction steps leading to the formation of D + A and B + C components were of a different nature.

Thermal decomposition [7] studies on these polymers showed that poly- α -methylstyrene samples prepared under different solvent conditions but having similar proportions of D + A and B + C components obeyed the following order of stability in the three solvents: bulk > p-dioxane > THF. Furthermore, a comparison of the decomposition results obtained with polymers made up of low and high molecular weight components and those made up exclusively of high molecular weight component showed that the presence of low molecular weight components enhanced the decomposition reaction in the former pairs.

Keeping in mind the results of these previous studies [1-7], it was thought of interest to explore the effect of these low molecular weight components on the glass transition temperatures (T_g) of their higher molecular weight counterparts as well as to compare the T_g values of multimodal and unimodal poly- α -methylstyrene samples [8] having the same number-average molecular weights M_n . The principal results of this study are outlined in the present paper.

EXPERIMENTAL

Materials

Anionically prepared [1-4] poly- α -methylstyrene samples showing by GPC bimodal or even multimodal molecular weight distributions and having \bar{M}_n values ranging from 2.6×10^3 to 40×10^3 were used in the present study (see Table 1 for polymerization data). Binary blends of polymer samples L-19, M-14 and L-19, L-15 were made in THF. The polymer mixtures were precipitated out with methanol and dried at 333°K under vacuum.

Gel-Permeation Chromatography (GPC)

Molecular weight distribution analyses of polymers were carried out with a Waters Associates Model 200 GPC operated in a constant temperature room ($298 \pm 0.5^\circ\text{K}$). The separating system consisted of five 8×1200 mm columns connected in series, each packed with crosslinked polystyrene gel having (by the Waters method) pore sizes of 1×10^6 , 1.5×10^5 , 3×10^3 , 250, and 60 Å, respectively. The flow of solvent, tetrahydrofuran degassed with nitrogen, was maintained at 1 ml/min while the concentration of polymer in the samples was limited to 0.25 wt % in order to render negligible "concentration effects" on the peak position in the chromatograms. Calibration of the instrument was performed with quasi monodispersed poly- α -methylstyrene samples whose weight-average molecular weights \bar{M}_w were calculated from intrinsic viscosity data at 303°K in toluene by using the relation reported in the literature [9]. Molecular weights were then computed by the summation method [10].

T_g Measurements

The T_g values were determined with a Perkin-Elmer model DSC-2 differential scanning calorimeter [8]. Polymer samples weighing 10 mg each were heated for a few seconds to a temperature 30°K above the estimated T_g in order to have a homogeneous system. After homogenizing, the sample was quenched through the glass transition region at a rate of $320^\circ\text{K}/\text{min}$ as suggested in the literature [11]. After quenching, T_g values of the polymer samples were determined by heating these at various rates q ($^\circ\text{K}/\text{min}$). To compare the present

TABLE I. Anionic Polymerization of α -Methylstyrene under Different Reaction Conditions

Sample	[Monomer] ₀ (mole/liter)	Initiator	[Initiator] (mole/liter)	Solvent	Initiation time at 298°K (min)	Reaction tempera- ture (°K)	Yield (base-mole) liter ^a
L-11	4.50	Potassium	0.23	THF	5	313	2.10
65	6.25	Potassium	0.63	THF	30	328	3.85
L-12	4.50	Potassium	0.28	THF	5	313	2.70
L-6	4.20	Potassium	0.10	p-dioxane	5	313	1.00
B	1.60	Potassium	0.08	p-dioxane	2	298	0.80
M-14	Bulk	BuLi-TMEDA	0.08	-	5	323	2.00
M-28	5.80	Potassium- anthracene	0.06	THF	2	248	1.00
59	5.80	Potassium	0.09	THF	10	323	1.31
43	5.80	Potassium	0.22	cyclohexane	5	313	3.20
64	6.70	Potassium	0.12	THF	20	333	1.47
L-15	2.20	Potassium- naphthalene	0.01	THF	2	195	1.90
L-26	4.50	Potassium	0.25	THF	5	313	3.00
L-1	2.75	Potassium- naphthalene	0.05	p-dioxane	2	298	0.90
47	5.17	Potassium	0.12	cyclohexane	5	313	1.92
L-5	2.75	Potassium	0.04	THF	2	298	0.90

L-3	2.75	Potassium	0.05	p-dioxane	2	298	0.84
L-27	4.50	Potassium	0.24	THF	5	313	3.43
69	6.45	Potassium	0.11	THF	15	323	2.00
58	5.85	Potassium	0.04	THF	10	323	0.78
44	5.17	Potassium	0.11	cyclohexane	5	313	2.15
63	6.70	Potassium	0.07	THF	20	333	2.10
57	6.44	Potassium	0.08	THF	15	323	1.88
L-4	2.75	Potassium	0.05	p-dioxane	2	278	1.74
56	5.82	Potassium	0.02	THF	10	323	0.63
26	5.55	Potassium	0.08	p-dioxane	5	313	2.80
L-19	6.00	Potassium	0.05	THF	10	298	5.10

^aAll polymerization runs were allowed to reach equilibrium before being quenched with methanol. Time of polymerization generally varied from 24 to 90 hr, depending on the experimental conditions.

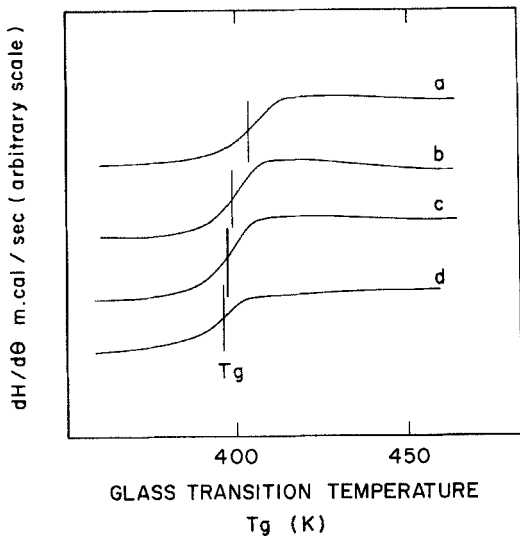


FIG. 1. Typical DSC-2 thermograms of unannealed poly- α -methylstyrene (sample L-5) obtained in the glass transition range at various heating rates: (a) 40°K/min; (b) 20°K/min; (c) 10°K/min; (d) 5°K/min. (See Table 2 for other data.)

data with those published earlier [8], a standard procedure was adopted whereby the T_g values at different heating rates were extrapolated to q values of 1°K/min (T_{g_e}) by using the plots of $\log q$ versus $1/T_g$ [12].

RESULTS AND DISCUSSION

In Fig. 1 are shown typical DSC-2 thermograms of an unannealed poly- α -methylstyrene sample L-5, obtained in the glass transition region at different q values. The T_g values determined at the $\Delta C_p/2$ point (the change in heat capacity with glass transition) for various heating rates were extrapolated to T_{g_e} . The principal results on the T_g values of bimodal poly- α -methylstyrene samples with \bar{M}_n ranging from 2.6×10^3 to 40×10^3 are summarized in Table 2. As might be expected, T_{g_e} increased with increasing \bar{M}_n of the polymer.

TABLE 2. Variation of T_g with Rate of Heating q ($^{\circ}\text{K}/\text{min}$) and with the Molecular Weight for Various Samples of Poly- α -methylstyrene

Sample	$\bar{M}_n \times 10^{-3}$	P_d	T_g ($^{\circ}\text{K}$)					$T_{g_c}^b$ ($^{\circ}\text{K}$)
			$q = 40$	$q = 20$	$q = 10$	$q = 5$	$T_{g_e}^a$ ($^{\circ}\text{K}$)	
L-11	2.6	3.1	311	310	309	308.5	307	358
65	2.9	8.6	322	321	318	315.5	310	353
L-12	2.9	3.1	324	323	322	-	319	364
L-6	2.9	2.0	333	333	331	330.5	328	352
B	2.9	1.4	350	347	345	345	341	348
M-14	3.0	1.2	368	366.5	364	363	361	350
M-28	3.8	2.8	382	380	377	376.5	371	372
L-3	4.0	1.6	372.5	370	367	366	361	375
59	4.4	6.1	348	344.5	343	338	331	385
43	4.5	7.0	363.5	361	360.5	-	354	386
64	4.6	5.7	359	358	357	-	354	387
L-15	4.7	1.3	396	393	391	389	387	387
L-26	4.7	6.1	351	346	342	-	328	380
L-1	4.8	1.7	381.5	379	377.5	377	373	387
47	4.9	5.7	367	364	363.5	363	359	390

(continued)

TABLE 2 (continued)

Sample	$\bar{M}_n \times 10^{-3}$	P_d	T_g ($^{\circ}\text{K}$)				T_{ge} ($q = 1$) ($^{\circ}\text{K}$) ^a	T_{gc} ^b ($^{\circ}\text{K}$)
			$q = 40$	$q = 20$	$q = 10$	$q = 5$		
L-5	5.1	1.7	402	398	397	396	390	391
L-27	5.5	7.9	341	338	335	-	325	394
69	5.9	11.2	355	353	351	-	345	403
58	6.0	7.0	387.5	386	385.5	385	383	401
44	6.0	5.3	375	374	373.5	373	372	409
63	10.3	8.7	417	414	411	410	404	424
57	10.5	6.8	401	400	399	-	397	430
L-4	10.7	1.6	418	414	411	409.5	402	425
56	11.7	5.5	421	419	418	416.5	413	425
26	17.1	3.5	436	434	433	431.5	428	435
L-19	39.7	3.2	453.5	450	449	447	444	444

^a Values extrapolated by using the relation $\log q = a - b/T_g$ [8, 12, 13].

^b Calculated by using Eq. (6) of Blanchard et al. [12].

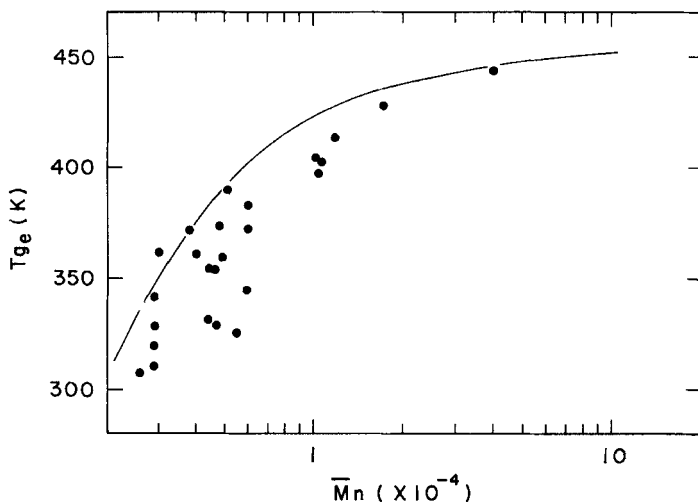


FIG. 2. Fitting of the extrapolated ($q = 1$) T_{g_e} values of the present study on the T_{g_e} vs. \bar{M}_n curve prepared with unimodal poly- α -methylstyrene samples [8]. (See Table 2 for other data.)

In Fig. 2 is shown a fit of the present data on the plot of T_{g_e} as a function of \bar{M}_n for low polydispersity ($P_d = \bar{M}_w/\bar{M}_n$) samples of poly- α -methylstyrene [8]. Polymers with high polydispersity do not fall on the curve. Furthermore, polymers with identical \bar{M}_n but different polydispersity showed interesting results, the T_{g_e} values in the case of higher polydispersity polymers being generally lower and deviating more from the curve. These results are similar to those obtained in the glass transition temperature studies carried out with polystyrene [12] and poly(*p*-isopropyl α -methylstyrene) samples [13] of varying polydispersity, where it was suggested that the shorter chain segments in the dispersed polymers initiate and bring about the transition at a lower temperature.

In the case of polymers having broad molecular weight distributions, \bar{M}_n and polydispersity values may be reasonably sufficient to characterize them for T_g purposes. This however, may not be so with polymers having bimodal molecular weight distributions, where,

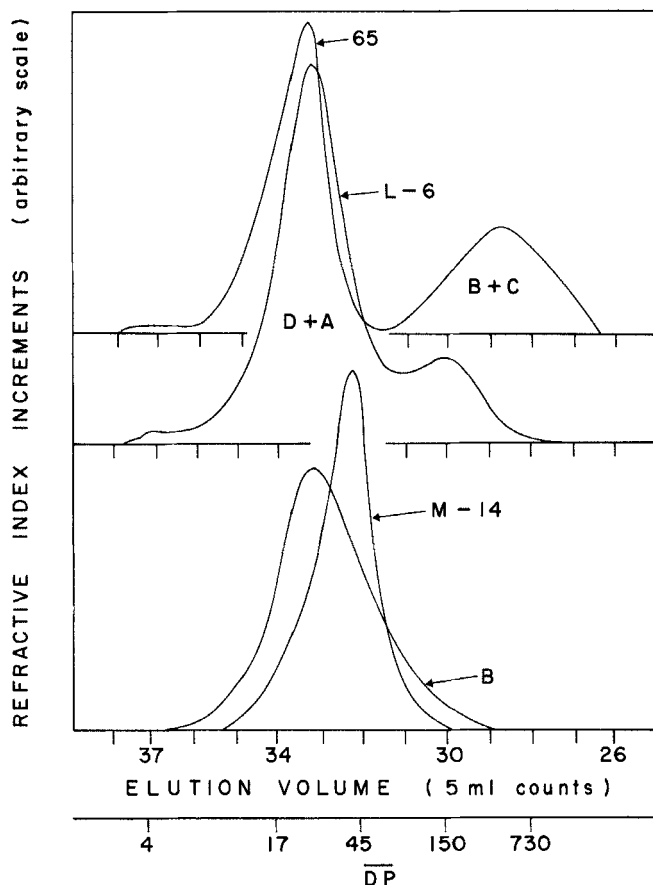


FIG. 3. GPC molecular weight distributions of poly- α -methylstyrene samples 65, L-6, B, and M-14. (See Table 1 for other data.)

for similar overall \overline{M}_n values, the proportion of low and high molecular weight components, their individual molecular weights, and their polydispersity may not be the same. As a consequence, different T_g values would result. In such cases a correlation between the glass transition data of polymers and their GPC molecular weight distributions may yield valuable information.

In Fig. 3 are shown the GPC molecular weight distributions of

poly- α -methylstyrene samples 65, L-6, B, and M-14, whose average \bar{M}_n values are the same ($\sim 2.9 \times 10^3$) but whose T_{ge} values are different. The analyses of these curves, in terms of the proportions and the \bar{M}_n values of low as well as high molecular weight components, are presented in Table 3 which also carries GPC and NMR data for all of the polymers listed in Table 2. From Fig. 3 it is evident that as one moves from poly- α -methylstyrene sample 65 to L-6, to B and finally to M-14, the peak maxima of component D + A move toward a lower elution volume (higher molecular weight) and those of component B + C move toward a higher elution volume (lower molecular weight) resulting in a decrease of their polydispersity but, keeping the \bar{M}_n constant around 2.9×10^3 .

The T_{ge} values of polymer samples 65 (310°K), L-6 (328°K), B (341°K), and M-14 (361°K) which show regular increases may now be related directly to the increasing \bar{M}_n of component D + A and decreasing \bar{M}_n of component B + C. The glass transition value (noted from the curve in Fig. 2) for a narrowly dispersed polymer with an \bar{M}_n of 2.9×10^3 is in the vicinity of 350°K. The calculated T_g values (T_{gc}) for samples 65, L-6, B, and M-14, based on the proportions of components D + A and B + C and their individual \bar{M}_n data [12], were 353, 352, 348 and 350°K, respectively, which are higher than their respective T_{ge} values. In the case of polymer samples 65 and L-6 (both with an \bar{M}_n of 2.9×10^3 but one carrying 63% of component D + A with an \bar{M}_n of 1.9×10^3 and the other 83% of component D + A with an \bar{M}_n of 2.6×10^3 , respectively), their overall T_{ge} of 310 and 328°K correspond to T_{ge} of narrowly dispersed polymers having an \bar{M}_n of 2.1×10^3 and an \bar{M}_n of 2.4×10^3 , respectively. This would suggest that the overall T_{ge} values of polymer samples 65 and L-6, are in reality the T_{ge} values of their respective lower molecular weight components D + A.

If it is true that the glass transition temperatures of polymers with bimodal molecular weight distributions are controlled by their lower molecular weight components D + A, it should also be interesting to see the role played by the steric configuration of this component on the overall T_{ge} . It is well known that poly(methyl methacrylate) samples of identical \bar{M}_n but carrying varying proportions of isotactic (mm), heterotactic (mr), and syndiotactic (rr) sequences yield different

TABLE 3. Intensities Associated with Various Configurations of the Low (D + A) and High (B + C) Molecular Weight Components (Deduced from Their Methyl Protons) of Poly- α -methylstyrene by Use of NMR Spectroscopy and GPC Analyses of These Polymers

Sample	GPC data ^a						NMR data ^b						
	D + A		B + C		D + A		B + C		D + A		B + C		
	%	$\bar{M}_n \times 10^{-3}$	%	$\bar{M}_n \times 10^{-3}$	%	mm	mr	rr	P_m	%	P_m	%	P_m
L-11	77	2.1	23	19.5	55	0.14	0.51	0.35	0.39	45	0.27	45	0.27
65	63	1.9	37	29.5	52	0.19	0.51	0.30	0.45	48	0.28	48	0.28
L-12	64	2.2	36	25.0	53	0.14	0.53	0.33	0.39	47	0.27	47	0.27
L-6	83	2.6	17	14.6	53	0.13	0.51	0.36	0.38	47	0.27	47	0.27
B	100	2.9	-	-	47	0.11	0.46	0.43	0.34	53	0.26	53	0.26
M-14	100	3.0	-	-	49	0.08	0.41	0.51	0.29	51	0.22	51	0.22
M-28	70	2.8	30	20.0	35	0.11	0.48	0.42	0.35	65	0.26	65	0.26
L-3	50	2.5	50	10.0	33	0.12	0.43	0.45	0.34	67	0.25	67	0.25
59	50	2.3	50	38.0	38	0.16	0.50	0.34	0.40	62	0.26	62	0.26
43	63	3.0	37	40.0	27	0.11	0.46	0.43	0.33	73	0.25	73	0.25
64	45	2.3	55	31.0	37	0.16	0.47	0.37	0.40	63	0.26	63	0.26
L-15	100	4.7	-	-	23	0.09	0.29	0.62	$P_{m/r} = 0.62$	77	0.26	77	0.26
									$P_{r/m} = 0.19$				

L-26	56	2.4	44	40.0	35	0.15	0.51	0.34	0.39	65	0.28
L-1	67	3.6	33	13.0	30	0.16	0.46	0.38	0.40	70	0.21
47	60	3.2	40	24.0	22	0.10	0.45	0.45	0.33	78	0.26
L-5	60	3.6	40	13.0	24	0.11	0.40	0.49	0.33	76	0.25
L-27	44	2.5	56	60.0	33	0.14	0.50	0.36	0.39	67	0.30
69	38	2.4	62	58.0	30	0.16	0.50	0.34	0.40	70	0.25
58	50	3.2	50	50.0	26	0.15	0.44	0.41	0.38	74	0.26
44	60	3.8	40	50.0	21	0.10	0.44	0.46	0.33	79	0.25
63	19	3.0	81	41.0	18	0.14	0.44	0.42	0.36	82	0.25
57	27	3.3	73	53.0	20	0.15	0.45	0.40	0.38	80	0.24
L-4	26	4.4	74	21.5	13	0.12	0.38	0.50	0.34	87	0.24
56	22	3.4	78	40.0	16	0.15	0.44	0.41	0.38	84	0.25
26	37	8.0	63	51.0	-	-	-	-	-	100	0.26
L-19	6	-	94	40.0	2	-	-	-	-	98	0.26

^aData of Leonard and Malhotra [1-4].

^bData of Malhotra [5, 6].

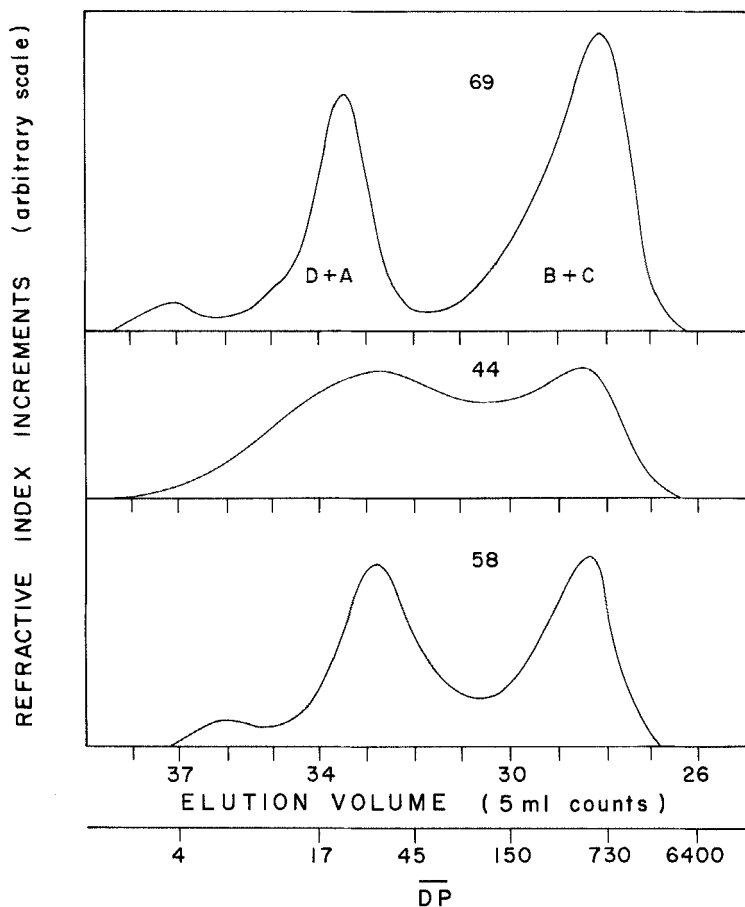


FIG. 4. GPC molecular weight distributions of poly- α -methylstyrene samples 69, 44, and 58. (See Table 1 for other data.)

T_{g_e} values, the value of the syndiotactic polymer being generally higher than that of the isotactic polymer [14]. In Table 3 are listed the intensities of mm, mr, rr triads as well as the Bernoullian propagation statistics value P_m of various polymers. One notes that the increasing order of T_{g_e} values and that of the increasing syndiotacticity (decreasing P_m value) follow the same pattern: M-14 > B > L-6 > 65.

In Fig. 4 are shown the GPC molecular weight distributions of poly- α -methylstyrene samples 69, 44, and 58 having the same \bar{M}_n ($\sim 6.0 \times 10^3$) but showing T_{ge} values of 345, 372, and 383°K, respectively. From Fig. 4 it may be noted that as one moves from samples 69 to 44 and finally to 58 the peak maxima of lower molecular weight component D + A shifts towards a lower elution count whereas that of component B + C remains stationary at an elution count of about 28.5 (142.5 ml).

The increasing T_{ge} values of polymer samples 69, 44, and 58 may be ascribed to varying proportions of components D + A and B + C as well as the increasing \bar{M}_n of the former component (see Table 3). The glass transition temperature for a narrowly dispersed polymer with an \bar{M}_n of 6.0×10^3 (noted from the curve in Fig. 2) is about 402°K. The T_{gc} values of polymer samples 69, 44, and 58, computed from the proportions of their components D + A and B + C and their individual \bar{M}_n values, are 403, 409, and 401°K, respectively, which are higher than their T_{ge} values but which agree well with those noted from the curve in Fig. 2. In the case of polymer samples 69 and 58 (both with $\bar{M}_n = 6.0 \times 10^3$ but one carrying 38% of component D + A with an \bar{M}_n of 2.4×10^3 and the other 50% of component D + A with an \bar{M}_n of 3.2×10^3), the overall respective T_{ge} values of 345 and 383°K correspond to T_{ge} of narrowly dispersed polymers having \bar{M}_n of 2.8×10^3 and \bar{M}_n of 4.5×10^3 . This would mean that the overall T_{ge} values of polymer samples 69 and 58 do not correspond rigorously to the T_{ge} of their components D + A and that the control of component D + A on the overall T_{ge} starts to decrease once its \bar{M}_n is greater than 2.5×10^3 and its proportion in the mixture is less than 50%.

In Fig. 5 are shown the GPC molecular weight distributions of poly- α -methylstyrene samples 57, L-4, and 63 having the same \bar{M}_n ($\sim 10.5 \times 10^3$) and showing similar T_{ge} values of 397, 402, and 404°K. The glass transition temperature of a narrowly dispersed polymer with an \bar{M}_n of 10.5×10^3 is about 433°K. The T_{ge} values of polymer samples 57, L-4, and 63 computed from the proportions of components D + A and B + C and their individual \bar{M}_n were 430, 425, and 424°K, respectively. One notes that, in spite of the low proportions ($\sim 25\%$) of component D + A as well as the relatively higher

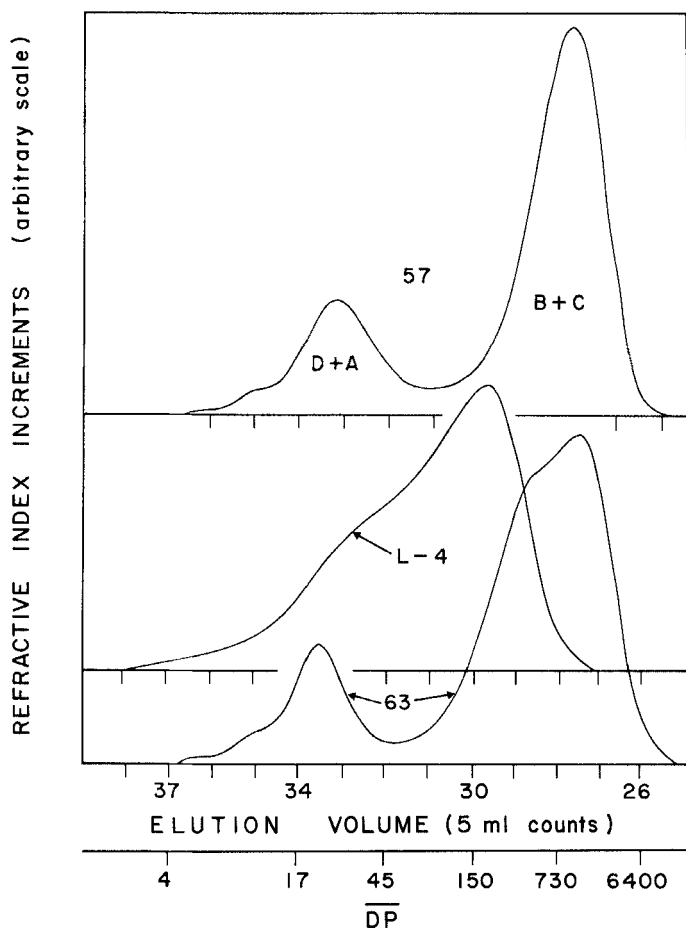


FIG. 5. GPC molecular weight distributions of poly- α -methylstyrene samples 57, L-4, and 63. (See Table 1 for other data.)

\bar{M}_n (3.0×10^3 for sample 63, 3.3×10^3 for sample 57, 4.4×10^3 for sample L-4, see Table 3), the effect of component D + A on the overall T_{ge} of these polymers is still significant. Furthermore, it would appear that the T_g values recorded for polymer samples 57, L-4, and 63 are also being affected by the higher molecular weight

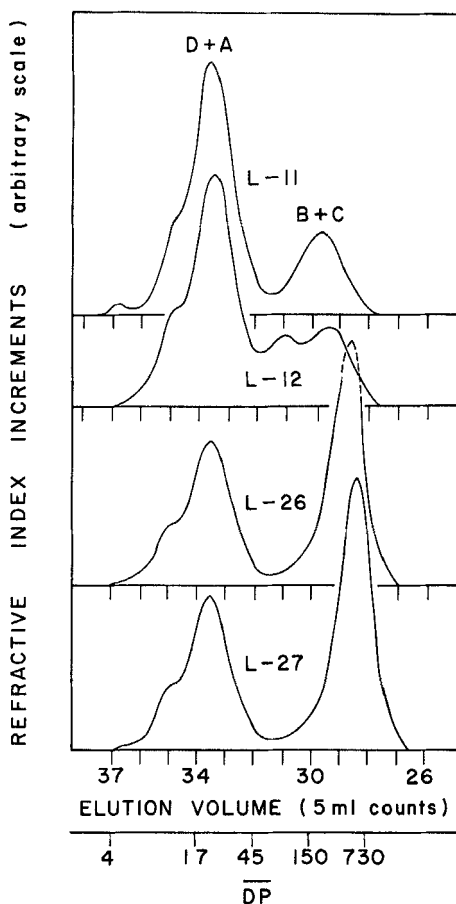


FIG. 6. GPC molecular weight distribution of poly- α -methylstyrene samples L-11, L-12, L-26, and L-27. (See Table I for other data.)

component B + C, whose similar proportions ($\sim 75\%$) but different individual \bar{M}_n (21.5×10^3 for sample L-4, 41.0×10^3 for sample 63 and 53×10^3 for sample 57) contribute to different extents towards the overall T_{g_e} values.

Based on the results of these studies, the overall low T_{g_e} of poly- α -methylstyrene samples may be attributed to the combined effect of

the following variable parameters: (a) proportion, \bar{M}_n , and steric configuration of component D + A; (b) \bar{M}_n of component B + C.

In order to study the individual importance of these parameters a few other polymer samples were selected where at a given time one or two of the above mentioned parameters were kept under control.

In Fig. 6 are shown the GPC molecular weight distributions of poly- α -methylstyrene samples L-11, L-12, L-26, and L-27 having different \bar{M}_n values and carrying different proportions of components D + A which in turn possess similar \bar{M}_n and identical steric configurations (see Table 3). The overall T_{ge} values of polymer samples L-11, L-12, L-26, and L-27 are 310, 319, 328, and 325°K, respectively. The glass transition temperature values of component D + A alone for polymer samples L-11, L-12, L-26, and L-27 are 310, 316, 326, and 330°K, respectively, indicating clearly the dominating effect of this component on the overall T_g measurements.

Based on these results one would have to conclude that the presence of low molecular weight ($\sim 2.5 \times 10^3$) component D + A in the bimodal polymers initiates the glass transition phenomenon at an earlier stage compared to other samples having the same \bar{M}_n but with less significant proportion of component D + A in them. These results agree well with those of Odani et al. [15], who measured dynamic viscoelastic properties of copolymer (styrene-butadiene-styrene) samples at low frequencies and reached the conclusion that in each polystyrene domain the mobility of two thirds or more segments is enhanced to the level of the rest of the segments.

Studies related to the glass transition (T_g) and liquid-liquid transition ($T_{\ell\ell}$) of polystyrene binary blends have been reported in the literature [16]. These studies showed that when the molecular weights of both components in the binary mixture were below the critical molecular weight M_c ($< 2.0 \times 10^4$), T_g and $T_{\ell\ell}$ versus $1/\bar{M}_n$ plots yielded straight lines, indicating that these transitions depended on the total number of chains regardless of the degree of dispersity. When the molecular weight (9.6×10^3) of one of the components is less than M_c and the molecular weight (111×10^3) of the second component is greater than M_c , a single glass transition temperature was observed, although $T_{\ell\ell}$ showed a complex behavior. In the T_g versus $1/\bar{M}_n$ plot, two linear regions were observed which intersected at an \bar{M}_n of $\sim 5.0 \times 10^4$.

With a view to exploring further this glass transition behavior of

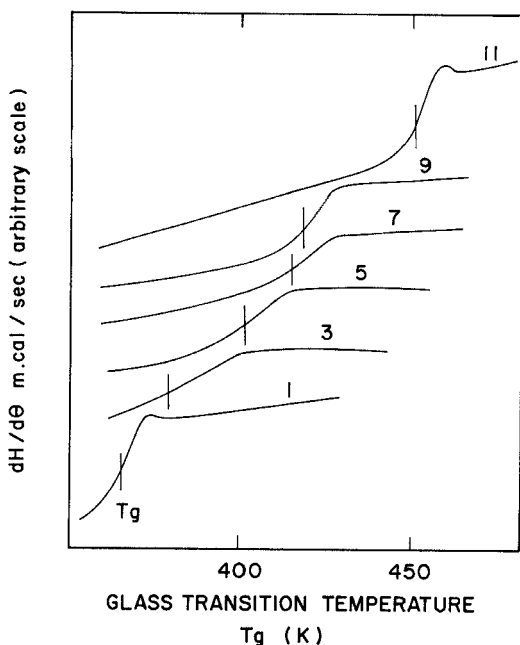


FIG. 7. DSC-2 thermograms obtained in the glass transition range at a q value of $20^\circ\text{K}/\text{min}$ with binary blends of poly- α -methylstyrene samples L-19 and M-14. (See Table 4 for other data.)

binary blends, two sets of polymer mixtures were prepared: (a) those involving poly- α -methylstyrene samples M-14 (\bar{M}_n of 3.0×10^3) and L-19 (\bar{M}_n of 39.7×10^3); (b) those involving poly- α -methylstyrene samples L-15 (\bar{M}_n of 4.7×10^3) and L-19 (\bar{M}_n of 39.7×10^3).

The primary reason for selecting polymer samples M-14 and L-15 for this study is that these fall in the molecular weight range (2.5 to 5.0×10^3) where the effect of component D + A on the overall T_{g_e} of the polymers studied earlier is very significant.

In Figs. 7 and 8 are shown the DSC-2 thermograms obtained in the glass transition range at a q value of $20^\circ\text{K}/\text{min}$ with various binary blends of poly- α -methylstyrene samples L-19 and M-14 (Fig. 7) as well as samples L-19 and L-15 (Fig. 8). These DSC-2 curves resemble those obtained with differential thermal analysis (DTA) [16] for polystyrene blends of molecular weights $\bar{M}_n = 2.05 \times 10^3$

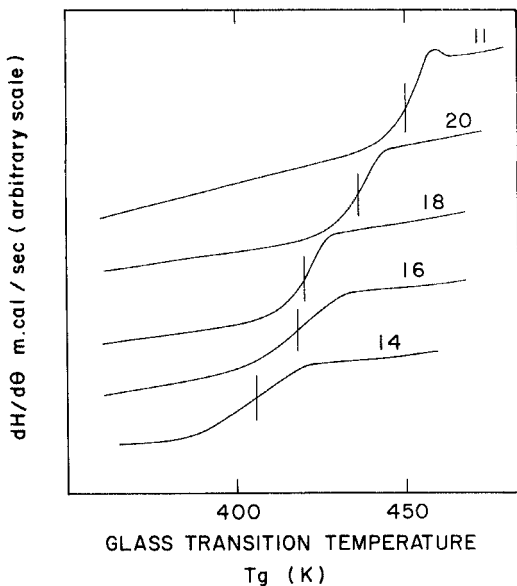


FIG. 8. DSC-2 thermograms obtained in the glass transition range at a q value of $20^\circ\text{K}/\text{min}$ with binary blends of poly- α -methylstyrene samples L-19 and L-15. (See Table 5 for other data.)

and $\bar{M}_n = 20.2 \times 10^3$ where T_g depended solely on the total number of chain ends. They are different, however, from those prepared with polystyrene blends of molecular weights $\bar{M}_n = 9.6 \times 10^3$ and $\bar{M}_n = 111 \times 10^3$ [16].

From the DSC-2 curves recorded at different q values with binary blends of poly- α -methylstyrene samples L-19 and M-14 as well as samples L-19 and L-15, T_{g_e} (at $q = 1$) data were collected and are presented in Tables 4 and 5, respectively. By making use of these data, T_{g_e} versus $1/\bar{M}_n$ plots were traced, and these are shown in Figs. 9 and 10. One notes that the plots of T_{g_e} versus $1/\bar{M}_n$ in Figs. 9 and 10 do not resemble those prepared for polystyrene blends of $\bar{M}_n = 2.05 \times 10^3$ and $\bar{M}_n = 20.2 \times 10^3$ but correspond to polystyrene blends of $\bar{M}_n 9.6 \times 10^3$ and $\bar{M}_n = 111 \times 10^3$ [16]. The two linear regions in the T_{g_e} versus $1/\bar{M}_n$ plots prepared with poly- α -methylstyrene

TABLE 4. Variation of T_g with Rate of Heating q ($^{\circ}\text{K}/\text{min}$) and with the Molecular Weight for Various Blends of Poly- α -methylstyrene Samples L-19 and M-14

Sample	Proportion (%)		$\bar{M}_n \times 10^{-3}$	P_d	T_g ($^{\circ}\text{K}$)					T_{ge} ($^{\circ}\text{K}$)	T_{gc} ($^{\circ}\text{K}$)
	L-19	M-14			$q = 40$	$q = 20$	$q = 10$	$q = 5$			
1	0	100	3.0	1.2	368	366.5	364	363	361	361	361
2	10	90	3.3	4.8	368.5	367	365	363.5	361	361	369
3	20	80	3.7	7.6	380.5	378	375.5	-	367	367	378
4	30	70	4.15	9.8	386	384	382	381.5	377	377	386
5	40	60	4.8	11.0	402	400	399.5	395.5	391	391	394
6	50	50	5.6	11.7	400	399	-	-	395	395	402
7	60	40	6.7	11.5	413	410	408	407.5	402	402	411
8	70	30	8.5	10.6	412	410	408	-	402	402	419
9	80	20	11.5	8.9	422	417.5	417	416	413	413	427
10	90	10	17.9	6.4	431.5	428.5	426	424.5	419	419	436
11	100	0	39.7	3.2	453.5	450	449	447	444	444	444

TABLE 5. Variation of T_g with Rate of Heating q ($^{\circ}\text{K}/\text{min}$) and with the Molecular Weight for Various Blends of Poly- α -methylstyrene Samples L-19 and L-15

Sample	Proportion		$\bar{M}_n \times 10^{-3}$	P_d	T_g ($^{\circ}\text{K}$)				T_{ge} ($^{\circ}\text{K}$)	T_{gc} ($^{\circ}\text{K}$)
	L-19	L-15			$q = 40$	$q = 20$	$q = 10$	$q = 5$		
12	0	100	4.7	1.3	396	393	391	389	387	387
13	10	90	5.1	3.5	401	399	398.5	398	395	393
14	20	80	5.7	5.3	406	404	402	401.5	397	398
15	30	70	6.4	6.6	410	408	407	405.5	402	404
16	40	60	7.3	7.5	416	413	411.5	411	406	410
17	50	50	8.4	7.9	422	418	417	416.5	410	415
18	60	40	10.0	7.9	423	419	418	417	411	421
19	70	30	12.3	7.4	432	429	427	425.5	420	427
20	80	20	16.0	6.4	439	435	432	431.5	424	433
21	90	10	22.7	5.1	443	439	437	435	428	438
11	100	0	39.7	3.2	453.5	450	449	447	444	444

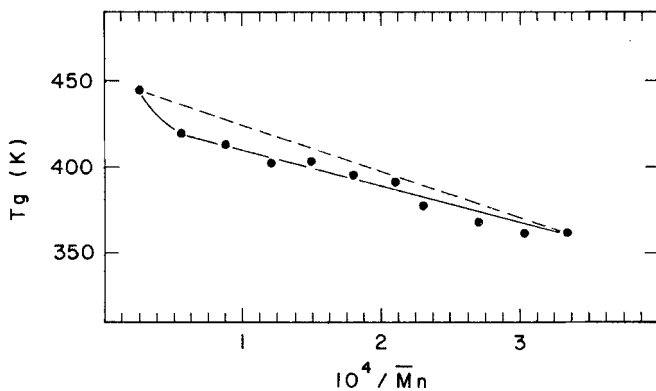


FIG. 9. Extrapolated T_{g_e} values (to $q = 1$) as a function of $1/\bar{M}_n$ for blends of poly- α -methylstyrene samples L-19 and M-14. (See Table 4 for other data.)

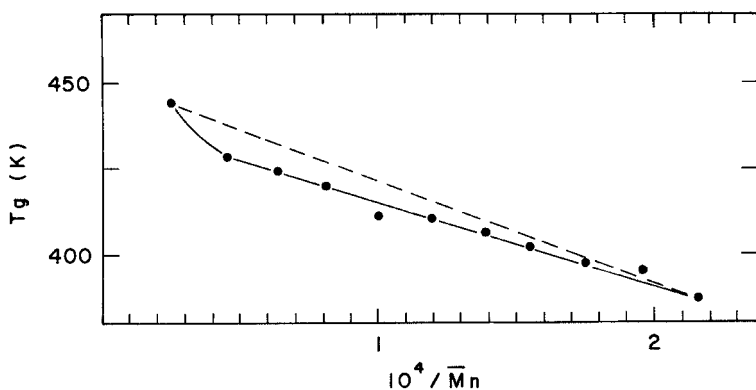


FIG. 10. Extrapolated T_{g_e} values (to $q = 1$) as a function of $1/\bar{M}_n$ for blends of poly- α -methylstyrene samples L-19 and L-15. (See Table 5 for other data.)

samples intersect at $\bar{M}_n = 17.9 \times 10^3$ (for L-19 and M-14) and $\bar{M}_n = 22.7 \times 10^3$ (for L-19 and L-15). It is probable that with other binary blends, this point of intersection may be still higher.

Another observation which is relevant to this study is that in the binary blends of polymer samples L-19 and M-14 ($\bar{M}_n = 3 \times 10^3$) the effect of the latter polymer in lowering the T_{g_e} is more significant than noted with L-15 ($\bar{M}_n = 4.7 \times 10^3$) in the L-19 and L-15 blends.

The T_{g_e} results of binary blends presented in Tables 4 and 5, however, do not correspond to the T_{g_e} of the lower molecular weight component M-14 (Table 4) or L-15 (Table 5) and are different from those obtained with poly- α -methylstyrene samples (Tables 1 to 3) having bimodal or multimodal distributions made up of components D + A and B + C where component D + A seemed to initiate T_g at a lower temperature. The T_{g_e} results in Tables 4 and 5 tend to refute the concept that the low molecular weight component of a dispersed polymer may initiate an earlier transition to glass.

A plausible explanation for the T_{g_e} in binary blends of M-14 and L-19 as well as L-15 and L-19 not corresponding to those of their low molecular weight counterparts may be found in their steric structures. The propagation reaction of the NMR-characterized [5, 6] low molecular weight component D + A in M-14 obeys Bernoullian statistics with a P_m value of 0.29. That of the corresponding NMR-characterized B + C component has a P_m of 0.22. The propagation reaction of the NMR characterized component D + A in L-15 follows first-order Markov statistics with a $P_{m/r}$ of 0.62 and a $P_{r/m}$ of 0.19. That of component B + C obeys Bernoullian statistics with a P_m of 0.26. The NMR-characterized components D + A in poly- α -methylstyrene samples L-11, L-12, L-26, L-27, 65, and L-6 where the overall T_{g_e} values correspond to those of component D + A have P_m values of 0.39 or higher. This would mean that component D + A has to have more of the isotactic sequences to be effective in bringing down the overall T_{g_e} values.

As reported earlier [1-6], the character of component D + A, i. e., its dormant nature, limiting molecular weight, and different steric structure to that of component B + C, may have a specific influence on T_g . A comparison of the thermal decomposition [7] results obtained with polymers built up of low (D + A) and high (B + C) molecular weight components and those made up exclusively of the high

molecular weight component also showed that the presence of component D + A enhanced the decomposition reaction. It appears that in poly- α -methylstyrene samples, prepared anionically [1-4] and made up of components D + A and B + C, the presence of the former component improves the total chain packing, reduces the steric hindrance and consequently lowers the overall T_{ge} . In binary blends of poly- α -methylstyrene samples, the introduction of component D + A to another component B + C somehow does not achieve the same goal. It is quite probable that the structure of component D + A may not be of much significance in the chain packing phenomenon and it is the mode of polymer preparation which is responsible for the quality of chain packing thus resulting in different T_{ge} values in the above cases.

CONCLUSIONS

The principal conclusions to be drawn from the present study may be summed up as follows.

In poly- α -methylstyrene samples prepared with potassium as initiator and built up of components D + A and B + C, the overall T_{ge} values are influenced by the following factors: (a) proportion, \bar{M}_n value, and steric configuration of component D + A. (b) \bar{M}_n of component B + C.

A comparison of T_{ge} data obtained for binary blends of poly- α -methylstyrene samples L-19 and M-14 as well as L-19 and L-15 with those obtained with anionically prepared bimodal poly- α -methylstyrene samples (having D + A and B + C components) showed that in the latter polymers the chains are well packed with less steric hindrance and consequently lower T_{ge} values. In binary blends of poly- α -methylstyrene the chain packing is not adequate to have the same effect.

Further work is in progress on the effect of different substituents on the glass transition of polystyrene and will be reported on in due course.

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