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

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ABSTRACT

Glass transition temperature (T_g) studies on poly-α-methylstyrene having $\overline{M}_n$ values ranging from 2.9×10^3 to 7.0×10^4 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) = $453 - 3.1 \times 10^5/\overline{M}_n$. The enthalpy change ΔH observed near the glass transition temperature drops to zero for zero annealing time and zero extrapolated heating rate conditions, suggesting that it is not necessary to postulate a first order transition to account for energy absorption. Operating with longer annealing periods or low heating rates yields similar trends as far as the ΔH values are concerned. T_g extrapolated to zero ΔH for zero extrapolated heating rate conditions was found to increase with increasing annealing time.

INTRODUCTION

The glass transition temperature T_g of polymers has been the subject of numerous studies during the past decades. The principal observations retained from the literature and pertaining to these studies are discussed in recent review articles [1-3]. The glass transition process is generally defined as an apparent second-order transition originating from kinetic [4-7] or thermodynamic [8, 9] limitations on the rates of internal adjustments required by changes in temperature. This is further confirmed from the experimental data, which show that the measured T_g values vary on changing both the heating [10-16] and the cooling rates [17, 18]. Furthermore, the time and temperature of annealing [19-23] used to condition a polymer sample prior to making a T_g measurement are known to affect the final value. The T_g of polymers are also dependent on their molecular characteristics, e.g., molecular weights [4-7, 15, 24, 25], substituents and their bulk size [1, 26-30], tacticity [24, 31-34], and polydispersity [15].

In an earlier report from this laboratory [15] in which the effects of molecular weight and polydispersity on the glass transition temperature of polystyrene had been studied with a Perkin Elmer DSC-1 differential scanning calorimeter, it was speculated that the glass transition phenomenon carried with it a positive heat effect, at least in the case of polystyrene, where an experimental enthalpy of 0.6 cal/g was obtained at conditions extrapolated to zero heating rate.

To verify this unusual observation whereby enthalpy was associated with the T_g of polystyrene, it was thought of interest to see if similar results would be obtained with a better instrument and a different polymer. With this in view, T_g measurements were made on poly-α-methylstyrene by use of the more recent DSC-2 instrument, which enables one to obtain T_g values at very low heating rates. The results of this study are the subject of the present communication.

EXPERIMENTAL

Materials

Anionically prepared [35, 36] poly-α-methylstyrene samples showing unimodal molecular weight distributions by gel-permeation chromatography (GPC) and having number-average molecular weights $\overline{M}_n$ ranging from 2.9×10^3 to 7.0×10^4 were used in the present study (see

Table 1 for polymerization data). The GPC instrument was calibrated with monodisperse poly-α-methylstyrene samples whose weight-average molecular weights $\overline{M}_w$ were calculated from intrinsic viscosity data obtained at 30°C in toluene by using a relation reported in the literature [37].

T_g Measurements

The T_g values were determined with a Perkin-Elmer model DSC-2 differential scanning calorimeter equipped with an auto-zero scanning device that provides near-perfect base lines. The polymer samples, weighing 10 mg each, were placed in standard DSC aluminum pans. A similar but empty aluminum pan was used on the reference side of the instrument. Both sample and reference pans were closed with aluminum covers and sealed with the special press designed for the purpose. The pans were then placed in the cell compartments of the DSC instrument, where a continuous stream of pure dry helium is made to flow at a rate of 20 cm^3/min. In order to have a homogeneous polymer sample, it was heated for a few seconds to a temperature 30°C above the T_g estimated from a preliminary run. After homogenizing, the sample was quenched through the glass transition region at a rate of 320°K/min as is suggested in the literature [3]. After quenching, T_g values of the polymer samples were determined by heating these at various rates. Measurements were also made on annealed samples where prior to quenching, the samples were heated for given times at a temperature slightly below their T_g.

RESULTS AND DISCUSSION

In Fig. 1 are shown typical DSC thermograms of an unannealed poly-α-methylstyrene (sample 3), obtained in the glass transition region at different heating rates, q (°K/min). The T_g values determined as suggested in the literature [3] at the $\Delta C_p/2$ point (the change in heat capacity with glass transition) were found to increase with increasing values of q. To compare DSC data with values obtained by other techniques (e.g., DTA), a standard procedure was adopted whereby the T_g values were measured at several heating rates after which the extrapolated T_{g_e} values at a heating rate of 1°K/min were obtained from plots of log q versus $1/T_g$. The

TABLE 1. Anionic Polymerization of α-Methylstyrene under Different Reaction Conditions

Sample	$[\text{Monomer}]_0$ (mole/ liter)	Initiator	[Initiator] $\times 10^2$ (mole/ liter)	Solvent	Reaction time (hr)	Reaction temperature (°C)	Yield (base-mole/ liter)	Molecular weight (GPC) $\times 10^{-3}$		$\overline{M}_w / \overline{M}_n$
								$\overline{M}_w$	$\overline{M}_n$	
B	1.6	K	8.0	p-dioxane	96	25	0.8	4.0	2.9	1.4
M-14	7.2	BuLi-TMEDA	8.0	NONE	96	50	2.0	3.7	3.0	1.2
L-16	2.1	K	4.3	THF	24	15	0.65	4.7	3.6	1.3
L-15	2.2	K + naphthalene	9.7	THF	24	-78	1.90	6.1	4.7	1.3
M-11	2.0	K + anthracene	4.7	THF	2	-78	1.85	10.2	6.4	1.6
M-10	3.0	K + anthracene	4.7	THF	24	-25	2.4	20.7	12.2	1.7
E-5	7.2	BuLi-TMEDA	1.0	NONE	96	25	0.92	17.3	10.9	1.6
M-3	5.0	K + anthracene	6.7	THF	24	25	5.5	40.6	19.3	2.1
M-8	3.0	K + anthracene	2.1	THF	24	25	2.13	49.0	24.3	2.0
M-9	4.0	K + anthracene	6.6	THF	24	-78	5.0	45.2	18.1	2.5
L-45	5.0	K	3.9	THF	24	-25	5.0	60.4	30.2	2.0
62	7.2	K	1.0	THF	96	60	1.58	187.0	35.4	5.3
L-22	4.2	K	2.3	THF	24	-25	4.5	88.2	46.4	1.9
L-19	6.0	K	5.0	THF	24	25	5.1	127.0	39.7	3.2
4	2.6	K	0.8	p-dioxane	96	5	2.1	143.0	59.6	2.4
5	3.0	K	0.9	p-dioxane	96	5	2.5	163.0	65.2	2.5
3	2.4	K	0.6	p-dioxane	96	5	1.8	198.0	70.7	2.8

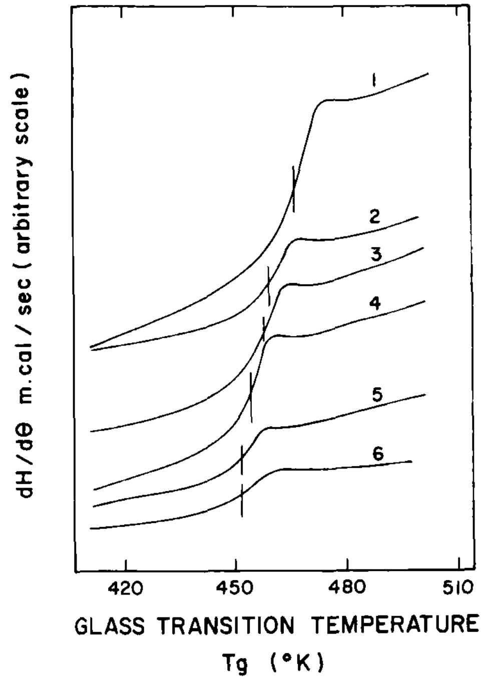

FIG. 1. Typical DSC-2 thermograms of unannealed poly-α-methylstyrene (sample 3) obtained in the glass transition range at various heating rate (q): (1) 80°K/min; (2) 40°K/min; (3) 20°K/min; (4) 10°K/min; (5) 5°K/min; (6) 2.5°K/min.

principal experimental results on the T_g values of poly-α-methylstyrene samples with $\overline{M}_n$ ranging from 2.9×10^3 to 7.0×10^4 are summarized in Table 2. 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 located in the vicinity of 6 to 7×10^4.

A plot of T_{g_e} as a function of $1/M_n$, shown in Fig. 3, yielded a straight line corresponding to Eq. (1).

$$T_{g_e}\ (°K) = 453 - 3.1 \times 10^5/\overline{M}_n \qquad (1)$$

TABLE 2. Variation of T_g with the Heating Rate q and with Molecular Weight

Sample	$\overline{M}_n \times 10^{-3}$	T_g (°K) q = 40°K/min	 q = 20°K/min	 q = 10°K/min	 q = 5°K/min	 q = 2.5°K/min	T_{g_e} at q = 1 (°K)[a]
B	2.9	350	347	345	345	344	341
M-14	3.0	368	366.5	364	363	362	361
L-16	3.6	376	374	374	375	374	369
L-15	4.7	396	393	391	389	387	387
M-11	6.4	400.5	397	395.5	393	391	390
E-5	10.9	437.5	435.5	434	433	432.5	431
M-10	12.2	441	440.5	441	437	434	432
M-9	18.1	451	449	448.5	448	446.5	443
M-3	19.3	445	442.5	441	438	437	437
M-8	24.3	453	450	448	448.5	446.5	444
L-45	30.2	453.5	450	449	447	444.5	444
62	35.4	455	451	450	447.5	446.5	444
L-19	39.7	453.5	450	449	447	446	444
L-22	46.4	454	450.5	448.5	447	446	444
4	59.6	459	455	454.5	449	448	448
5	65.2	458.5	456.5	455.5	454.5	454	452
3	70.3	458	456	454	452.5	451	451

[a] Extrapolated values by using the equation: $\log q = a - b/T_g$ [15].

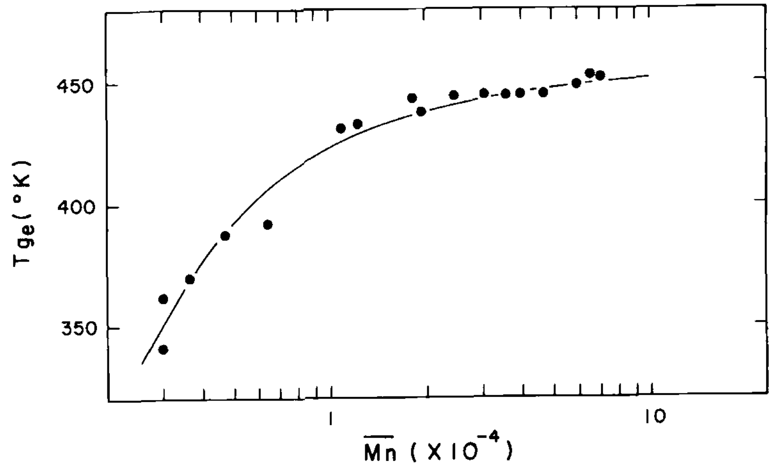

FIG. 2. Extrapolated T_{g_e} values (to q = 1) as a function of $\overline{M}_n$. See Table 2 for other data.

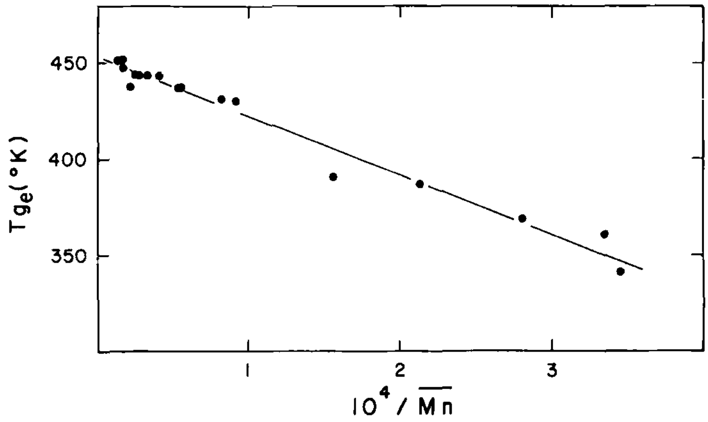

FIG. 3. Extrapolated T_{g_e} values (to q = 1) as a function of $1/\overline{M}_n$. See Table 2 for other data.

Cowie and Toporowski [25], using the DTA technique, reported a slightly different equation for their atactic poly-α-methylstyrene samples:

$$T_g\ (°K) = 446 - 3.6 \times 10^5/\overline{M}_n \qquad (2)$$

The poly-α-methylstyrene samples with $\overline{M}_n > 6.4 \times 10^3$ used in the present study obeyed Bernoullian propagation with a P_m of 0.26 (atactic polymers). The other samples, viz., B, M-14, L-16, and L-15, had unimodal GPC molecular weight distributions, but their NMR spectra recorded in o-dichlorobenzene at 100°C showed them to be built up of two different types of polymers. These are thought to originate from two different propagation steps, each obeying Bernoullian statistics but with different P_m (values ranging from 0.26 to 0.40). Though the stereoregularity in the above four polymers may be slightly better than that present in the other samples listed in Table 1, they can nevertheless be classified as atactic polymers similar to those of Cowie and Toporowski [25]. The difference in T_g (446°K in the literature [25] and 453°K in the present study) thus originates in all probability from the different techniques used in the two studies.

In Fig. 4 are shown four DSC-2 thermograms obtained in the glass transition temperature range at a q value of 5°K/min with poly-α-methylstyrene (sample 3) annealed at 440°K during different periods of time. The peak astride ΔC_p near the glass transition temperature is seen to increase with increasing annealing time. This endotherm is thought to be a consequence of the delayed response of the polymer in going from the glassy to the rubbery state as the temperature is raised rapidly. The enthalpy continues to increase even after the T_g of a given polymer is reached. This delayed change in enthalpy ΔH depends, besides other factors, on the heating rate [10-16] and on the temperature and time of annealing [19-23]. The values of T_g and ΔH in Fig. 4 also show an increase with increasing annealing time.

In the study mentioned earlier [15] involving the variation of T_g with $\overline{M}_n$ in the case of polystyrene, it was speculated that the enthalpy change observed (ΔH) might not arise solely from the delayed response of the polymer in passing from the glassy to the rubbery state but might also be associated with the glass transition itself, which would make the phenomenon a first-order transition having a positive heat effect instead of the generally conceived second-order transition.

In an attempt to confirm the unusual observation made with polystyrene and the DSC-1 instrument, poly-α-methylstyrene (sample 3) was studied on the DSC-2 instrument. The values of T_g and ΔH were measured at six values of q following different annealing periods at a temperature of 440°K. The results obtained are listed in Table 3. Based on these data, three plots of enthalpy change ΔH versus heating rates are presented in Fig. 5 for poly-α-methylstyrene (sample 3) annealed for different periods of time. The results clearly show that

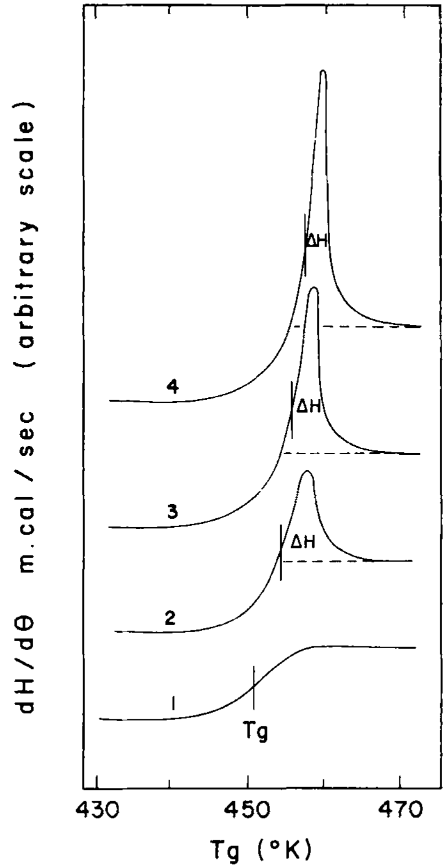

FIG. 4. DSC-2 thermograms obtained in the glass transition range at a q value of 5°K/min for poly-α-methylstyrene (sample 3) annealed for various periods: (1) zero hr; (2) 1 hr; (3) 3.5 hr; (4) 12 hr. See Table 3 for other data.

at an extrapolated zero heating rate value, ΔH tends towards zero. This is contrary to what was observed in the case of polystyrene [15], where a positive ΔH value of 0.6 cal/g was obtained. The present results dealing with poly-α-methylstyrene clearly show that the glass transition temperature is not a first-order transition.

In Fig. 4 it was noted that both T_g and ΔH of poly-α-methylstyrene (sample 3) increased with increasing annealing time. These measurements were made at a heating rate of 5°K/min. Data were also

TABLE 3. Variation of T_g and ΔH on Annealing Poly-α-methylstyrene (Sample 3) at 440°K for Various Periods of Time and Heating of the Samples at Different Rates

	T_g at various heating rates (°K)							ΔH at various heating rates (cal/g)						
Annealing time (hr)	1.25 °K/ min	2.5 °K/ min	5 °K/ min	10 °K/ min	20 °K/ min	40 °K/ min	80 °K/ min	1.25 °K/ min	2.5 °K/ min	5 °K/ min	10 °K/ min	20 °K/ min	40 °K/ min	80 °K/ min
0.0	-	451	452.5	454	456	458	461.5	-	-	-	-	-	-	-
0.17	450	451.5	453	455	457	459	465	-	-	0.06	0.11	0.19	0.23	0.24
0.5	450	452	453.5	455	458	462	465	-	0.10	0.16	0.21	0.28	0.30	0.35
1.0	450.5	453	455.5	456	460.5	464	466	-	0.13	0.19	0.27	0.35	0.41	0.48
2.0	451.5	453.5	456	458	461	465	468	-	0.17	0.31	0.35	0.38	0.55	0.57
3.5	452	454.5	457	458	462	466	470	-	0.19	0.33	0.40	0.50	0.60	0.62
12.0	454.5	456.5	459	461	465	467	470.5	-	0.26	0.48	0.59	0.67	0.71	0.79
23.0	455	457	459.5	461.5	466	469	471	0.34	0.44	0.58	0.61	0.75	0.79	0.84

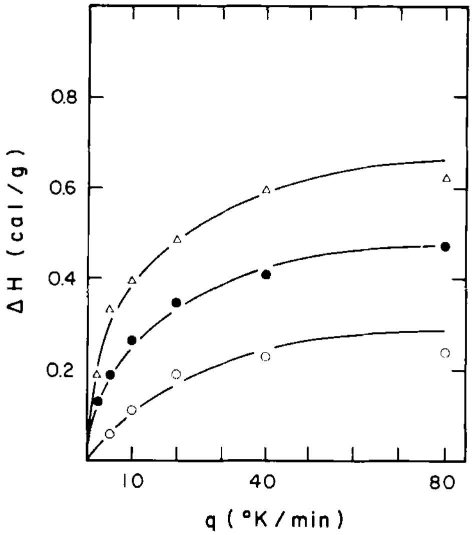

FIG. 5. Enthalpy change ΔH as a function of heating rate q for poly-α-methylstyrene (sample 3) annealed for various periods: (○) 10 min; (●) 1 hr; (△) 3.5 hr. See Table 3 for other data.

collected at other heating rates and are presented in Table 3. Based on these data, plots of ΔH as a function of annealing time are presented in Fig. 6 and this for four different heating rates. The results again show that ΔH tends towards zero as the annealing time goes to zero.

In Fig. 7 are shown plots of ΔH (associated with annealing at 440°K) as a function of T_g. Each curve, obtained with ΔH values determined at six different heating rates, shows a shift towards higher temperatures with increasing annealing time. At the point of intersection of any two curves, where ΔH and T_g are the same for two different annealing times, the heating rate required to obtain a given ΔH and T_g with a more annealed sample is always lower than that required by the less annealed sample to attain the same values. For instance, annealing at 440°K for 30 min, then heating at 15°K/min (interpolated value) (fast heating) or annealing at 440°K for 12 hr, then heating at 2.5°K/min (slow heating) yields the same ΔH and T_g values. Thus, annealing a polymer sample for increasing periods of time yields the same results (as far as ΔH and T_g are concerned) as decreasing the heating rate.

The effect of fast cooling and slow heating during a T_g determination

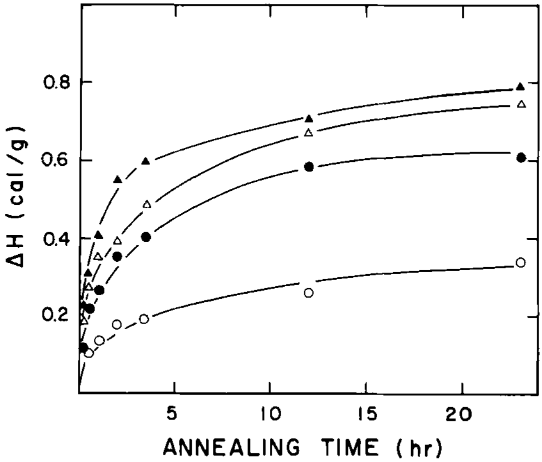

FIG. 6. Enthalpy change ΔH of poly-α-methylstyrene (sample 3) as a function of annealing time measured at q values of: (○) 2.5°K/min; (●) 10°K/min; (△) 20°K/min; (▲) 40°K/min. See Table 3 for other data.

has been discussed by Wunderlich et al. [11] and by Roberts and Sherliker [38], who suggested that under these conditions a relatively larger number of holes are frozen in. On subsequent slow heating, the polymer chains have sufficient time to rearrange to their equilibrium configurations involving smaller free volume fractions. On heating rapidly, equilibrium is not achieved immediately since, at the fast heating rate, insufficient time is available for the necessary molecular rearrangements to occur. During this rapid heating process, the polymer achieves its equilibrium free volume fraction by absorbing heat as it does and producing an endothermic peak in the thermogram. Because of the fast cooling and subsequent slow heating, the diminishing fractional free volume reduces the excess enthalpy required by the polymer. The introduction of annealing which lowers the heating rate reduces the excess enthalpy of the polymer, however, its T_g, with increasing annealing time, increases. Similar results with annealing were also reported by Petrie [21].

CONCLUSIONS

The main conclusions to be drawn from this study may be summed up as follows.

In the case of polystyrene and poly-α-methylstyrene samples having

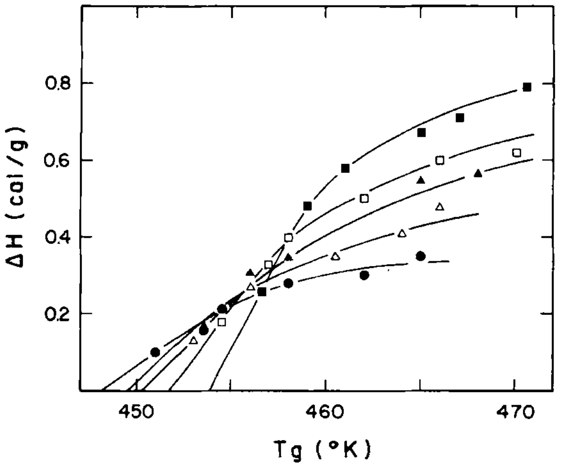

FIG. 7. Enthalpy change ΔH of poly-α-methylstyrene (sample 3) as a function of T_g measured at various annealing times: (●) 30 min; (△) 1 hr; (▲) 2 hr; (□) 3.5 hr; and (■) 12 hr. See Table 3 for other data.

the same $\overline{M}_n$, the T_g of the latter is higher because of the increased steric hindrance in it due to the substituent methyl group. Furthermore, the T_{g_∞} of the latter is also higher than that of the former [15].

The T_{g_∞} values obtained with the DSC-2 instrument used in the present study are different from those reported by Cowie and Toporowski [25], who used the DTA technique.

The observed enthalpy change ΔH tends towards zero as the annealing time and the heating rate are reduced to zero, suggesting that it is not necessary to postulate a first-order transition to account for the energy absorption.

The use of longer annealing periods or lower heating rates yields similar trends as far as the values of ΔH are concerned.

T_g extrapolated to zero ΔH for zero heating rate (Fig. 7) was found to increase with increasing annealing time.

Studies on the glass transition temperatures of poly p-isopropyl α-methylstyrene and other substituted styrenes are in progress. Results will be reported in due course.

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