The Thermal Decomposition and Glass Transition Temperature of Poly-p-methoxystyrene

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The Thermal Decomposition and Glass Transition Temperature of Poly-p-methoxystyrene

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ABSTRACT

The thermal decomposition and the glass transition temperature of poly p-methoxystyrene (PpOMeS) were studied with a (DSC-2) differential scanning calorimeter. The undecomposed and decomposed polymers were analyzed by gel permeation chromatography for molecular weight distributions and by DSC-2 for changes in the polymer glass transition temperatures. Decomposition of PpOMeS under isothermal conditions during 50 min intervals at various temperatures or at a fixed temperature (320°C) during various intervals leads increasing quantities of high molecular weight material to yield low molecular weight products. Random scissions have been shown to break down the polymer chains which then volatilize via depolymerization. Activation energy for the decomposition of PpOMeS has been found to be less than that for the decomposition of polystyrene (PS). Variation of T_{g_e} (at q = 1°K/min) with $\overline{M}_n$ obeys the relation:

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$T_{g_e}(^\circ K) = 386 - 4.67 \times 10^5/\overline{M}_n$. The value of $386^\circ K$ for the T_{g_∞} of PpOMeS is greater than the value ($362^\circ K$) reported in the literature. A comparison of T_{g_∞} for PS ($379^\circ K$) for poly p-methylstyrene ($384^\circ K$) and for PpOMeS ($386^\circ K$) reveals that the presence of p-CH3 or p-OCH3 groups neither influences the chain flexibility nor causes further steric hindrance than already exists in PS.

INTRODUCTION

Thermal decomposition [1-9] and glass transition temperature studies [7-13] of polystyrene (PS) [1, 2, 10], poly(α-methylstyrene) (PαMeS) [3, 4, 11, 12], poly(p-isopropyl α-methylstyrene) (PpiPrαMeS) [5, 6, 13], poly(p-methylstyrene) (PpMeS) [7], poly(p-isopropylstyrene) (PpiPrS) [8], and poly(p-tert-butylstyrene) (PptBuS) [9] have been reported on earlier. The results of the isothermal treatments showed that while the substituents p-methyl and p-isopropyl in substituted polystyrene are either involved or actually cause cross-linking of polymer chains, the other substituents, viz., α-methyl and p-tert-butyl, do not lead to such reactions. Furthermore, for identical weight-loss values, α, the treatment temperatures for PαMeS were the lowest; however, the other substituents led to relatively small decreases in the decomposition temperatures. The activation energy for the decomposition of polystyrene and its homologs followed the order $E_{PS} > E_{P\alpha MeS} > E_{PpMeS} = E_{PpiPrS} > E_{PptBuS}$. It is thought that this order corresponds to the radical yielding capacity of these substituents.

A comparison of the T_{g_e} values for PS ($363^\circ K$), PαMeS ($437^\circ K$), PpMeS ($364^\circ K$), PpiPrS ($335^\circ K$), and PptBuS ($399^\circ K$) samples having an $\overline{M}_n$ of 1.4×10^4 revealed that the chain flexibility and steric hindrance are related to the effective bulk size (i.e., the packing ability of the polymer) rather than to the apparent bulk size. This conclusion was based on the fact that although the apparent bulk size of various groups follows the order $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_3 > -H$, the effective bulk size determined from the T_{g_e} data obtained with polymers carrying these groups are α-CH3 > p-t-C(CH3)3 > p-CH3 > -H > p-i-CH(CH3)2 .

Keeping this in mind, a study of the thermal decomposition and the glass transition temperature of another homolog of polystyrene, namely, poly (p-methoxystyrene) (PpOMeS), was carried out and the data obtained were compared with those of PS carrying other substituents as well as with those reported on the decomposition [14-16] and T_g [17-19] of PpOMeS itself. The principal results obtained are outlined in the present article.

EXPERIMENTAL

PpOMeS from Aldrich Chemical Co. was used as received. The weight average molecular weight $\overline{M}_w$ of the polymer was calculated from the intrinsic viscosity data obtained with toluene at 30°C using the relation reported in the literature [20]. Molecular weight distributions of PpOMeS samples were obtained with a Waters Associates (Model 200) gel permeation chromatograph [1-9] calibrated with standard PS and PpOMeS samples.

A Perkin-Elmer (Model DSC-2) differential scanning calorimeter operating with pure dry helium was used for the isothermal decomposition of PpOMeS whereas a Perkin-Elmer (Model TGS-1) thermogravimetric scanning balance operating in pure dry nitrogen was used for the dynamic decomposition of PpOMeS. The T_g values of the undecomposed and decomposed samples of PpOMeS were determined with the DSC-2 apparatus [10-13].

RESULTS AND DISCUSSION

Thermal Decomposition of PpOMeS

In Table 1 are summarized values of the weight loss α (in %), the molecular weights ($\overline{M}_w$ and $\overline{M}_n$), and the polymolecularity ($\overline{M}_w/\overline{M}_n$ ratios) obtained with PpOMeS both before and after its isothermal treatment at various temperatures for different periods. Using the 50-min isothermal treatment data, a curve showing the variation of α with temperature is given in Fig. 1. For comparison purposes, data for 50 min isothermal treatments of PS [2] samples are also plotted in this figure. For α values of less than 5%, the respective decomposition temperatures of PS and PpOMeS are nearly the same. For identical values of α ($>5\%$), however, the respective decomposition temperature of PpOMeS is 22°K lower than that of PS.

In Fig. 2 are shown the normalized GPC molecular weight distribution curves of six PpOMeS samples subjected to 50 min isothermal treatments at various temperatures. The maxima in the GPC distribution curves of the decomposed polymers move toward higher elution counts, i.e., toward lower molecular weights. Furthermore, as the treatment temperature is raised, an increase is noted in the quantity of lower molecular weight polymer present between elution counts 27 and 34. This behavior is similar to that observed in the case of PS [2] where random scission and depolymerization reactions operate.

In Fig. 3 is shown the variation of $\overline{M}_w$ with treatment temperature for PpOMeS samples subjected to 50 min decomposition periods at various temperatures. $\overline{M}_w$ decreases regularly with increasing temperature.

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TABLE 1. Data on PpOMeS Samples Subjected to Isothermal Treatments at Various Temperatures for Different Periods

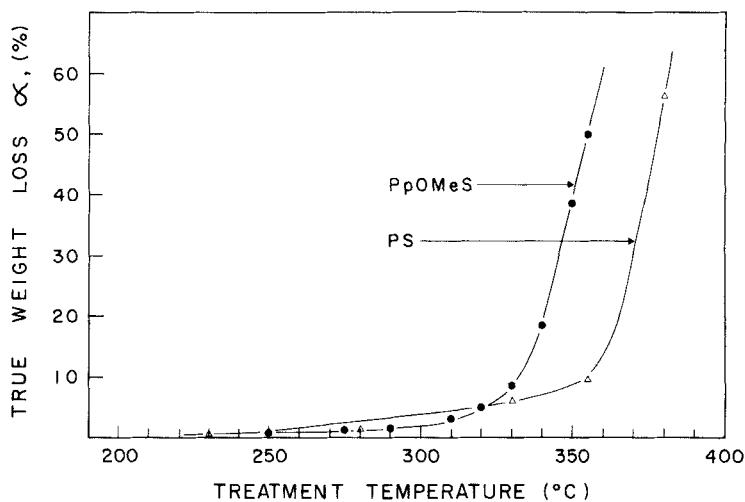| Sample no.	Treatment temperature (°C)	Treatment time (min)	Weight loss α (%)	$\overline{M}_w$ (GPC) $\times 10^{-4}$	$\overline{M}_n$ (GPC) $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PpOMeS-0	Undecomposed	–	0	67.0	3.9	17.1
PpOMeS-1	250	50	0.8	47.0	3.5	13.6
PpOMeS-2	275	50	1.3	41.8	3.9	10.6
PpOMeS-3	290	50	1.4	48.7	4.3	11.2
PpOMeS-4	300	50	1.5	31.5	3.25	9.7
PpOMeS-5	310	50	2.9	26.4	3.2	8.2
PpOMeS-6	320	50	4.8	22.4	2.9	7.7
PpOMeS-7	330	50	8.3	14.2	2.5	5.7
PpOMeS-8	340	50	17.9	10.4	2.3	4.6
PpOMeS-9	350	50	38.4	8.3	2.0	4.2
PpOMeS-10	355	50	49.8	7.4	1.9	3.9
PpOMeS-11	320	10	1.6	35.0	3.4	10.2
PpOMeS-12	320	20	2.1	26.7	3.4	8.5
PpOMeS-13	320	30	2.7	27.3	3.3	8.2
PpOMeS-14	320	90	8.6	19.6	3.0	6.5
PpOMeS-15	320	120	12.4	15.1	2.8	5.4
PpOMeS-16	320	180	18.6	13.7	2.6	5.2

FIG. 1. Variation of weight loss α (%) with treatment temperature T (°C) for PS ($\overline{M}_w$ = 4.3 × 10^5 [2]) and PpOMeS ($\overline{M}_w$ = 6.7 × 10^5) samples. See Table 1 for other data.
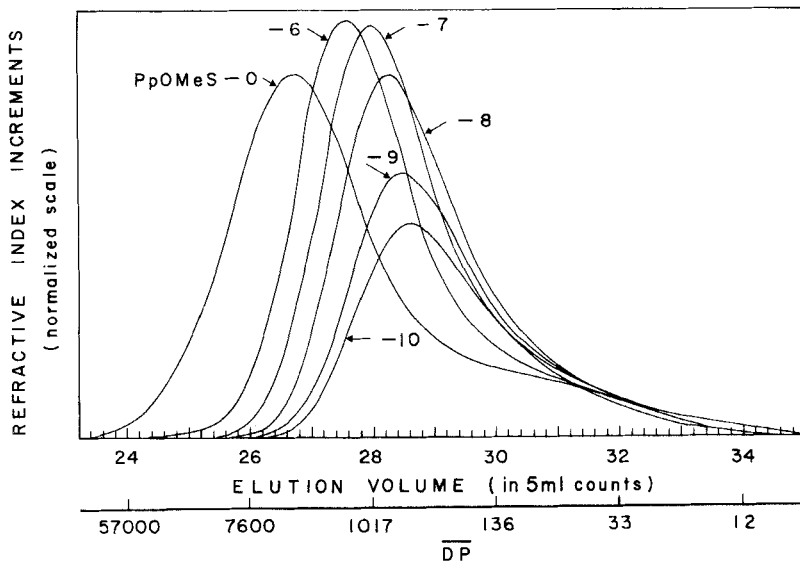
FIG. 2. Normalized GPC molecular weight distributions of PpOMeS samples subjected to 50 min decomposition periods at various temperatures. See Table 1 for other data.
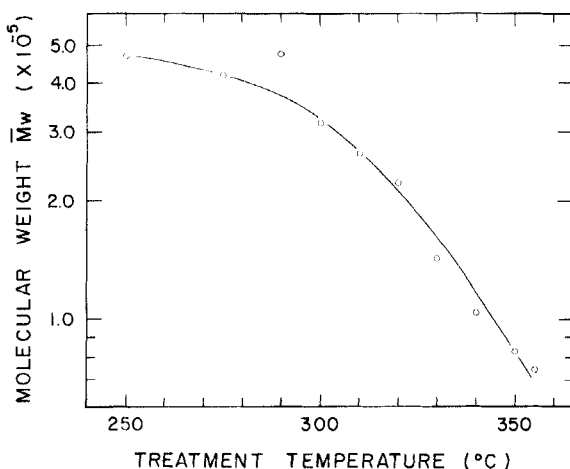
FIG. 3. Variation of molecular weight with treatment temperature for PpOMeS samples subjected to 50 min decomposition periods. See Table 1 for other data.

In Fig. 4 are shown, for different modes of operation, curves of the variation in molecular weight as a function of α. In general, the molecular weights decrease with increasing values of α. For identical α values obtained with 50 min isothermal treatments at various temperatures or at 320°C using different decomposition periods, the decrease in molecular weight is not the same.

Based on the data presented in Table 1 and on an analysis of Figs. 1 to 4, it may be said that the presence of an OCH$_3$ group in the aromatic rings of PS facilitates the formation of radicals which bring about the random scission and the depolymerization of the polymer chains.

To better understand the decomposition of PpOMeS,,the normalized GPC distribution curve of the undecomposed polymer was compared successively with like curves of other samples decomposed during 50 min periods at different temperatures. Subtracting from the initial distribution curve of the undecomposed polymer the distribution of any subsequently decomposed polymer, the changes, both positive and negative, that take place as a result of the decomposition of the initial higher molecular weight species can be visualized. For the PpOMeS samples studied, these changes are shown in Figs. 5 and 6, where the distributions over the negative sign (-) between elution counts 23 and 28) represent the volatilized fraction due to decomposition and those over the positive sign (+) (between elution counts 25 and 31) represent the newly formed products.

The characteristics of the various (-) and (+) GPC molecular weight distributions shown in Figs. 5 and 6 are summarized in Table 2 which
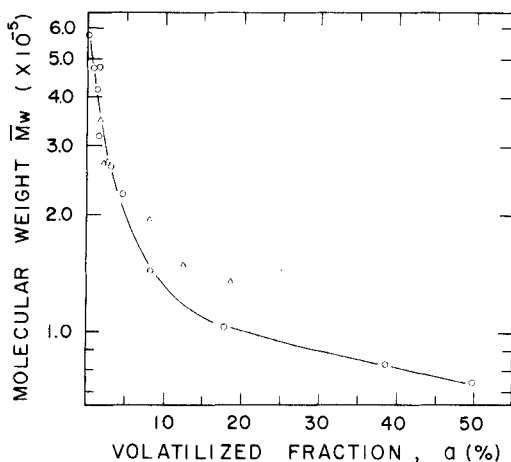
FIG. 4. Variation of molecular weight as a function of weight loss: ($\circ$) α (%) for 50 min decomposition periods at different temperature and ($\triangle$) α (%) for different periods at 320°C.

includes α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values. For 50 min isothermal decompositions, as the temperature is raised from 25 to 355°C, increasing quantities of high molecular weight material with $\overline{M}_w$ of (24.3 to 9.5) $\times 10^5$ and $\overline{M}_w/\overline{M}_n$ of 1.5 to 2.2 (located between elution counts 23 and 28 on the GPC curves) decompose to yield products (appearing on the GPC curves between elution counts 25 and 31) having $\overline{M}_w$ values of (54.0 to 7.0) $\times 10^4$ and $\overline{M}_w/\overline{M}_n$ values varying from 1.8 to 3.5.

In Fig. 7 are shown the normalized GPC molecular weight distributions of three PpOMeS samples subjected to thermal decomposition at a fixed temperature (320°C) for different periods ranging from 10 to 180 min. Their α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values are listed in Table 1. It may be noted that as α increases, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ decrease regularly.

In Fig. 8 are shown changes that occur in the GPC molecular weight distributions of seven PpOMeS samples subjected to thermal decomposition at 320°C, where the decomposition time is varied from zero to 10, 10 to 20, 20 to 30, 30 to 50, 50 to 90, 90 to 120, and 120 to 180 min, respectively. The values of α, $\overline{M}_w$, $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$, associated with both the (-) and the (+) distributions shown in Fig. 8, are summarized in Table 2. These data show that the isothermal treatment of PpOMeS during the initial 10 min period results in the
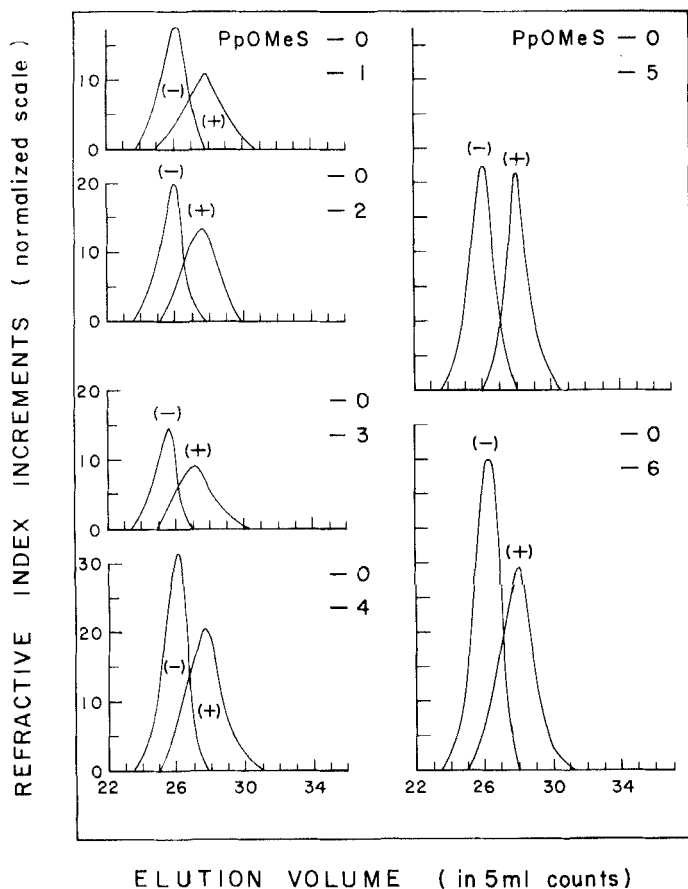
ELUTION VOLUME (in 5ml counts)

FIG. 5. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of PpOMeS samples subjected to 50 min decomposition periods in the temperature range of 250 and 320°C. See Table 2 for other data.

decomposition of 19.2% of the polymer having an $\overline{M}_w$ of 18.8×10^5 and an $\overline{M}_n$ of 11.0×10^5 ($\overline{M}_w/\overline{M}_n = 1.7$) and yielding a product (17.7%) with an $\overline{M}_w$ of 17.9×10^4 and an $\overline{M}_n$ of 9.3×10^4 ($\overline{M}_w/\overline{M}_n = 1.9$). In the intervals of 10 to 20, 20 to 30, 30 to 50, 50 to 90, 90 to 120, and 120 to 180 min, 7.8, 2.8, 14.2, 6.9, 14.1, and 7.0% of the polymer volatilize yielding 6.9, 1.0, 9.9, 3.4, 10.0, and 1.5%, respectively, of lower
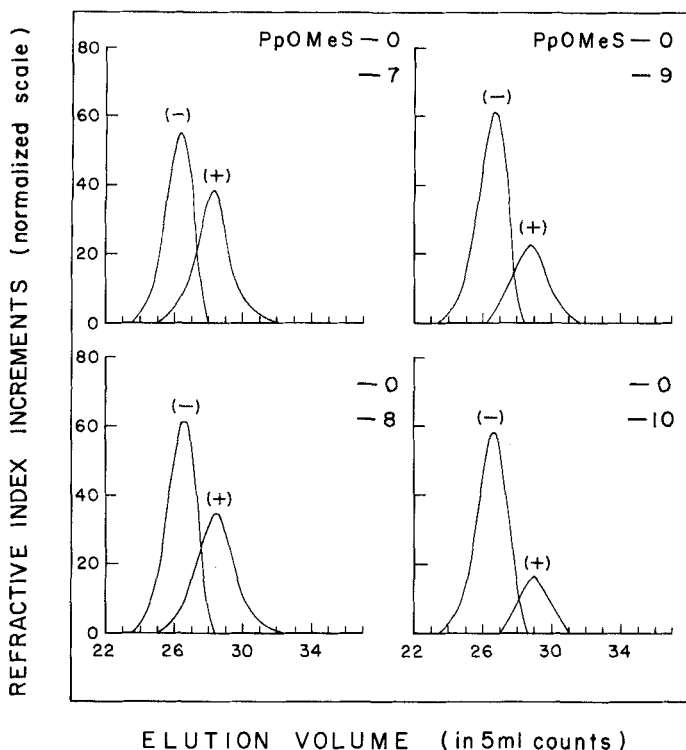
FIG. 6. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of PpOMeS samples subjected to 50 min decomposition periods in the temperature range of 330 and 355°C. See Table 2 for other data.

molecular weight products with an $\overline{M}_w$ of $(18.5 \text{ to } 2.8) \times 10^4$ and $\overline{M}_w/\overline{M}_n$ ratios close to 2.0.

Based on these GPC molecular weight results derived from both undecomposed and decomposed PpOMeS samples, one notes the following:

1. In the 50-min isothermal treatment of PpOMeS at various temperatures or in decompositions carried out at 320°C during various intervals, the mechanism of random scission breaks down the polymer chains which then volatilize via depolymerization. The decomposition behavior, in general, resembles that of PS [2]. Due to the presence of the OMe group in the PS aromatic ring, the thermal decomposition of PpOMeS is facilitated; however, the decreases in

TABLE 2. Characteristics of Polymers Appearing in Two GPC Elution Count Ranges: The Case of PpOMeS Decomposed for 50 min at Different Temperatures and for Different Periods at 320°C[a]

Polymer-pairs analyzed	Elution count range							
	(23–28) (−)				(26–32) (+)			
	α (%)	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	α (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
PpOMeS-0 → PpOMeS-1	16.9	15.4	8.7	1.8	14.3	31.1	9.5	3.3
PpOMeS-0 → PpOMeS-2	16.4	18.8	10.9	1.7	16.1	34.2	14.9	2.3
PpOMeS-0 → PpOMeS-3	10.7	24.3	16.0	1.5	11.0	53.6	20.9	2.6
PpOMeS-0 → PpOMeS-4	26.5	18.2	11.2	1.6	25.6	32.8	10.5	3.1
PpOMeS-0 → PpOMeS-5	29.8	15.0	8.2	1.8	25.0	16.2	8.9	1.8
PpOMeS-0 → PpOMeS-6	42.0	16.2	9.2	1.8	35.8	27.3	9.3	2.9
PpOMeS-0 → PpOMeS-7	53.6	12.1	6.5	1.9	44.9	21.9	7.1	3.1
PpOMeS-0 → PpOMeS-8	66.3	10.2	5.1	2.0	47.4	16.5	4.7	3.5
PpOMeS-0 → PpOMeS-9	69.5	9.5	4.5	2.1	28.3	10.1	4.0	2.5
PpOMeS-0 → PpOMeS-10	66.3	9.5	4.4	2.2	16.8	6.9	3.6	1.9
PpOMeS-0 → PpOMeS-11	19.2	18.8	11.0	1.7	17.7	17.9	9.3	1.9
PpOMeS-11 → PpOMeS-12	7.8	9.9	6.1	1.6	6.9	18.5	9.5	2.0
PpOMeS-12 → PpOMeS-13	2.8	7.9	5.3	1.5	1.0	11.0	8.6	1.3
PpOMeS-13 → PpOMeS-6	14.2	6.0	3.6	1.7	9.9	14.0	8.3	1.7

PpOMeS-6	PpOMeS-14	6.9	6.0	2.7	2.2	3.4	9.0	4.6	2.0
PpOMeS-14	PpOMeS-15	14.1	4.5	2.8	1.6	10.0	12.9	4.6	2.8
PpOMeS-15	PpOMeS-16	7.0	2.7	1.8	1.5	1.5	2.8	2.3	1.2

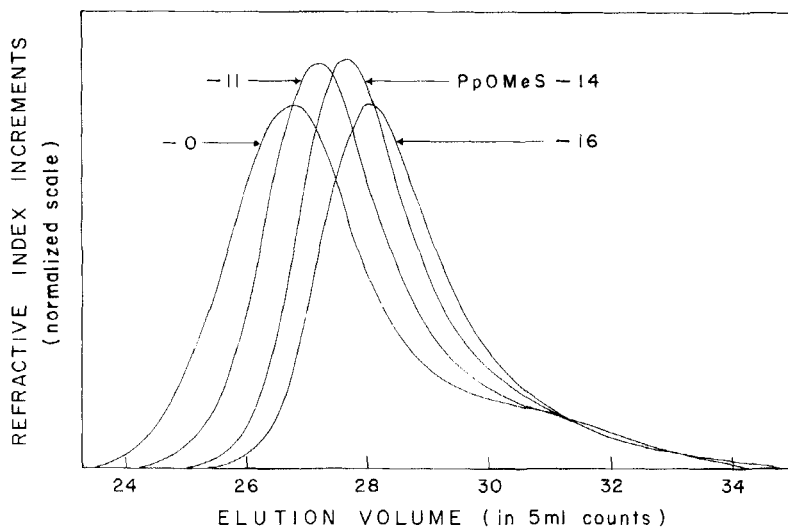[a]See Table 1 for decomposition reaction conditions.

FIG. 7. Normalized GPC molecular weight distributions of PpOMeS samples subjected to isothermal treatments at 320°C for different periods. See Table 1 for other data.

the values of α, $\overline{M}_w$, or $\overline{M}_n$ as a function of temperature or time are not as regular as those for the thermal decomposition of PS [2].

2. The results of the present study do not agree with those reported on by Inagaki et al. [16], who suggested that PpOMeS is thermally more stable than PS because of the electron-repelling OMe group in the former polymer. The present results, however, agree well with those of Still and Whitehead [14, 15] who suggested that PS and PpOMeS degrade in a similar manner and the latter polymer has a low activation energy (37 kcal/mole) of decomposition.

In Fig. 9 are shown curves representing the dynamic thermogravimetric decomposition at a heating rate of 20°K/min of PS and PpOMeS samples using the method of Coats and Redfern [21]. Activation energies were calculated assuming successively orders of reaction of zero and one. The values obtained are presented in Table 3. The activation energy values for PS are found to be higher than those for PpOMeS. For the zero-order reaction the value of 39.6 kcal/mole as the activation energy of decomposition of PpOMeS is close to that (37.4 kcal/mole) found by Still and Whitehead [15].
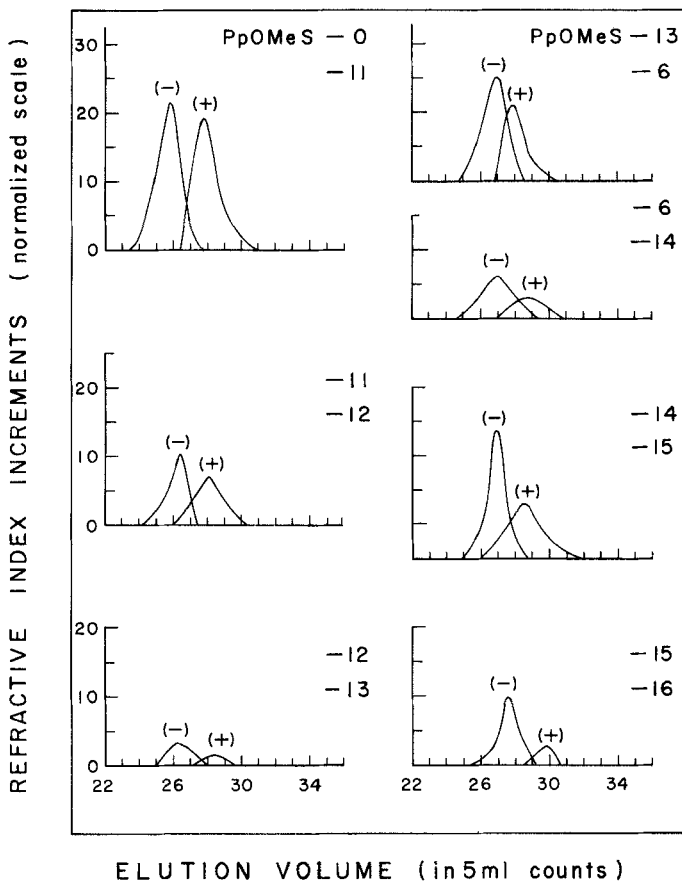
FIG. 8. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of PpOMeS samples subjected to isothermal treatments at 320°C for different periods. See Table 2 for other data.

Glass Transition of PpOMeS

The glass transition temperature (T_g) of a polymer is a heating-rate dependent [7-13] as well as cooling-rate dependent [22, 23]. Although recent work [7-9] on PpMeS, PpiPrS, and PptBuS has shown that in the case of substituted polystyrenes the cooling rate has no effect on T_g, it was thought pertinent to study the effects that the cooling rate might have on the T_g of PpOMeS.
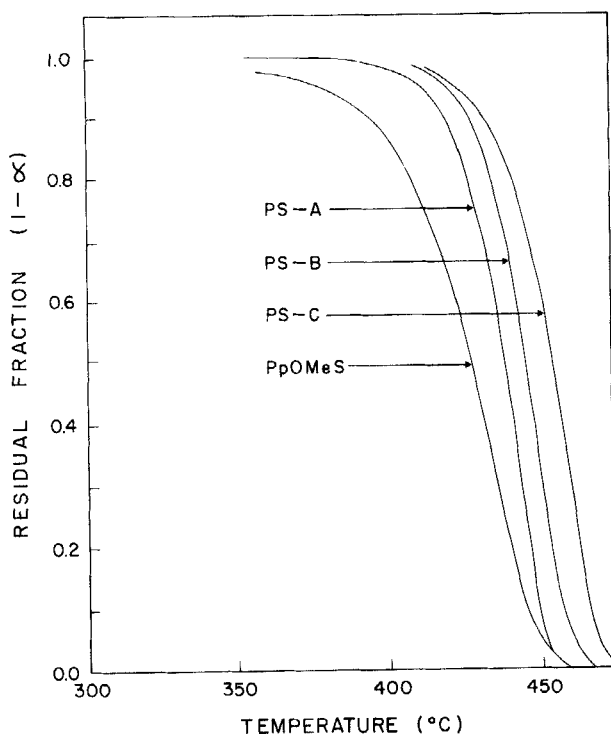
FIG. 9. Dynamic thermogravimetric decomposition of PS and PpOMeS samples at a heating rate of 20°K/min. See Table 3 for other data.

In Fig. 10 are shown typical DSC thermograms obtained with the undecomposed polymer and recorded in the glass transition range at a fixed heating rate of 40°K/min. Various cooling rates were used to bring the samples to a temperature approximately 30°K below their expected T_g value prior to tracing the thermogram in the heating mode. The T_g values determined at the $\Delta Cp/2$ point [7-13] remained constant as the cooling rate was increased. T_g values of the undecomposed polymer subjected to three cooling rates are presented in Table 4. T_{g_e} values (extrapolated to a heating rate of 1°K/min) are likewise listed. These remain constant at 370.5 ± 0.5°K. Subsequent T_g measurements on the decomposed polymer samples were made after they had been cooled below T_g at a rate of 320°K/min.

TABLE 3. Activation Energy Values Calculated by the Method of Coats and Redfern [21] for the Thermal Decomposition of Poly-styrene (PS) and Substituted Polystyrenes

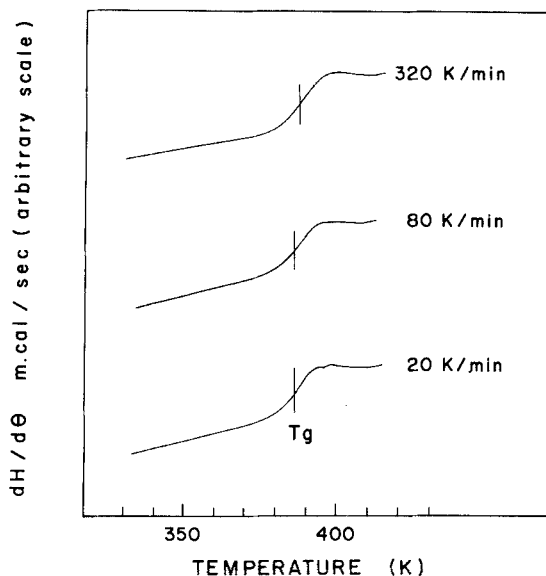| Sample	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	Activation energy (kcal/mole)[a]	
			For n = 0	For n = 1
PS-A	78.0	1.1	-	111.0
PS-B	4.6	1.1	-	103.0
PS-C	1.8	1.1	51.4	88.5
PpOMeS	3.9	17.1	39.6	77.4

[a]n is the order of reaction.

FIG. 10. Typical DSC thermograms of an undecomposed polymer sample of PpOMeS recorded in the glass transition region at a heating rate of 40°K/min following cooling at various rates. See Table 4 for other data.

TABLE 4. Effect of Thermal History on T_{g_e} Determination of an
Undecomposed PpOMeS Sample

Sample cooling rate ($°K/min$)	T_g at various heating rates ($°K/min$)				T_{g_e} a ($1°K/min$)
	80	40	20	10	
320	386.0	383.5	381.0	378.5	370.5
80	385.5	382.5	381.5	379.0	370.5
20	385.5	382.5	381.0	378.5	370.0

aExtrapolated value at a heating rate (q) of $1°K/min$ using equation
$\log q = a - b/T_g$ [10].

In Fig. 11 are shown typical DSC thermograms of an undecomposed
PpOMeS polymer sample recorded in the glass transition region at
various heating rates. As expected, T_g was found to increase with
increasing heating rate. The T_g data obtained with a sample cooling
rate of $320°K/min$ and heating rates of 80, 40, 20, and $10°K/min$ for
the undecomposed and a number of decomposed PpOMeS samples are
summarized in Table 5. The values of T_{g_e} are found to increase with
increasing $\overline{M}_n$.

In Fig. 12 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 constant. The critical value is
located at an $\overline{M}_n$ value of 3.0×10^4. A plot of T_{g_e} as a function of
$1/\overline{M}_n$, shown in Fig. 13, yields a straight line best described by

$$T_{g_e}(°K) = 386 - 4.67 \times 10^5/\overline{M}_n \tag{1}$$

The value of $386°K$ for the T_{g_∞} of PpOMeS is greater than the
value $362°K$ reported in the literature [17-19].

In earlier work from this laboratory [10] the T_{g_e} of PS (Eq. 2)
and PpMeS (Eq. 3) were related to $\overline{M}_n$ as follows:

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

$$T_{g_e}(°K) = 384 - 2.65 \times 10^5/\overline{M}_n \tag{3}$$

The addition of methyl and methoxy substituents in the aromatic
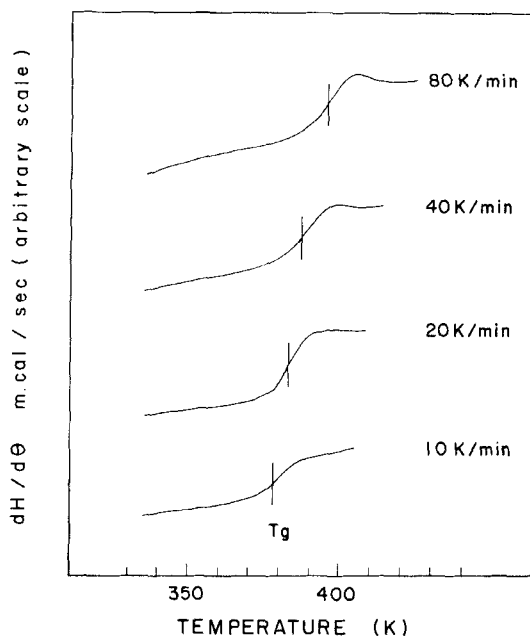rings increases the value of T_{g_∞} from $379°K$ for PS to $384°K$ for

FIG. 11. Typical DSC thermograms of an undecomposed polymer sample of PpOMeS recorded in the glass transition region at various heating rates. See Table 4 for other data.

PpMeS and on to $386°K$ for PpOMeS. The values of the constant K, which is related to the free volume of the polymer, are quite different for PS (2.1×10^5), PpMeS (2.65×10^5), and PpOMeS (4.67×10^5). It would appear that the introduction of substituents, e.g., p-CH₃ and p-OCH₃ groups in the aromatic ring of PS, does not influence the chain flexibility or cause further steric hindrances to affect much the T_{g_∞} values of these substituted polymers.

The principal conclusions to be drawn from this study may be summed up as follows:

1. In the isothermal decomposition of PpOMeS, random scissions reduce the chain length of the polymer and depolymerization reactions account for the weight loss. These conclusions find support from the work of Still and Whitehead [15].

2. The presence of the p-OCH₃ group in the aromatic ring lowers its thermal stability, and a lower activation energy of decomposition is required as compared to that for PS. These findings are in contradiction with the work of Inagaki et al. [16].

TABLE 5. Variation of T_g as a Function of Heating Rates for Undecomposed and Decomposed Samples of PpOMeS

| Sample no.	Weight loss α (%)	$\bar{M}_n$ (GPC) $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	T_g at various heating rates (°K/min)				T_{ge} (1°K/min)
				80	40	20	10	
PpOMeS-0	Undecomposed	3.93	17.1	386.0	383.5	381.0	378.5	370.5
PpOMeS-17	1.4	3.21	10.6	385.5	383.0	381.0	380.0	373.5
PpOMeS-18	2.6	3.01	8.1	383.0	381.0	378.5	377.0	370.0
PpOMeS-19	3.7	2.59	9.1	383.5	382.0	379.0	377.0	369.5
PpOMeS-20	10.7	2.22	5.9	376.0	374.5	373.0	372.0	367.5
PpOMeS-21	14.0	1.65	5.9	372.5	371.0	370.0	368.5	364.5
PpOMeS-22	16.4	1.47	6.8	371.0	368.0	368.0	365.5	361.0
PpOMeS-23	18.7	1.46	6.2	369.0	367.0	366.0	365.0	360.5
PpOMeS-24	22.8	1.77	5.1	367.0	365.0	363.0	362.0	356.0
PpOMeS-25	25.1	1.59	5.1	367.0	364.5	363.0	362.5	356.5
PpOMeS-26	32.2	1.53	4.6	362.0	359.5	357.5	356.0	349.0
PpOMeS-27	39.1	1.38	4.4	358.0	356.0	355.0	353.5	348.5
PpOMeS-28	45.8	1.25	4.5	357.0	355.0	353.5	352.5	347.0
PpOMeS-29	49.9	1.14	4.5	353.5	352.0	351.0	350.0	346.0
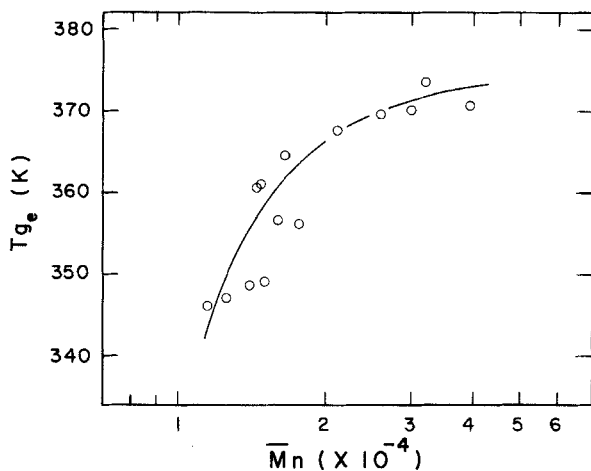
FIG. 12.   Extrapolated T_{g_e} values (to q = 1°K/min) of PpOMeS as a function of $\overline{M}_n$.   See Table 5 for other data.
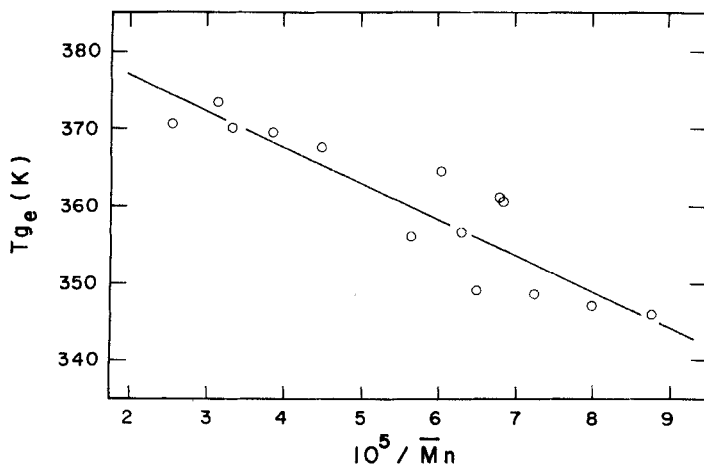

FIG. 13.   Extrapolated T_{g_e} values (to q = 1°K/min) of PpOMeS as a function of $1/\overline{M}_n$.   See Table 5 for other data.

3. T_g measurements made on the undecomposed and decomposed PpOMeS samples yield T_{g_∞} of 386°K which is different from the value of 362°K reported in the literature [17-19]. A comparison of T_g for PS (379°K), PpMeS (384°K), and PpOMeS (386°K) reveals that the presence of p-CH₃ and p-OCH₃ groups neither influences the chain flexibility nor causes further steric hindrance in PS.

Further studies on the effect of other substituents on the thermal decomposition of polystyrene as well as on T_{g_∞} are in progress and will be reported on in due course.

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