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Thermal Decomposition and Glass-Transition Temperature Study of Poly-p-methylstyrene

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ABSTRACT

Thermal decomposition and glass-transition temperature studies have been carried out on poly-p-methylstyrene (PpMeS) with the DSC-2 differential scanning calorimeter. The undecomposed and decomposed polymers were analyzed by gel-permeation chromatography (GPC), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR). Decompositions of PpMeS under isothermal conditions during 50-min periods in the 25-330°C temperature range did not affect $\overline{M}_w$ values; however, $\overline{M}_n$ values decreased from 5.1×10^4 to 1.5×10^4. The decomposed polymers following treatments at temperatures above 330°C are only partially soluble in THF, o-$C_6H_4Cl_2$, and CCl_4. These products may therefore contain certain crosslinked materials. The results of the IR analyses show that in the polymers decomposed at temperatures above 330°C, the aromatic content is lower than that observed for polymers decomposed in the 25-330°C temperature range. The variation of T_{g_e} (at $q = 1$°K/min) with $\overline{M}_n$ obeys the relation; $T_{g_e}(K) = 384 - 2.65 \times 10^5/\overline{M}_n$. The

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value of 384°K for the T_g of PpMeS at infinite molecular weight is close to that found for PS (379°K) but is far below that (453°K) obtained for PαMeS. This illustrates the relative importance of the methyl substitution in the vinyl chain as compared to that in the aromatic rings.

INTRODUCTION

In studies related to the thermal decomposition of poly p-methylstyrene (PpMeS) [1, 2] and its glass-transition temperature T_g [3-7], it was shown [2] that the introduction of an electron-withdrawing methyl group in the para position of the aromatic rings of polystyrene (PS) lowers its thermal stability, while the activation energy for chain scission [2] was found to be higher in the case of PpMeS than in the case of PS.

T_g values obtained from specific volume data at various temperatures [3], from differential thermal analyses [5] and from mechanical damping measurements [6] showed that, due to the presence of the p-methyl groups in the PS aromatic rings, the glass-transition temperature of PpMeS is lower than that of PS.

Most of the results on the thermal decomposition and glass-transition temperature of PpMeS, however, were obtained with but a limited number of samples whose $\overline{M}_w$ and $\overline{M}_n$ values were not comparable with those of the PS samples used. Keeping in mind that the activation energy values for chain scission [8] or depolymerization [9, 10] encountered in thermal decompositions are molecular weight-dependent plus the fact that T_g values are also molecular weight-dependent [11-13], it was thought of interest to study, for comparison purposes, the thermal decomposition of a sample of PpMeS having $\overline{M}_w$ and $\overline{M}_n$ values similar to those of the PS [8] and PαMeS [10] previously studied. Furthermore, with a view to comparing the T_g values (at infinite molecular weight) of PpMeS with those of PS [11] and PαMeS [13], decomposed PpMeS samples having different $\overline{M}_n$ were investigated in a differential scanning calorimeter to determine their T_g values. A discussion of the principal results of this study is the object of the present communication.

EXPERIMENTAL

Poly-p-methylstyrene (PpMeS) (Aldrich Chemical Co.) was used as received in this study. Its weight-average molecular weight $\overline{M}_w$ was calculated from intrinsic viscosity data obtained in toluene at 30°C by using the relation reported in the literature [14]. Molecular weights of PpMeS samples both before and after thermal decomposition were determined with a Waters Associates model 200 gel-permeation chromatograph [8-13]. The instrument was calibrated with standard PS and PpMeS samples and the molecular weight values of the decomposed PpMeS samples were computed by the summation method suggested by the supplier [15].

A Perkin-Elmer model DSC-2 differential scanning calorimeter operating with pure dry helium in the cell zone was used to decompose 10-mg samples of PpMeS at a heating rate of 20°K/min. A Perkin-Elmer model TGS-1 thermogravimetric scanning balance operating in a pure dry nitrogen atmosphere was also used to follow the dynamic decomposition of 2-mg samples of the polymer at a heating rate of 20°K/min.

IR spectra of undecomposed and decomposed samples of PpMeS on KBr pellets were recorded with a Perkin-Elmer model 521 grating spectrometer. A series of experiments were performed in which, for a constant weight (50 mg) of KBr and undecomposed PpMeS, the content of the latter was varied from 2 to 6%. It was observed that the ratios of aromatic to aliphatic ν_{CH} increased with increasing PpMeS content. This increase resulted from the enhanced intensity of the aromatic ν_{CH} (rather than the aliphatic ν_{CH}) with increasing PpMeS content; best results were obtained with KBr pellets carrying 6% (3 mg polymer + 47 mg KBr) of PpMeS.

Nuclear magnetic resonance (NMR) analyses of the undecomposed PpMeS were carried out with a 220 MHz NMR spectrometer using 7, 11, 15, and 20 wt % solutions in CCl_4 at 75°C, tetramethylsilane being the internal standard. As variations of the PpMeS concentration under these conditions did not affect the various proton-proton ratios, the spectra of the decomposed PpMeS samples were subsequently observed with 7 wt % solutions.

The T_g values of the decomposed and undecomposed PpMeS samples were also determined with the Perkin-Elmer DSC-2 apparatus [12, 13].

RESULTS AND DISCUSSION

Thermal Decomposition of PpMeS

In Table 1 are summarized data on the percent weight loss α, the molecular weights $\overline{M}_w$ and $\overline{M}_n$, and the polydispersity ratio $\overline{M}_w/\overline{M}_n$ of PpMeS samples subjected to isothermal treatments at various temperatures for different periods. For values of α between 0 and 14%, $\overline{M}_w$ varied little while $\overline{M}_n$ decreased steadily, with a consequent increase in the value of $\overline{M}_w/\overline{M}_n$. For values of α greater than 14%,

LE 1. Data on PpMeS Samples Subjected to Isothermal Treatments at Various Temperatures a
ent Time Periods

le	Decomposition temperature (°C)	Decomposition time (min)	True weight loss α (%)	$M_w \times 10^{-4}$ (GPC)	$M_n \times 10^{-4}$ (GPC)
S-0	Undecomposed	-	0.0	13.5	5.1
S-1	250	50	0.8	11.1	4.1
S-2	275	50	1.0	11.4	4.2
S-3	300	50	2.0	10.8	3.6
S-4	310	50	4.6	10.3	3.1
S-5	315	50	5.8	10.5	3.0
S-6	320	50	6.9	10.3	2.8
S-7	325	50	10.6	11.4	2.3
S-8	330	50	14.1	11.8	1.5
S-9[a]	340	50	24.9	-	-
S-10[a]	350	50	43.5	-	-
S-11[a]	355	50	53.9	-	-
S-12[a]	365	50	74.3	-	-
S-13	330	10	4.9	10.3	2.5
S-14	330	20	6.2	9.4	2.3

S-15	330	30	8.4	10.2	2.2	4
S-16	330	60	20.1	45.1	1.6	28

olymers not completely soluble in THF.

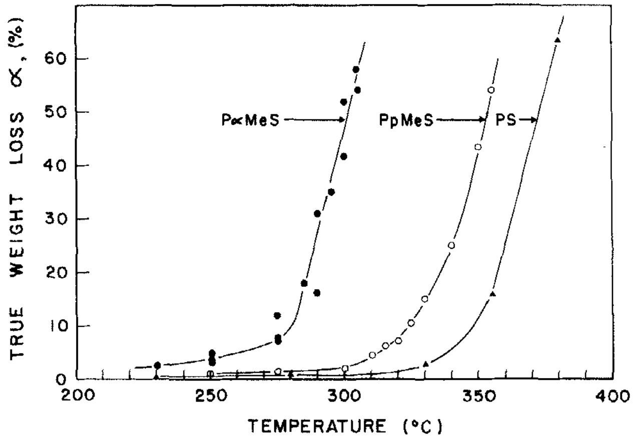

FIG. 1. Variation of weight loss α with temperature for PS, PpMeS, and PαMeS samples of similar $\overline{M}_w$.

the residual decomposed PpMeS samples were only partly soluble in THF. Their exact $\overline{M}_w$ and $\overline{M}_n$ values could not therefore be determined by GPC.

By using the 50 min isothermal decomposition data of Table 1 and the corresponding data published previously on polystyrene (PS) [8] and poly-α-methylstyrene (PαMeS) [10], curves representing the variation of α with temperature were plotted (Fig. 1) for comparision purposes. For identical values of α above the initial few percentage points, the respective decomposition temperatures for PpMeS and PαMeS are some 22 and 72°K lower than that for PS. This indicates that the presence of methyl groups facilitates the decomposition process, the influence being more significant when the substituent methyl is on the vinyl chain than when it is on the aromatic ring.

In Fig. 2 are shown four GPC distribution curves of PpMeS samples subjected to 50 min isothermal treatments at various temperatures. The peak in the GPC distributions of the decomposed polymers moves toward higher elution counts (i. e., lower molecular weights). Furthermore, as the treatment temperature increases, an increase is noted in the quantity of low molecular weight polymer between elution counts 28 and 34. This behavior is similar to that observed in the case of PS [8], where random scission and depolymerization reactions operate but is different to that of PαMeS [10] where only depolymerization has been shown to be responsible for its decomposition. Unlike the case of the decomposition of PS, in degraded PpMeS, crosslinked materials are believed to be present. These appear in the GPC distribution curves below elution count 26 (130 ml).

To better understand the decomposition of PpMeS, the normalized GPC distribution curve of an undecomposed sample was compared

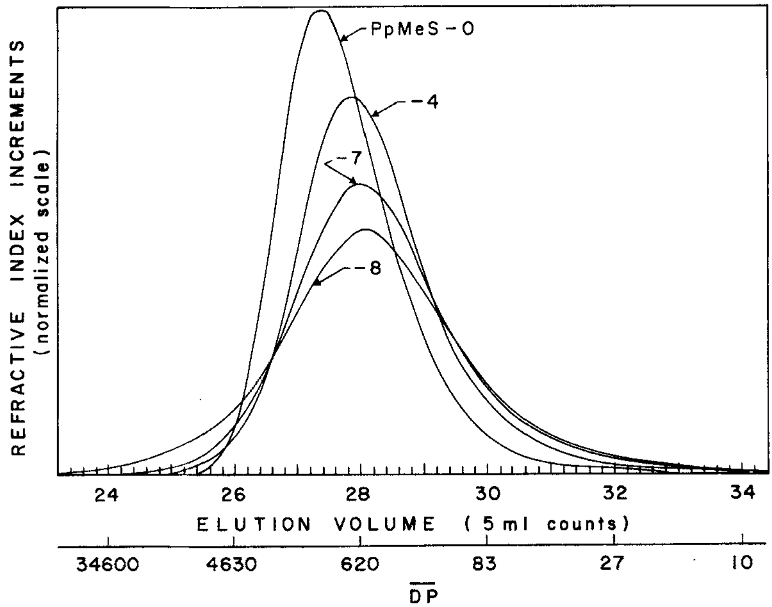

FIG. 2. GPC distribution curves of PpMeS samples subjected to 50 min isothermal treatments at various temperatures. See Table 1 for other data.

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 sample, the changes, both positive and negative, that take place as a result of the decomposition of the initial higher molecular weight species can readily be visualized. For the PpMeS samples studied, these changes are shown in Fig. 3, where the negative (-) distribution (between elution counts 26 and 29) represents the volatilized fraction due to decomposition and the positive (+) distributions (between elution counts 26 and 34 and between 22 and 26) represent newly formed nonvolatile products.

The characteristics of the various (-) and (+) GPC molecular weight distributions shown in Fig. 3 are summarized in Table 2 which lists their 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 250 to 315°C, increasing quantities of high molecular weight (between elution counts 26 and 29) with $\overline{M}_w$ of $(20\text{-}30) \times 10^4$ and $\overline{M}_w/\overline{M}_n$ of 1.2 decompose to yield products having $\overline{M}_w$ values of 7.0×10^4 (between elution counts

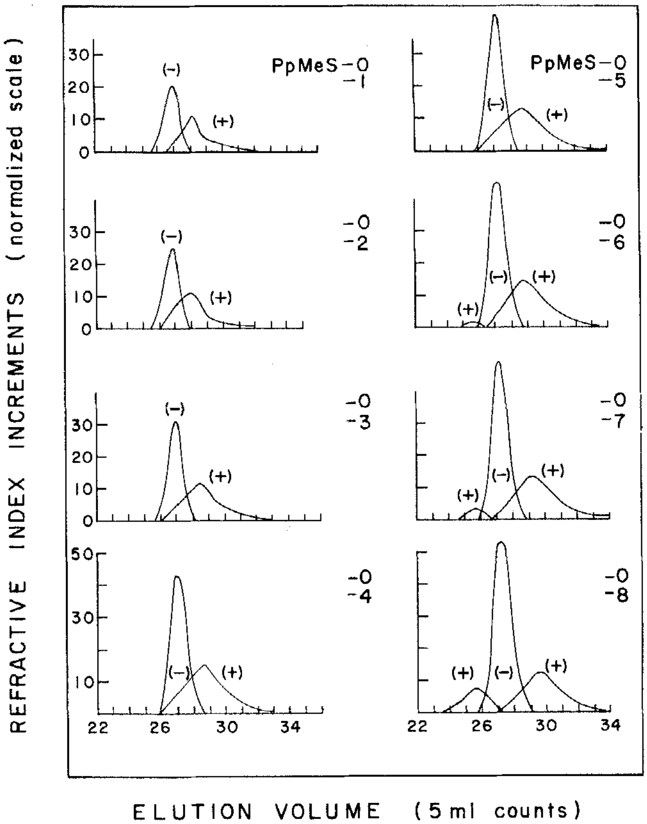

FIG. 3. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into their various components for the case of PpMeS samples subjected to 50 min isothermal treatments at different temperatures. See Table 2 for other data.

26 and 34) and $\overline{M}_w/\overline{M}_n$ ratios varying from 2.6 to 3.9. Between 315 and 330° C, the polymer appearing between elution counts 26 and 29 continues to decompose, yielding lower molecular weight residues; however, crosslinked products also appear between elution counts 22 and 26, their $\overline{M}_w$ values ranging from 8.6×10^5 to 11.8×10^5 and their $\overline{M}_w/\overline{M}_n$ ratios from 1.1 to 1.8. The α values associated with the crosslinked products increase from 0.8% (315°C) to 7.2% (330°C).

With a view to studying the evolution of the crosslinked products as a function of time, PpMeS samples were decomposed at a fixed temperature (330°C) for different periods ranging from 10 to 60 min.

2. Characteristics of the Polymers Appearing in Three GPC Elution Count Ranges: Decompo
S for 50 min at Different Temperatures and at 330°C for Different Periods^a

	GPC elution count range										
	22-26				26-29				27-34		
r pairs d	α (%)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	α (%)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	α (%)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$
0-PpMeS-1	-	-	-	-	11.6	26.6	22.0	1.2	9.8	7.25	2.83
0-PpMeS-2	-	-	-	-	14.0	28.8	23.4	1.2	13.1	9.65	2.84
0-PpMeS-3	-	-	-	-	17.2	23.6	19.5	1.2	15.7	6.86	1.96
0-PpMeS-4	-	-	-	-	27.8	20.1	15.9	1.3	21.6	6.63	1.87
0-PpMeS-5	-	-	-	-	26.7	19.6	15.7	1.3	20.6	6.18	1.60
0-PpMeS-6	0.8	86.0	77.8	1.1	29.3	18.6	14.6	1.3	21.1	4.35	1.36
0-PpMeS-7	2.2	86.0	68.8	1.3	33.3	17.7	13.6	1.3	19.8	3.09	1.03
0-PpMeS-8	7.2	118.0	65.3	1.8	39.4	16.7	12.1	1.4	17.7	2.36	0.93
0-PpMeS-13	-	-	-	-	23.0	21.2	16.6	1.3	16.3	6.2	1.80
13-PpMeS-14	-	-	-	-	12.0	19.8	14.4	1.4	8.9	6.15	1.75
14-PpMeS-15	2.8	35.5	26.4	1.4	5.0	11.5	7.7	1.5	-	-	-
15-PpMeS-8	5.4	69.0	31.7	2.2	11.2	11.5	6.9	1.7	-	-	-
8-PpMeS-16	5.4	524.0	204.0	2.6	16.9	12.4	6.5	1.9	4.4	0.65	0.41

Table 1 for reaction conditions.

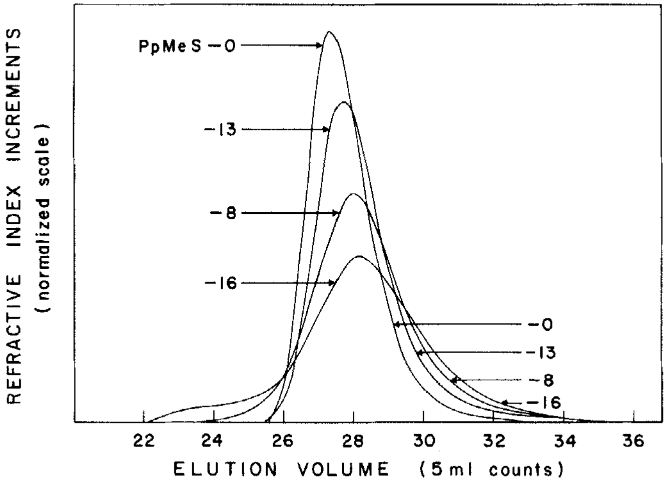

FIG. 4. GPC molecular weight distributions of PpMeS sample subjected to isothermal treatments at 330°C for different periods. See Table 1 for other data.

Their α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values are listed in Table 1. Within experimental limits (± 1%) at 330°C, the values of α increase linearly with time (graph not shown here). For isothermal decompositions carried out at 330°C, between zero and 10 min, $\overline{M}_w$ decreases from 13.5×10^4 to 10.3×10^4 and $\overline{M}_n$ goes from 5.1×10^4 to 2.55×10^4. Between 10 and 50 min, $\overline{M}_w$ remains constant while $\overline{M}_n$ continues to decrease. At 60 min of isothermal decomposition, $\overline{M}_w$ increases to 4.5×10^4, while $\overline{M}_n$ remains constant at 1.5×10^4.

The normalized GPC molecular weight distributions of PpMeS decomposed at 330°C during various periods are shown in Fig. 4. These are much the same as those shown in Fig. 2 which were obtained after 50 min isothermal decompositions of PpMeS at different temperatures. Decompositions carried out at 310°C for 50 min (PpMeS-4) or 330°C for 10 min (PpMeS-13) both yield α values of about 5%, and their corresponding $\overline{M}_w$ and $\overline{M}_n$ values do not differ by much. Similarly, decompositions carried out at 315°C for 50 min (PpMeS-5) or 330°C for 20 min (PpMeS-14) both yield α values of about 6%. Their corresponding $\overline{M}_w$ and $\overline{M}_n$ values are likewise very similar. It would appear that in the early stages of the reaction ($\alpha < 6\%$) the mode of decomposition is not controlled by the reaction conditions. In the more advanced stages of decomposition ($\alpha > 6$)

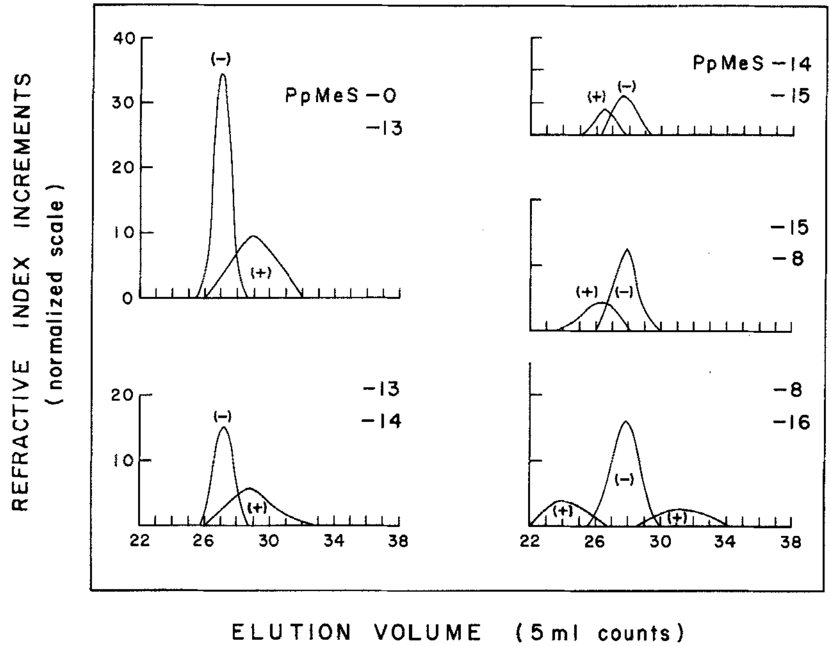

FIG. 5. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into their various components for the case of PpMeS samples subjected to isothermal treatments at 330°C for different periods. See Table 2 for other data.

where very high molecular weight polymer appears, the reaction conditions under which data are obtained become more important. In this connection, the results gathered (with time as the variable) may yield important information regarding the precise conditions under which crosslinking takes place.

In Fig. 5 are shown changes that occur in the GPC molecular weight distributions of five PpMeS samples subjected to decompositions at 330°C for various periods. The changes noted for any given sample are those relative to the distribution of the same material decomposed during the nearest shorter time. Thus, in Fig. 5 are shown the changes when the decomposition time is varied from 0 to 10, from 10 to 20, from 20 to 30, from 30 to 50, and from 50 to 60 min, respectively. The values of α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$, associated with (-) and (+) distributions shown in Fig. 5, are summarized in Table 2. These data show that the isothermal treatment of PpMeS during the initial 20-min period results in the decomposition of polymer 35% (23.0 + 12.0) having an average $\overline{M}_w$ of 20×10^4 and $\overline{M}_n$ of 15×10^4

yielding a product 25.2% (16.3 + 8.9) having an average $\overline{M}_w$ of 6.2×10^4 and $\overline{M}_n$ of 1.8×10^4. In the intervals 20 to 30, 30 to 50, and 50 to 60 min, the decomposed polymer has an average $\overline{M}_w$ of 11.5×10^4 and $\overline{M}_n$ of 7.0×10^4, a part of which crosslinks to yield high molecular weight products with $\overline{M}_w$ and $\overline{M}_n$ ranging from 35.5×10^4 to 524×10^4 and 26.4×10^4 to 204×10^4 respectively. The quantity of crosslinked product also increases with the time of decomposition going from 2.8% at 30 min, to 8.2% (2.8 + 5.4) at 50 min and to 13.6% (2.8 + 5.4 $\pm$ 5.4) at 60 min. In the time intervals 20 to 30 and 30 to 50 min, there were no low molecular weight products. For decompositions up to 60 min, 4.4% of the products observed were of very low molecular weight ($\overline{M}_w = 6.5 \times 10^3$ and $\overline{M}_n = 4.1 \times 10^3$). From these results, one is led to believe that the decomposition of polymer with an $\overline{M}_w$ of 20×10^4 and an $\overline{M}_n$ of 15×10^4 results in the formation of lower molecular weight polymer with an $\overline{M}_w$ of 11.5×10^4 and an $\overline{M}_n$ of 7.0×10^4 which intercrosslinks or which crosslinks with undecomposed parts of the high molecular weight polymer having an $\overline{M}_w$ of 20×10^4 and an $\overline{M}_n$ of 15×10^4.

Based on the results of the GPC molecular weight distribution study on both the undecomposed and decomposed PpMeS samples, one may conclude the following.

(1) The mechanism of random scissions lowers to an $\overline{M}_w$ value ranging anywhere from 2×10^3 to 20×10^4, the molecular weight of that part of the polymer having an $\overline{M}_w$ of 20×10^4 and an $\overline{M}_n$ of 15×10^4; (2) part of these low molecular weight products depolymerize to low molecular weight oligomers (dimers, trimers, etc.) that volatilized; and (3) part of the low molecular weight polymers (with $\overline{M}_w$ of 11.5×10^4 and $\overline{M}_n$ of 7×10^4) intercrosslink or crosslink with very high molecular weight polymer molecules which have not yet decomposed.

To gain insight into the mechanism of the crosslinking reactions, it was thought of interest to elucidate the structural changes that take place when the undecomposed PpMeS samples are subjected to isothermal treatments at various temperatures. This was carried out by IR and NMR spectroscopy.

In Fig. 6 are shown IR spectra of undecomposed (PpMeS-0) and decomposed (PpMeS-6, PpMeS-10) samples of PpMeS. The spectrum of the undecomposed material shows important peaks [16] at the following frequencies: 3100, 3080, 3040 and 3910 (aromatic ν_{CH}), 2910 (ν_{CH_3}), 2840 (ν_{CH_2}), 2000-1600 (shape typical of p-substitution), 1495 (phenyl ring) 1430, 1390 (δ_{CH_3}, δ_{CH_2}), 1360 (δ_{CH_3}), 1160, 1090,

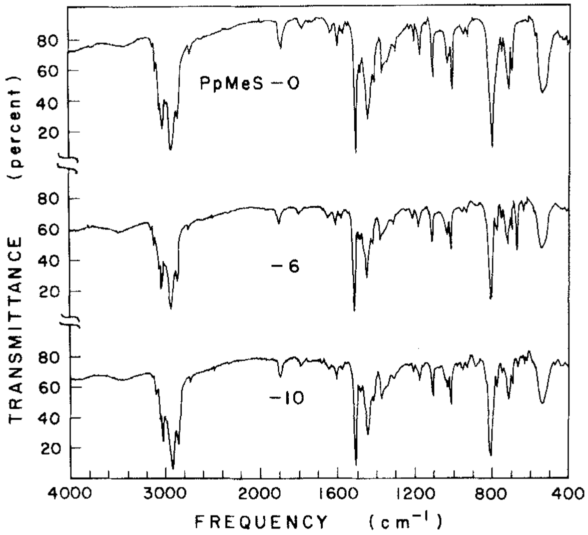

FIG. 6. IR spectra of undecomposed and decomposed samples of PpMeS. See Table 3 for other data.

1000 (in-plane CH bending of phenyl) and 790 cm^{-1} (out-of-plane CH bending of two adjacent aromatic hydrogens). All of these peaks are present in the spectra of the decomposed samples though their intensities may or may not be the same as those of the PpMeS-0 sample.

In Table 3 are summarized the intensity ratios of undecomposed and decomposed samples of PpMeS. In the temperature range 25 to 325°C, the ν_{CH} intensity ratios: CH_3/CH_2, CH_3/arom and CH_2/arom, remain nearly constant at 1.41 ± 0.03, 0.58 ± 0.03, and 0.41 ± 0.01, respectively. At 350°C, however, the CH_3/CH_2 ratio decreases to 1.33 while the CH_3/arom and CH_2/arom ratios increase. This indicates that between 325 and 350°C the $\nu_{\mathrm{CH_3}}$ and ν_{arom} intensities decrease, whereas the $\nu_{\mathrm{CH_2}}$ intensity increases. At a yet higher temperature (365°C), the CH_3/CH_2 ratio remains constant at 1.31 while the CH_3/arom and CH_2/arom ratios continue to increase, suggesting that between 350 and 365°C, it is only the ν_{arom} intensity that decreases. This decrease suggests that one of the sites involved in the crosslinking reactions observed with the PpMeS samples decomposed isothermally at 350 and 365°C by the GPC data (Figs. 2-5 and Tables 1 and 2), may be located at their aromatic rings. The decrease in the ν_{arom} intensity could also arise from an artifact in the IR

TABLE 3. IR ν_{CH} Intensity Ratios of Undecomposed and Decomposed Samples of PpMeS

Sample	Decomposition temperature (°C)	ν_{CH} intensity ratios		
		CH_3/CH_2	CH_3/arom	CH_2/arom
PpMeS-0	(Undecomposed)	1.38	0.56	0.40
PpMeS-1	250	1.38	0.57	0.41
PpMeS-6	320	1.48	0.61	0.41
PpMeS-7	325	1.41	0.57	0.41
PpMeS-10	350	1.33	0.66	0.50
PpMeS-12	365	1.31	0.76	0.58

spectra of the decomposed polymers; however, for the time being, the concept of side reactions leading to the involvement of the aromatic ring in the crosslinking reactions is retained.

As mentioned earlier in the text, the PpMeS samples decomposed at temperatures higher than 330°C are not soluble in THF, o-$C_6H_4Cl_2$, or CCl_4 and thus their NMR spectra cannot be recorded. PpMeS samples decomposed below 330°C, however, are completely soluble in CCl_4. With a view to confirming the IR results obtained with the PpMeS samples (PpMeS-0, PpMeS-6, and PpMeS-7), their NMR spectra were observed at 75°C in CCl_4 as solvent and are shown in Fig. 7. The highlights of these spectra are as follows: benzene protons (H_{arom}) at $\tau = 2.8$-4.0; p-methyl protons (pCH_3) at $\tau = 7.3$-8.0; methine protons (CH) at $\tau = 8.0$-8.4; and methylene protons (CH_2) at $\tau = 8.4$-9.0.

The relative abundances of the different protons in a polymer may best be expressed in the form of ratios. In PpMeS there are six possible combinations of proton/proton ratios and these are presented in Table 4 for the monomer, pMeS, the undecomposed polymer PpMeS-0, and decomposed polymer (PpMeS-1, PpMeS-6, and PpMeS-7) samples. A comparison of the proton/proton ratios of pMeS and PpMeS-0 shows that besides the H_{arom}/p-CH_3 ratio none of the other ratios, viz., H_{arom}/CH, H_{arom}/CH_2, p-CH_3/CH, p-CH_3/CH_2, and CH_2/CH are the same. This suggests that PpMeS-0 is not 100% pure. On close examination of the NMR proton/proton ratios, it appears that these ratios correspond to a 95% PpMeS and 5% PS mixture.

A comparison of the proton/proton ratios for the PpMeS-1, PpMeS-6, and PpMeS-7 samples with those of the PpMeS-0 sample

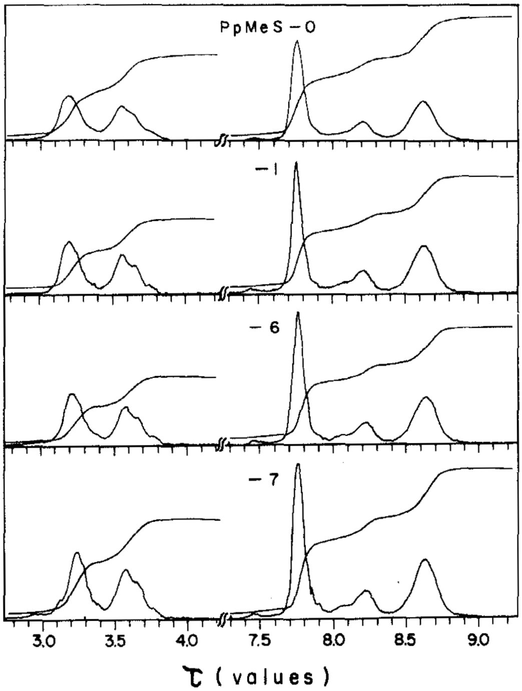

FIG. 7. NMR spectra of undecomposed and decomposed samples of PpMeS. See Table 4 for other data.

reveals that H_{arom} and CH_2 protons decrease slightly whereas the p-CH_3 and CH protons remain constant for samples exposed to isothermal conditions between 25 and 325°C. These results show that H_{arom} as well as CH_2 protons may be involved somehow in the crosslinking reactions. They also support the IR results discussed earlier when the participation of H_{arom} in such reactions was suggested. Because the magnitude of the changes in H_{arom} and CH_2 proton intensities observed here was small, no attempt was made to postulate the reaction mechanisms leading to crosslinking.

In Fig. 8 are shown the curves representing dynamic thermogravimetric decomposition at a heating rate of 20°K/min, of PS, PpMeS, and PαMeS samples of similar molecular weights $\overline{M}_n$. By use of the method of Coats and Redfern [17, 18], activation energies were calculated for the decomposition of PS, PpMeS, and PαMeS, on assuming successively orders of reaction of zero and one. The values are

E 4. Values of Proton/Proton Ratios Obtained from NMR Spectra of Undecomposed and Decom
es of PpMeS

	pMeS (monomer)[a]	PpMeS-0[b]	PpMeS-1	PpMeS-6	Pp
/p-CH_3	1.33	1.36 ± 0.03	1.23	1.18	1.2
/CH	4.0	3.93 ± 0.10	3.62	3.54	3.6
/CH_2	2.0	1.87 ± 0.03	1.84	1.78	1.8
/CH	3.0	2.91 ± 0.10	2.93	2.99	2.9
/CH_2	1.5	1.38 ± 0.02	1.49	1.50	1.5
H	2.0	2.10 ± 0.06	1.97	1.99	1.9

eoretical values.

verage of values obtained from NMR spectra observed with 7, 11, 15 and 20 wt % solutions.

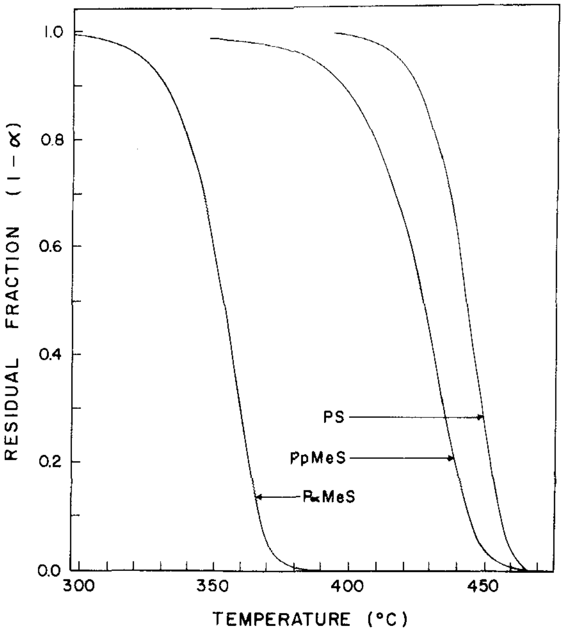

FIG. 8. Dynamic thermogravimetric decomposition of PS, PpMeS, and PαMeS samples of similar $\overline{M}_n$ at a heating rate of 20°K/min. See Table 5 for other data.

presented in Table 5. One notes that PpMeS and PαMeS have much the same activation energies for their decomposition though both are lower than that for PS. It is thought that the presence of methyl groups in the vinyl chain or in the aromatic ring facilitates the formation of radicals that bring about the decomposition reactions and consequently lower activation energies are involved.

Glass Transition of PpMeS

It is well known that glass-transition temperature values T_g of polymers are dependent on both sample heating rate [11-13, 19-24] and sample cooling rate [25, 26].

In earlier studies carried out in this laboratory [11-13], T_g values were determined as suggested in the literature [27] at the $\Delta C_p/2$ point (ΔC_p being the change in heat capacity observed at the glass transition). These were found to increase with increasing values of

TABLE 5. Activation Energy Values for the Thermal Decomposition of Polystyrene (PS) and Two of its Derivatives (PαMeS and PpMeS)[a]

Sample	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	Activation energy (kcal/mole)	
			n = 0	n = 1
PS	4.6	1.1	-	103.0
PαMeS	4.6	1.9	56.1	62.3
PpMeS	5.1	2.7	45.7	62.2

[a] Method of Coats and Redfern [17, 18]; n is the order of reaction.

the heating rate q (°K/min). 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 extrapolated T_{g_e} values at a heating rate of 1°K/min were obtained from plots of log q versus $1/T_g$.

Though various heating rates were used to measure T_g in earlier studies [11-13], T_g was not determined while cooling and only a single high cooling rate of 320°K/min was employed. In order to establish the influence of sample cooling rate on T_{g_e} values, in the present study T_g values of PpMeS sample were determined while cooling as well as heating at different rates.

In Fig. 9 are shown typical DSC-2 thermograms of a PpMeS sample recorded in the glass transition region at cooling rates of 320, 80, 10, and 1.25°K/min. A heating rate of 40°K/min was used in this case to return the sample to a temperature above T_g. One notes that the rate of cooling does not affect the T_g values of PpMeS. In Table 6 are summarized T_g values obtained at heating rates of 80, 40, 20, and 10°K/min for different sample cooling rates. The extrapolated T_{g_e} (to q = 1°K/min) values, regardless of the sample cooling rate (1.25, 2.5, 5, 10, 20, 40, 80, and 320°K/min), all fall within ±1°K of 378.5. As a consequence and for the sake of convenience, T_g determinations were made on the decomposed samples of PpMeS after they had been cooled to a temperature below T_g at a rate of 320°K/min.

The principal experimental T_g results obtained on isothermally decomposed PpMeS samples with $\overline{M}_n$ ranging from 1.8×10^4 to

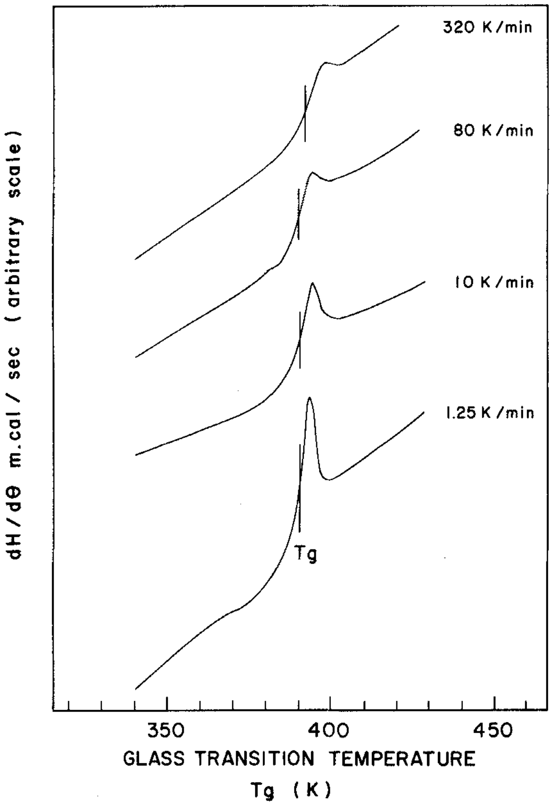

FIG. 9. Typical DSC-2 thermograms of a PpMeS sample, recorded in the glass transition region at various cooling rates; heating rate constant at 40°K/min. See Table 6 for other data.

5.1×10^4 are summarized in Table 7. The values of T_{g_e} were found to increase with increasing $\overline{M}_n$.

In Fig. 10 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 of the molecular weight is located at 5.0×10^4. A plot of T_{g_e} as a function of $1/\overline{M}_n$, shown in Fig. 11, yields a straight line corresponding to Eq. (1):

$$T_{g_e}\ (^\circ K) = 384 - 2.65 \times 10^5/\overline{M}_n \qquad (1)$$

ABLE 6. Effect of Thermal History on T_{g_e} Determinations of an Undecomposed PpMeS Sampl

e g rate in)	T_g at various heating rates (°K)				T_{g_e} (1°K
	80°K/min	40°K/min	20°K/min	10°K/min	
	392.5	389.0	387.0	386.0	378.
	392.5	388.5	387.5	387.0	379.
	393.0	389.0	387.5	387.0	378.
	393.0	389.0	387.5	387.0	378.
	392.5	389.0	387.5	387.0	379.
	393.5	389.0	388.0	387.0	378.
	393.5	390.0	387.5	387.0	378.
	393.5	389.5	388.0	387.0	378.

trapolated value at a heating rate q of 1°K/min by using the equation: $\log q = a - b/T_g$ [11].

T_g vs Heating Rate Data for Undecomposed and Decomposed Samples of PpMeS (Decompositi
min)

	Weight loss α (%)	Molecular weight $\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	T_g at various heating rates (°K)				T_{ge}
				80°K/min	40°K/min	20°K/min	10°K/min	(1°K/
	0.0	5.1	2.7	392.5	389.0	387.0	386.0	378.0
	0.6	4.5	2.7	392.0	390.0	387.5	386.0	379.0
	1.0	3.95	3.0	392.0	389.5	386.5	385.5	377.5
	3.7	3.4	3.5	389.0	387.0	382.0	382.5	376.0
	6.7	4.3	3.8	388.0	386.0	383.0	382.0	374.0
	9.3	2.35	4.8	387.0	384.0	382.5	380.5	373.5
	12.5	2.15	5.9	384.5	383.0	381.5	379.0	373.5
	17.9	1.8	26.6	384.0	381.0	379.0	377.0	369.5
a	19.1	-	-	382.5	380.0	378.0	376.5	370.0
a	33.0	-	-	378.5	375.5	373.5	372.5	365.0
a	53.0	-	-	373.5	371.5	368.5	365.0	356.5
a	66.3	-	-	368.5	366.0	364.0	-	354.5

ers insoluble in THF.

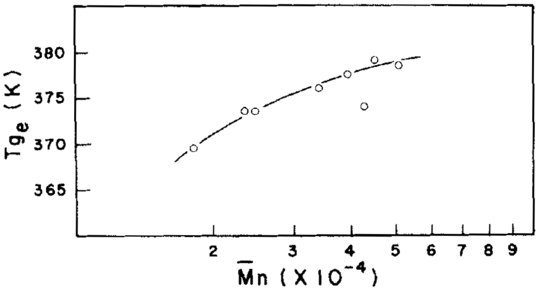

FIG. 10. Extrapolated T_{g_e} values (to q = 1°K/min) of PpMeS as a function of $\overline{M}_n$. See Table 7 for other data.

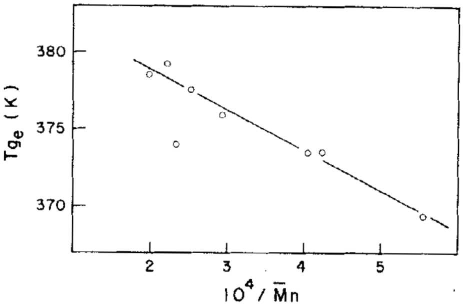

FIG. 11. Extrapolated T_{g_e} values (to q = 1°K/min) of PpMeS as a function of $1/\overline{M}_n$. See Table 7 for other data.

In earlier work from this laboratory [11, 13], T_{g_e} of PS [Eq. (2)] and PαMeS [Eq. (3)], respectively, were related to $\overline{M}_n$.

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

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

The addition of a methyl substituent in the aromatic ring (p-CH_3) increases the value of T_{g_∞} from 379°K (for PS) to 384°K (for PpMeS); however, the addition of a methyl substituent in the vinyl chain (α-methyl) increases the value of T_{g_∞} from 379°K (for PS) to 453°K (for PαMeS). It appears that substitution in the p-position does not result in increased steric hindrances or decreased chain flexibility as was the case for PαMeS [13].

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

(1) In the isothermal decomposition of PpMeS, random scissions reduce the chain length of the polymer, while depolymerization reactions account for volatilization. A part of the lower molecular weight decomposition products either intercrosslink or crosslink with undecomposed high molecular weight PpMeS species. The locus of crosslinking may reside in the aromatic ring.

(2) T_g measurements made on the decomposed PpMeS samples yield T_{g_∞} of 384°K, a value not far removed from that of PS (379°K) but well below that of PαMeS (453°K). This suggests that substitutions in the para position do not decrease chain flexibility or contribute towards greater steric hindrance.

(3) To determine T_{g_∞} of a polymer, samples with varying $\overline{M}_n$ values are required. These are generally obtained by the polymerization of monomer under different reaction conditions which is often laborious and time consuming. If, on the other hand, one has only small quantities of a high molecular weight polymer whose thermal decomposition takes place by random scissions as well as depolymerization reactions without alteration of its basic structure, various samples with different $\overline{M}_n$ values become readily obtainable for T_g determinations as shown by the present study.

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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REFERENCES

[1] Yu. A. Glagoleva and V. R. Regel, Polym. Sci. U. S. S. R., 12, 1078 (1970).

[2] N. Inagaki, Y. Takagi, and K. Katsuura, Eur. Polym. J., 13, 433 (1977).

[3] G. T. Kennedy and F. Morton, J. Chem. Soc., 1949, 2383.

[4] T. E. Davies, Brit. Plastics, 32, 283 (1959).

[5] K. R. Dunham, J. W. H. Faber, J. Vandenberghe, and W. F. Fowler, J. Appl. Polym. Sci., 7, 897 (1963).

[6] V. Frosini and P. L. Magagnini, Eur. Polym. J., 2, 129 (1966).

[7] L. C. Corrado, J. Chem. Phys., 50, 2260 (1969).

[8] S. L. Malhotra, J. Hesse, and L. P. Blanchard, Polymer, 16, 81 (1975).

[9] S. L. Malhotra, C. Baillet, H. H. Lam-Tran, and L. P. Blanchard, J. Macromol. Sci.–Chem., A12, 103 (1978).

[10] S. L. Malhotra, C. Baillet, L. Minh, and L. P. Blanchard, J. Macromol. Sci.–Chem., A12, 129 (1978).

[11] L. P. Blanchard, J. Hesse, and S. L. Malhotra, Can. J. Chem., 52, 3170 (1974).

[12] S. L. Malhotra, L. Minh, and L. P. Blanchard, J. Macromol. Sci.–Chem., A12, 149 (1978).

[13] S. L. Malhotra, L. Minh, and L. P. Blanchard, J. Macromol. Sci.–Chem., A12, 167 (1978).

[14] G. Tanaka, S. Imai, and H. Yamakawa, J. Chem. Phys., 52, 2639 (1970).

[15] Waters Associates, Gel Permeation Chromatograph Instruction Manual, Bull. No. 2, 2064 (1966).

[16] K. Nakanishi, Infrared Absorption Spectroscopy, Holden-Day, San Francisco, and Nankodo Co., Tokyo, 1962.

[17] A. W. Coats and J. P. Redfern, Nature, 201, 68 (1964).

[18] A. W. Coats and J. P. Redfern, J. Polym. Sci. B., 3, 917 (1965).

[19] S. Strella, J. Appl. Polym. Sci., 7, 569 (1963).

[20] B. Wunderlich, D. M. Bodily, and M. H. Kaplan, J. Appl. Phys., 35, 95 (1964).

[21] S. Strella and P. F. Erhardt, J. Appl. Polym. Sci., 13, 1373 (1969).

[22] A. Lambert, Polymer, 10, 319 (1969).

[23] S. M. Wolpert, A. Weitz, and B. Wunderlich, J. Polym. Sci., A-2, 9, 1887 (1971).

[24] M. J. Richardson and N. G. Savill, Polymer, 16, 753 (1975).

[25] B. Wunderlich and D. M. Bodily, J. Polym. Sci. C., 6, 137 (1964).

[26] J. Bourdariat, A. Berton, J. Chaussy, R. Isnard, and J. Odin, Polymer, 14, 167 (1973).

[27] W. P. Brennan, Perkin-Elmer DSC-2 Instruction Manuals, 7 and 8, Perkin-Elmer Co., Norwalk, Conn., 1973.

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