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### A Thermal Decomposition and Glass Transition Temperature Study of Poly(p-chlorostyrene)

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## A Thermal Decomposition and Glass Transition Temperature Study of Poly(p-chlorostyrene)

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### ABSTRACT

The thermal decomposition and the glass transition temperature of poly(p-chlorostyrene) (PpClS) were studied with a Model 2 differential scanning calorimeter (DSC). The undecomposed and decomposed polymers were analyzed by gel permeation chromatography for molecular weight distributions and by DSC for changes in the polymer glass transition temperature. The decomposition of PpClS under isothermal conditions during 50 min intervals at various temperatures or at a fixed temperature (320°C) but for different periods is characterized by the disappearance of increasing quantities of high molecular weight polymer and the appearance of low molecular weight products. Random scissions have been shown to break down the polymer chains which depolymerize into volatile products. Activation energy (72 kcal/mole) for the decomposition of PpClS is lower than that (103 kcal/mole) for the decomposition of polystyrene

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(PS). Variation of  $T_{g_e}$  (at  $q = 1^\circ \text{K}/\text{min}$ ) with  $\bar{M}_n$  obeys the relation:  $T_{g_e} (^\circ \text{K}) = 398 - 2.71 \times 10^5 / \bar{M}_n$ . The value of  $398^\circ \text{K}$  for the  $T_{g_\infty}$  of PpClS is higher than the value ( $383^\circ \text{K}$ ) reported in the literature. The presence of the chloro group in the p-position of PS results in an increased hindrance and decreased chain flexibility, thereby increasing its  $T_{g_\infty}$ .

## INTRODUCTION

Thermal decomposition [1-10] and glass transition temperature studies [7-14] of polystyrene (PS) [1, 2, 11], poly( $\alpha$ -methylstyrene) (P $\alpha$ MeS) [3, 4, 12, 13], poly(p-isopropyl  $\alpha$ -methylstyrene) (PpiPr $\alpha$ MeS) [5, 6, 14], poly(p-methylstyrene) (PpMeS) [7], poly(p-isopropylstyrene) (PpiPrS) [8], poly(p-tert-butylstyrene) (PptBuS) [9], and poly(p-methoxystyrene) PpOMeS) [10] have been reported on.

In polystyrenes substituted with p-methyl and p-isopropyl groups, crosslinking of polymer chains is observed; however, other substituents, viz.,  $\alpha$ -methyl, p-tert-butyl, and p-methoxy, do not cause such reactions. In polymers of similar molecular weights for identical weight-loss values,  $\alpha$ , the treatment temperatures for PS, PpMeS, and PpOMeS followed the order PS > PpOMeS > PpMeS. The activation energy for the decomposition of polystyrene and the same homologs, however, followed the order  $E_{\text{PS}} > E_{\text{PpMeS}} > E_{\text{PpOMeS}}$ .

A comparison of  $T_{g_\infty}$  values for PS ( $379^\circ \text{K}$ ), PpMeS ( $384^\circ \text{K}$ ), and PpOMeS ( $386^\circ \text{K}$ ) revealed that the presence of the p-CH<sub>3</sub> and p-OCH<sub>3</sub> groups neither influence the chain flexibility nor cause further steric hindrance in PS.

Keeping this in mind, a study of the thermal decomposition and the glass transition temperature of a quite different homolog of polystyrene, namely poly(p-chlorostyrene) (PpClS), was carried out. The data obtained were compared with those of PS chains carrying other substituents as well as those reported on the decomposition [15] and  $T_g$  [16-19] of PpClS. The principal results are outlined in the following paragraphs.

## EXPERIMENTAL

PpClS obtained from the Aldrich Chemical Co. was used as received. The weight-average molecular weight,  $\bar{M}_w$ , of the polymer was calculated from intrinsic viscosity data obtained with toluene at  $30^\circ \text{C}$  using the relation reported in the literature [20]. Molecular weight distributions of PpClS samples were obtained with a Waters Associates (Model 200) gel permeation chromatograph [1-10] which had been calibrated with standard PS and PpClS samples.

A Perkin-Elmer (Model 2) differential scanning calorimeter operating with pure dry helium as purge gas was used for the isothermal decomposition of PpClS whereas a Perkin-Elmer thermogravimetric scanning balance operating in a pure dry nitrogen atmosphere was used for the dynamic decomposition of PpClS. The  $T_g$  values of the undecomposed and decomposed samples of PpClS were determined with the DSC apparatus [7-10].

## RESULTS AND DISCUSSION

### Thermal Decomposition of PpClS

In Table 1 are summarized values of the weight loss ( $\alpha$  in %), the molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ), and the polydispersities ( $\bar{M}_w/\bar{M}_n$  ratios) obtained with PpClS 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  $\alpha$  with temperature is given in Fig. 1. For comparison purposes, data for the 50 min isothermal treatment of PS [2] and PpOMeS [10] are also plotted in this figure. For  $\alpha$  values below 10%, the respective treatment temperatures obey the order PS  $\geq$  PpOMeS  $>$  PpClS. For  $\alpha$  values of 10% and above, the order of treatment temperature is PS  $>$  PpOMeS = PpClS. This indicates that the presence of  $-\text{OCH}_3$  and  $-\text{Cl}$  substituents on the aromatic rings in PS facilitates the formation of radicals which bring about random scission and depolymerization of the polymer chains. For  $\alpha$  values of 10% and above, the  $-\text{OCH}_3$  and  $-\text{Cl}$  substituents have the same capacity to produce radicals; however, for  $\alpha$  values of less than 10% the  $-\text{OCH}_3$  substituent is more active than the  $-\text{Cl}$  substituent. In general, for identical values of  $\alpha$  ( $\alpha > 3\%$ ), the respective decomposition temperatures for PpClS are 15 to 20° K lower than the corresponding ones for PS.

In Fig. 2 are shown the normalized GPC molecular weight distribution curves of six PpClS at various temperatures. The maxima in the 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 28 and 36. This behavior is similar to that observed in the case of PS [2] where random scission and depolymerization reactions operate.

To better understand the decomposition of PpClS, 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. By subtracting from the initial distribution curve of the undecomposed polymer the distribution curve of any subsequently decomposed polymer, it is possible to

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

Sample no.	Treatment temperature (°C)	Treatment time (min)	Weight loss $\alpha$ (%)	$\bar{M}_w$ (GPC) $\times 10^{-4}$	$\bar{M}_n$ (GPC) $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
PpCIS-0	Undecomposed	-	0	25.2	6.1	4.1
PpCIS-1	200	50	2.3	20.7	6.4	3.2
PpCIS-2	220	50	2.3	21.3	6.9	3.1
PpCIS-3	265	50	2.9	17.4	5.1	3.4
PpCIS-4	275	50	3.1	17.2	5.6	3.0
PpCIS-5	285	50	3.2	16.3	4.0	4.1
PpCIS-6	300	50	3.6	17.1	5.1	3.4
PpCIS-7	320	50	7.6	14.0	4.1	3.4
PpCIS-8	340	50	17.7	8.3	2.5	3.3
PpCIS-9	350	50	35.4	4.7	1.4	3.3
PpCIS-10	355	50	46.2	3.2	1.0	3.1
PpCIS-11	360	50	66.5	1.9	0.7	2.7
PpCIS-12	320	10	4.0	18.0	4.9	3.7
PpCIS-13	320	20	5.0	17.0	4.5	3.8
PpCIS-14	320	30	5.6	17.0	4.4	3.8
PpCIS-15	320	90	9.6	13.0	3.3	3.9
PpCIS-16	320	120	11.5	12.0	3.6	3.5
PpCIS-17	320	180	14.4	11.0	3.1	3.6

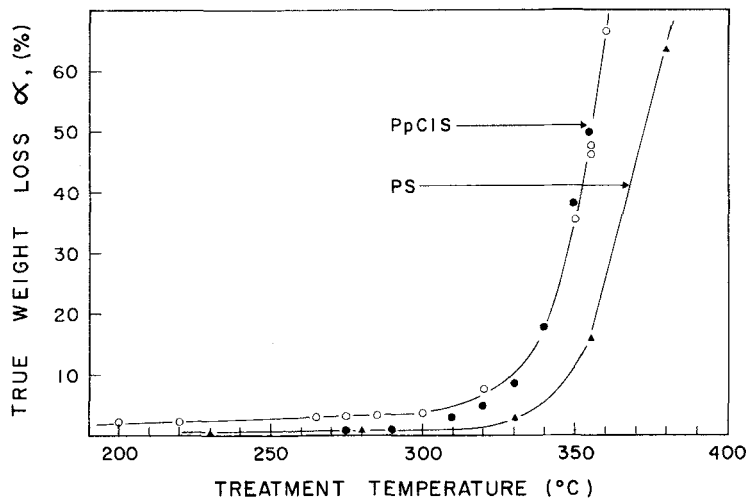


FIG. 1. Weight loss  $\alpha$  (%) vs treatment temperature  $T$  ( $^{\circ}\text{C}$ ) for PS ( $\blacktriangle$ ) ( $\overline{M}_w = 1.6 \times 10^5$  [2]) and PpClS ( $\circ$ ) ( $\overline{M}_w = 2.52 \times 10^5$ ) samples. Solid circles ( $\bullet$ ) are data obtained with PpOMeS ( $\overline{M}_w = 6.7 \times 10^5$  [10]). See Table 1 for other data on PpClS.

visualize the changes, both positive and negative, that take place as a result of the decomposition of the initial higher molecular weight species. For the PpClS samples studied, these changes are shown in Figs. 3 and 4, where the distribution over the negative sign (-) (between elution counts 25 and 28) represents the volatilized fraction due to decomposition and that over the positive sign (+) (between elution counts 26 and 32) represents 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 includes  $\alpha$ ,  $\overline{M}_w$ ,  $\overline{M}_n$ , and  $\overline{M}_w/\overline{M}_n$  values. For 50 min isothermal decompositions, as the temperature is raised from 25 to  $360^{\circ}\text{C}$  increasing quantities of high molecular weight material with  $\overline{M}_w$  of  $(74.6 \text{ to } 28.6) \times 10^4$  and  $\overline{M}_w/\overline{M}_n$  of 1.4 to 2.1 (located between elution counts 25 and 28 on the GPC curves) decompose to yield products (appearing on the GPC curves between elution counts 26 and 32) having  $\overline{M}_w$  values of  $(15.6 \text{ to } 0.7) \times 10^4$  and  $\overline{M}_w/\overline{M}_n$  values varying from 1.2 to 4.1.

In Fig. 5 are shown the normalized GPC molecular weight distributions of three PpClS samples subjected to thermal decomposition at a fixed temperature ( $320^{\circ}\text{C}$ ) for different periods ranging from 10 to 180 min. Their  $\alpha$ ,  $\overline{M}_w$ ,  $\overline{M}_n$ , and  $\overline{M}_w/\overline{M}_n$  are listed in Table 1. With

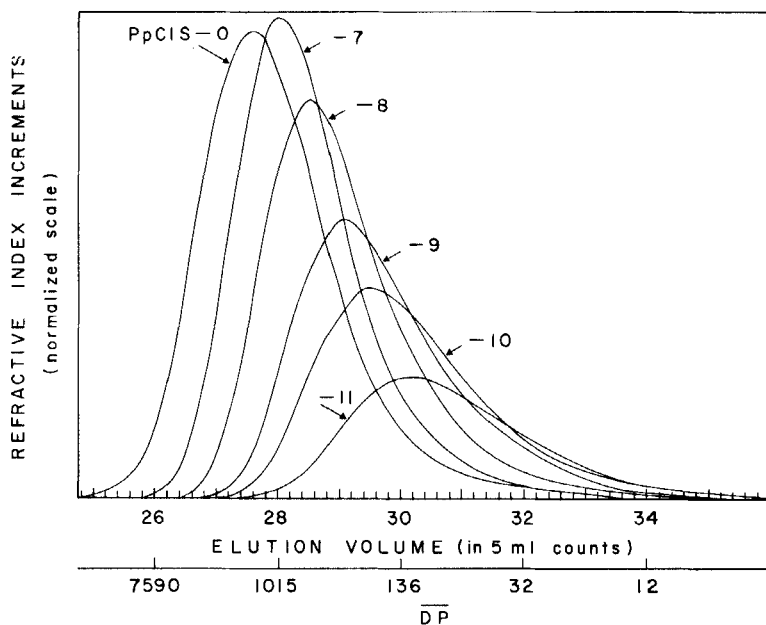


FIG. 2. Normalized GPC molecular weight distributions of PpClS samples subjected to 50 min decomposition periods at various temperatures. See Table 1 for other data.

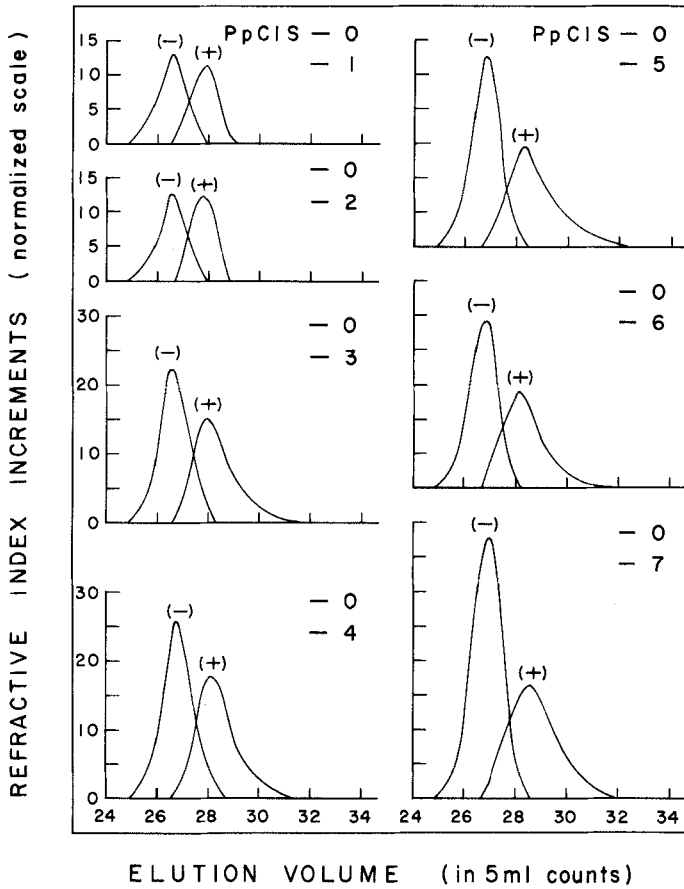


FIG. 3. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of PpCIS samples subjected to 50 min decomposition periods in the temperature range of 200 to 320°C. See Table 2 for other data.

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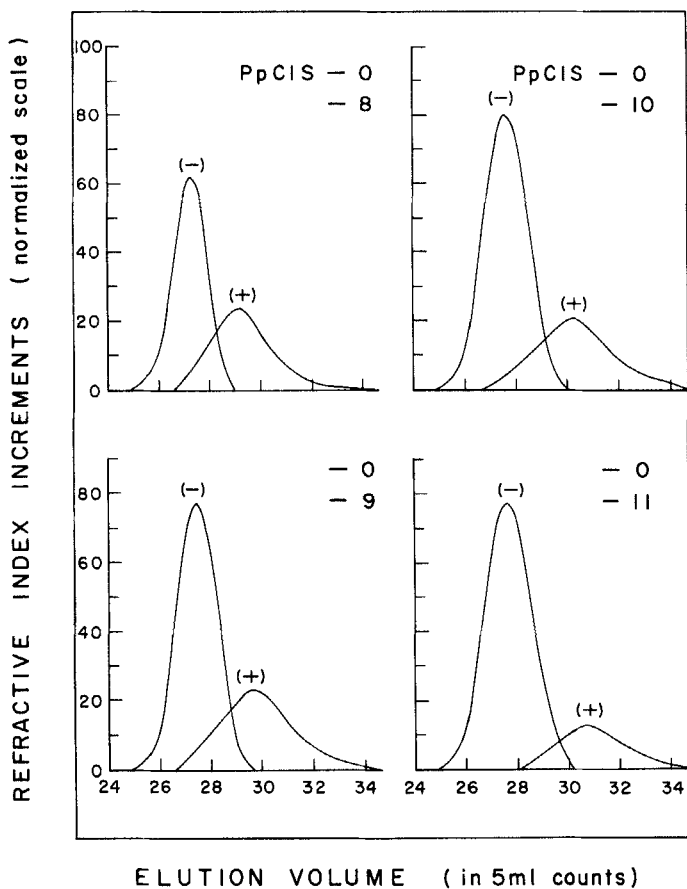


FIG. 4. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of PpClS samples subjected to 50 min decomposition periods in the temperature range of 340 to 360°C. See Table 2 for other data.

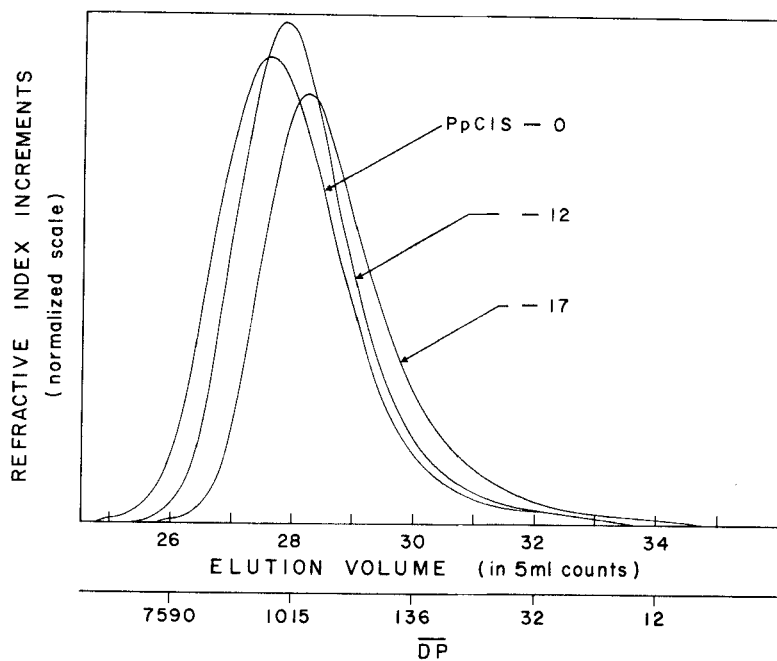


FIG. 5. Normalized GPC molecular weight distributions of PpClS samples subjected to isothermal treatments at 320°C for different periods. See Table 1 for other data.

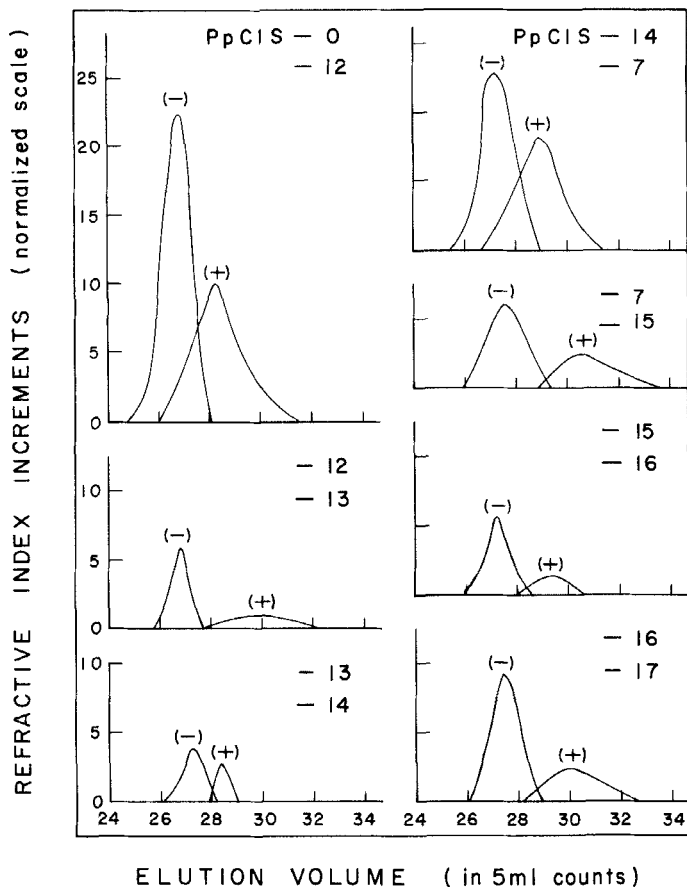


FIG. 6. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of PpClS samples subjected to isothermal treatments at  $320^{\circ}\text{C}$  for different periods. See Table 2 for other data.

increasing  $\alpha$  values,  $\bar{M}_w$  and  $\bar{M}_n$  decrease regularly whereas  $\bar{M}_w/\bar{M}_n$  stays within  $\pm 0.2$  of 3.7.

In Fig. 6 are shown changes that occur in the GPC molecular weight distributions of seven PpClS samples subjected to thermal decomposition at  $320^{\circ}\text{C}$ , 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  $\alpha$ ,  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $\bar{M}_w/\bar{M}_n$ , associated with both the (-) and the (+) distributions shown in Fig. 6 are summarized in Table 2. These data show that the isothermal treatment of PpClS

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

Polymer-pairs analyzed	Elution count range											
	(25-28)			(-)			(26-32)			(+) )		
	$\alpha$ (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\alpha$ (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\alpha$ (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
PpClS-0 - PpClS-1	8.5	74.6	55.0	1.4	6.9	19.7	15.6	1.3	6.9	19.7	15.6	1.3
PpClS-0 - PpClS-2	7.7	74.7	55.0	1.4	7.3	19.6	16.3	1.2	7.3	19.6	16.3	1.2
PpClS-0 - PpClS-3	16.4	65.8	46.4	1.4	13.9	13.8	6.9	2.0	13.9	13.8	6.9	2.0
PpClS-0 - PpClS-4	19.0	56.1	36.9	1.5	16.1	12.3	6.3	1.9	16.1	12.3	6.3	1.9
PpClS-0 - PpClS-5	19.2	57.3	40.5	1.4	15.4	10.3	3.8	2.7	15.4	10.3	3.8	2.7
PpClS-0 - PpClS-6	17.1	61.1	44.7	1.4	13.1	12.8	6.5	2.0	13.1	12.8	6.5	2.0
PpClS-0 - PpClS-7	27.3	51.7	36.4	1.4	19.3	9.7	3.9	2.5	19.3	9.7	3.9	2.5
PpClS-0 - PpClS-8	53.9	48.7	31.5	1.5	33.8	6.8	1.9	3.5	33.8	6.8	1.9	3.5
PpClS-0 - PpClS-9	74.4	32.0	18.4	1.7	39.1	5.0	1.2	4.1	39.1	5.0	1.2	4.1
PpClS-0 - PpClS-10	84.6	29.4	15.2	1.9	37.1	3.7	0.9	4.1	37.1	3.7	0.9	4.1
PpClS-0 - PpClS-11	88.2	28.6	13.4	2.1	19.2	1.5	0.7	2.3	19.2	1.5	0.7	2.3
PpClS-0 - PpClS-12	15.5	61.0	45.7	1.3	11.5	15.4	5.9	2.6	11.5	15.4	5.9	2.6
PpClS-12 - PpClS-13	2.4	51.7	45.7	1.1	1.3	3.0	1.4	2.1	1.3	3.0	1.4	2.1

(continued)

TABLE 2 (continued)

Polymer-pairs analyzed	Elution count range							
	(25-28)		(-)		(26-32)		(+)	
	$\alpha$ (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\alpha$ (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
PpCIS-13 - PpCIS-14	2.2	31.2	25.6	1.2	0.8	9.1	8.6	1.1
PpCIS-14 - PpCIS-7	10.9	34.7	23.3	1.5	9.0	8.4	3.9	2.2
PpCIS-7 - PpCIS-15	5.6	26.4	16.4	1.6	2.9	1.2	0.8	1.6
PpCIS-15 - PpCIS-16	3.8	30.6	22.0	1.4	0.9	4.8	3.8	1.3
PpCIS-16 - PpCIS-17	6.4	27.2	20.3	1.3	2.7	2.3	1.3	1.8

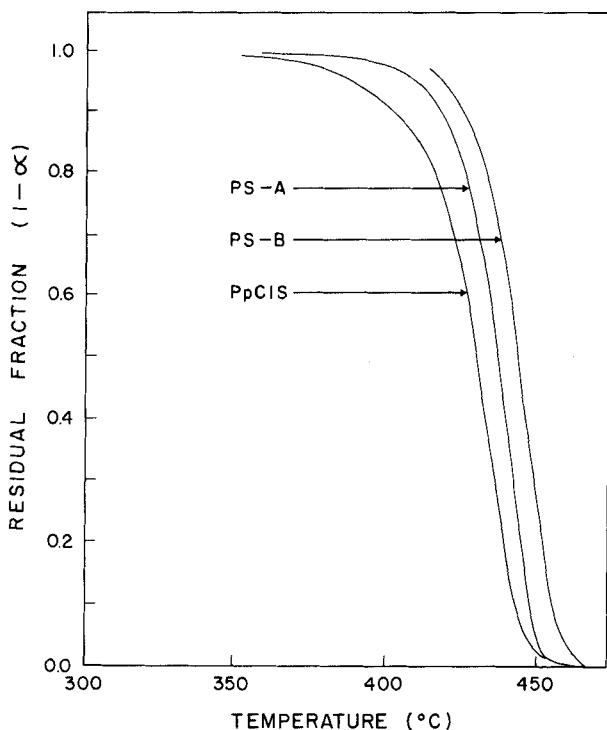


FIG. 7. Dynamic thermogravimetric decomposition of PS and PpClS samples at a heating rate of 20° K/min. See Table 3 for other data.

during the initial 10 min period results in the decomposition of 15.5% of the polymer having an  $\bar{M}_w$  of  $6.1 \times 10^5$  and an  $\bar{M}_n$  of  $4.6 \times 10^5$  ( $\bar{M}_w/\bar{M}_n = 1.3$ ) which yields a product (11.5%) with an  $\bar{M}_w$  of  $1.54 \times 10^5$  and an  $\bar{M}_n$  of  $0.59 \times 10^5$  ( $\bar{M}_w/\bar{M}_n = 2.6$ ). In the intervals 10 to 20, 20 to 30, 30 to 50, 50 to 90, 90 to 120, 120 to 180 min, 2.4, 2.2, 10.9, 5.6, 3.8, and 6.4% of the polymer with  $\bar{M}_w$ s of  $(51.7 \text{ to } 27.2) \times 10^4$  and  $\bar{M}_n$ s of  $(45.7 \text{ to } 20.3) \times 10^4$  decompose into volatile matter and new degradation products (1.3, 0.8, 9.0, 2.9, 0.9, and 2.7% respectively) of

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

Sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Activation energy (kcal/mole) <sup>a</sup>	
			n = 0	n = 1
PS-A	14.0	1.1	-	102.0
PS-B	4.6	1.1	-	103.0
PpMeS	5.1	2.7	45.7	62.2
PpOMeS	3.9	17.1	39.6	77.4
PpClS	6.1	4.1	52.4	72.3

<sup>a</sup> n is the order of reaction.

lower molecular weight with  $\bar{M}_w$ s of  $(9.1 \text{ to } 2.3) \times 10^4$  and  $\bar{M}_n$ s of  $(8.6 \text{ to } 1.3) \times 10^4$ . In the decomposition runs where  $\alpha$  values are significant, the polydispersities of the decomposed products are close to 2.0.

Based on these GPC molecular weight results derived from both undecomposed and decomposed PpClS samples, one may draw the following conclusions:

1. In the 50-min isothermal treatment of PpClS 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 depolymerize into volatile products. The decomposition behavior, in general, resembles that of PS [ 2 ]. Due to the presence of the -Cl group in the PS aromatic rings, the thermal decomposition of PpClS is facilitated; however, the decreases in the values of  $\alpha$ ,  $\bar{M}_w$ , or  $\bar{M}_n$  as a function of temperature or time are not as regular as those observed with PS [ 2 ]. The thermal decomposition of PpClS resembles very much more that of PpOMeS in this aspect.

2. The results of the present study agree well with those reported on by Inagaki et al. [ 15 ] who showed that PpClS is less stable than PS; however, the other conclusions by Inagaki et al. [ 15 ], that PpOMeS is more stable than PpClS because of the presence of an electron-repelling group (-OCH<sub>3</sub>) in the former and an electron-withdrawing group (-Cl) in the latter polymer, are not completely supported by this study. For  $\alpha$  values less than 5%, PpOMeS was found to be more stable than PpClS whereas for  $\alpha$  values > 5% the two polymers showed the same degree of thermal stability.

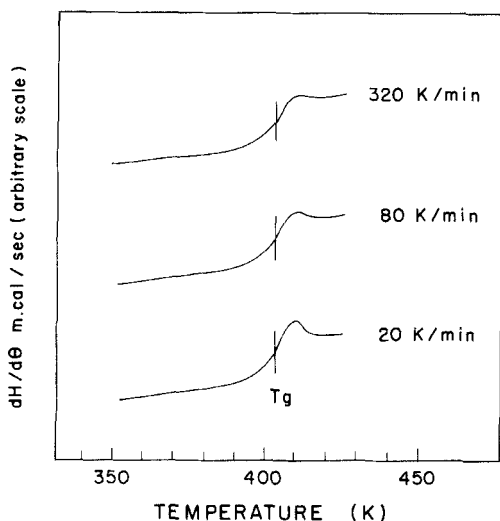


FIG. 8. Typical DSC thermograms of an undecomposed sample of PpClS recorded in the glass transition region at a heating rate of  $40^{\circ}$  K/min following cooling at various rates. See Table 4 for other data.

In Fig. 7 are shown curves representing the dynamic thermogravimetric decomposition, at a heating rate of  $20^{\circ}$  K/min, of PS and PpClS 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 along with those for PpMeS [7] and PpOMeS [10]. The activation energy for the decomposition of PpClS is lower than that for PS but is nevertheless close to the values of PpMeS and PpOMeS.

#### Glass Transition of PpClS

The glass transition temperature ( $T_g$ ) of a polymer is heating-rate dependent [7-14] and in some cases cooling-rate dependent [22, 23]. Though recent work [7-10] on PpMeS, PpiPrS, PptBuS, and PpOMeS showed that the cooling rate has no effect on the  $T_g$  of substituted polystyrenes, it was thought pertinent to verify the effects that the cooling rate might have on the  $T_g$  of PpClS.

In Fig. 8 are shown typical DSC thermograms obtained with the undecomposed polymer and recorded in the glass transition range at a fixed heating rate of  $40^{\circ}$  K/min. Various cooling rates were used



TABLE 4. Effect of Thermal History on the Determination of the  $T_g$  of an Undecomposed PpClS Sample

Sample cooling rate ( $^{\circ}\text{K}/\text{min}$ )	$T_g$ at heating rates (in $^{\circ}\text{K}/\text{min}$ ) of				$T_{ge}^a$ at $1^{\circ}\text{K}/\text{min}$
	80	40	20	10	
320	401.0	398.0	396.0	395.0	388.0
80	400.0	398.0	397.0	394.5	389.0
40	401.0	398.5	397.0	395.0	388.0

<sup>a</sup>Extrapolated value at a heating rate ( $q$ ) of  $1^{\circ}\text{K}/\text{min}$  using equation:  $\log q = a - b/T_g$  [11].

to bring the samples to a temperature approximately  $30^{\circ}\text{K}$  below their expected  $T_g$  value prior to tracing the thermogram in the heating mode. The  $T_g$  values, determined at the  $\Delta C_p/2$  point [7-14], remained constant as the cooling rate was increased from 40 to  $320^{\circ}\text{K}/\text{min}$ . The  $T_g$  values of the undecomposed polymer subjected to three cooling rates are presented in Table 4. The extrapolated  $T_{ge}$  values (at a heating rate of  $1^{\circ}\text{K}/\text{min}$ ) are likewise listed. These remain constant at  $388.5 \pm 0.5^{\circ}\text{K}$ . Subsequent  $T_g$  measurements on the decomposed polymer samples were made only after cooling the samples below  $T_g$  at the maximum rate of  $320^{\circ}\text{K}/\text{min}$ .

In Fig. 9 are shown typical DSC thermograms of an undecomposed PpClS 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  $320^{\circ}\text{K}/\text{min}$  and heating rates of 80, 40, 20, and  $10^{\circ}\text{K}/\text{min}$  for the undecomposed and a number of decomposed PpClS samples are summarized in Table 5. The values of  $T_{ge}$  are found to increase with increasing  $\bar{M}_n$ .

In Fig. 10 is shown a plot of  $T_{ge}$  as a function of  $\bar{M}_n$ .  $T_{ge}$  increases up to a point beyond which it remains constant. The critical value is located at an  $\bar{M}_n$  value of  $4.0 \times 10^4$ . A plot of  $T_{ge}$  as a function of  $1/\bar{M}_n$  shown in Fig. 11 yields a straight line corresponding to

$$T_{ge} (^{\circ}\text{K}) = 398 - 2.71 \times 10^5 / \bar{M}_n \quad (1)$$

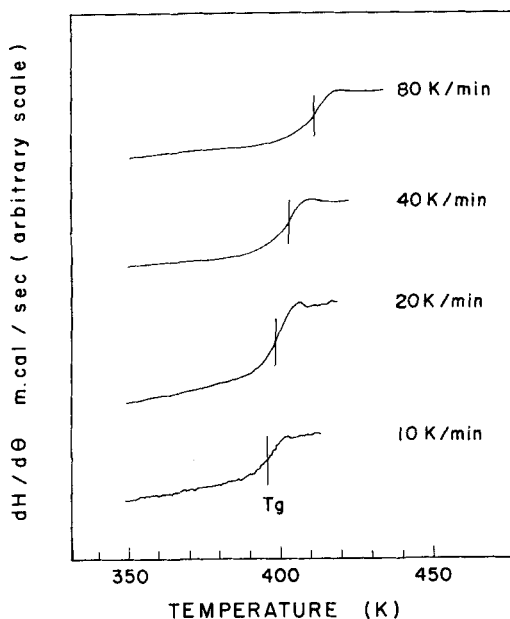


FIG. 9. Typical DSC thermograms of an undecomposed sample of PpClS recorded in the glass transition region at various heating rates using a cooling rate of  $320^{\circ}\text{K}/\text{min}$ . See Table 4 for other data.

The value of  $398^{\circ}\text{K}$  for the  $T_{g\infty}$  of PpClS is higher than the value  $383^{\circ}\text{K}$  reported in the literature [16-19].

In earlier work from this laboratory [11] the  $T_{g_e}$  of PS was related to  $\bar{M}_n$  as follows:

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

The addition of a chloro substituent in the aromatic ring increases the value of  $T_{g\infty}$  from 379 to PS to 398 for PpClS. The value of the constant  $K$ , which is related to the free volume of the polymer, is also higher for PpClS. It would appear that the presence of chloro groups results in increased steric hindrance and decreased chain flexibility, thereby increasing  $T_{g\infty}$ .

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

1. In the isothermal decomposition of PpClS, random scissions reduce the chain length of the polymer and depolymerization reactions account for the weight loss.

TABLE 5.  $T_g$  Data Obtained at Various Heating Rates on Undecomposed and Decomposed Samples of PpCIS

Sample no.	Weight loss $\alpha$ (%)	$\bar{M}_n$ (GPC) $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$T_g$ at heating rates (in $^{\circ}\text{K}/\text{min}$ ) of				$T_{ge}$ at $1^{\circ}\text{K}/\text{min}$
				80	20	40	10	
PpCIS-0	Undecomposed	6.16	4.1	401.0	396.0	398.0	395.0	388.0
PpCIS-18	3.3	5.80	3.6	403.0	399.5	401.0	398.5	393.0
PpCIS-19	4.6	4.15	4.1	404.0	400.5	402.0	399.0	393.0
PpCIS-20	6.8	3.52	4.2	403.5	399.5	401.5	398.0	391.0
PpCIS-21	9.9	2.70	3.8	398.0	394.5	396.0	393.0	386.5
PpCIS-22	13.2	2.46	3.8	394.0	391.0	392.5	389.0	383.0
PpCIS-23	18.7	2.38	3.4	396.0	392.0	394.0	390.5	389.0
PpCIS-24	29.2	1.25	3.5	385.5	382.5	384.0	382.0	377.5
PpCIS-25	35.2	1.40	3.5	391.5	387.5	389.5	385.5	379.0
PpCIS-26	48.2	0.80	3.6	377.0	372.0	375.0	371.0	364.0
PpCIS-27	56.8	0.72	3.2	374.5	369.5	372.0	367.0	359.5

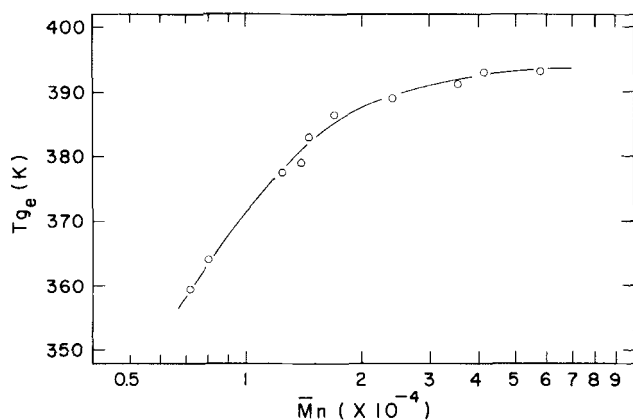


FIG. 10. Extrapolated  $T_{g_e}$  values (to  $q = 1^\circ\text{K}/\text{min}$ ) of PpClIS as a function of  $\bar{M}_n$ . See Table 5 for other data.

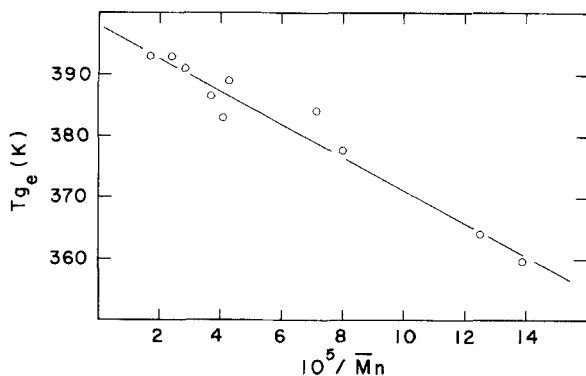


FIG. 11. Extrapolated  $T_{g_e}$  values (to  $q = 1^\circ\text{K}/\text{min}$ ) of PpClIS as a function of  $1/\bar{M}_n$ . See Table 5 for other data.

2. The presence of a p-chloro group in the PS aromatic rings lowers the thermal stability of PpClIS as evidenced by its lower activation energy of decomposition. The thermal stabilities of PpClIS, PpMeS, and PpOMeS have been found to be very much the same. These results are not in complete agreement with those reported by Inagaki et al. [15] which suggest that PpOMeS is more stable than PpMeS and PpClIS.

3. The addition of the chloro group in the p-position of the PS aromatic rings results in increased steric hindrance and decreased chain flexibility, thereby increasing  $T_{g\infty}$ .

Further studies on the effect of other substituents on the thermal decomposition and glass transition temperature of substituted polystyrenes are in progress and will be reported on in due course.

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