

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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

S. L. Malhotra^{ab}; P. Lessard^{ac}; L. P. Blanchard^a

^a D partement de G nie chimique Facult  des Sciences et de G nie Universit  Laval Qu bec, Groupe de Recherches en Sciences Macromol culaires, Qu bec, Canada ^b Xerox Research Centre of Canada, Mississauga, Ontario ^c Division de la propulsion, Centre de Recherche pour la Defense, Courcellette, Qu bec

To cite this Article Malhotra, S. L. , Lessard, P. and Blanchard, L. P.(1981) 'A Thermal Decomposition and Glass Transition Temperature Study of Poly(p-bromostyrene)', *Journal of Macromolecular Science, Part A*, 15: 8, 1577 – 1599

To link to this Article: DOI: 10.1080/00222338108056804

URL: <http://dx.doi.org/10.1080/00222338108056804>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

S. L. MALHOTRA,* P. LESSARD,† and L. P. BLANCHARD

Groupe de Recherches en Sciences Macromoléculaires
Département de Génie chimique
Faculté des Sciences et de Génie
Université Laval
Québec, Québec, Canada, G1K 7P4

ABSTRACT

The thermal decomposition and the glass transition temperature of poly(p-bromostyrene) (PpBrS) 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 glass transition temperatures. The decomposition of PpBrS under isothermal conditions during 50 min intervals at increasing temperatures or at a fixed temperature (320°C) for increasing periods results in increasing quantities of high molecular weight polymer yielding greater amounts of low molecular weight products. Random scissions have been shown to break the polymer chains which then volatilize via depolymerization. Activation energy for the decomposition of PpBrS at 118 kcal/mol is near that (102 kcal/mol) of polystyrene (PS). Variation of T_{ge} (at $q = 1$ K/min) with \overline{M}_n obeys the relation

*Present address: Xerox Research Centre of Canada, 2480 Dunwin Drive, Mississauga, Ontario L5L 1J9.

†Present address: Centre de Recherche pour la Défense, Division de la propulsion, Valcartier, C.P. 880, Courcelette, Québec G0A 1R0.

$$T_{g_e}(\text{K}) = 414 - 1.5 \times 10^5 / \bar{M}_n$$

The value 414 K for the T_{g_∞} of PpBrS is higher than that (391 K) reported in the literature. A comparison of T_{g_∞} for poly(p-chlorostyrene) (398 K) and PpBrS (414 K) shows that the p-bromo substituent causes more steric hindrance than its p-chloro homolog.

INTRODUCTION

Thermal decomposition [1-11] and glass transition temperature studies [7-15] of polystyrene (PS) [1, 2, 12], poly- α -methylstyrene (P α MeS) [3, 4, 13, 14] poly-p-isopropyl α -methylstyrene (PpiPr α MeS) [5, 6, 15], poly-p-methylstyrene (PpMeS) [7], poly-p-isopropylstyrene (PpiPrS) [8], poly-p-tert-butylstyrene (PptBuS) [9], poly-p-methoxystyrene (PpOMeS) [10], and poly-p-chlorostyrene (PpClS) [11] have been reported on earlier from this laboratory.

The p-methyl and p-isopropyl groups in substituted polystyrenes were found to participate in the cross-linking of polymer chains whereas the α -methyl, p-tert-butyl, p-methoxy, and p-chloro groups did not. A comparison of α weight-loss values for polymer samples having $\bar{M}_w > 10^5$ showed that for identical values, the treatment temperatures followed the order PS > PpOMeS \approx PpClS > PpMeS. The activation energy for the decomposition of these polymers, however, followed the order $E_{\text{PS}} > E_{\text{PpMeS}} \approx E_{\text{PpClS}} \approx E_{\text{PpOMeS}}$.

A comparison of the T_{g_∞} values for PS (379 K), PpMeS (384 K), PpOMeS (386 K), and PpClS (398 K) showed that, although the electron-repelling p-CH₃ and p-OCH₃ substituents do not influence the T_{g_∞} of Ps (379 K), the electron-withdrawing p-Cl substituent does raise this value to 398 K.

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

EXPERIMENTAL

PpBrS obtained from the Aldrich Chemical Co. in the United States was used as received. The weight-average molecular weight, \bar{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 PpBrS samples were obtained with a Waters Associates (Model 200) gel permeation chromatograph [1-11] calibrated with standard PS and PpBrS samples.

A Perkin-Elmer (Model DSC-2) differential scanning calorimeter operating with pure dry helium was used for the isothermal decomposition of PpBrS whereas a Perkin-Elmer (Model TGS-1) thermogravimetric scanning balance operating in pure dry nitrogen was used for the dynamic decomposition of PpBrS. The T_g values of the undecomposed and decomposed samples of PpBrS were determined with the DSC-2 apparatus [7-11].

RESULTS AND DISCUSSION

Thermal Decomposition of PpBrS

In Table 1 are summarized values of the percent weight-loss α , the molecular weights, \bar{M}_w and \bar{M}_n , and the polydispersities, \bar{M}_w/\bar{M}_n ratios, obtained with PpBrS 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 the 50 min isothermal treatment of PS [2], PpOMeS [10] and PpClS [11] are also plotted in this figure. For all values of α , the thermal stability of these homologs of PS obeys the following decreasing order PS > PpOMeS \approx PpClS = PpBrS. For identical values of α above 5%, the respective decomposition temperature of PpBrS is about 15 K lower than that of PS.

In Fig. 2 are shown the normalized GPC molecular weight distribution curves of six PpBrS 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 36. This behavior is similar to that observed with PS [2], PpOMeS [10], and PpClS [11] where random scission and depolymerization reactions operate.

In Fig. 3 is shown the variation of \bar{M}_w with treatment temperature for PpBrS samples subjected to 50-min decomposition periods at various temperatures, \bar{M}_w decreases regularly from 1.82×10^5 (\bar{M}_w of the undecomposed polymer) to 1.2×10^4 after a 50-min isothermal treatment at 355°C.

In Fig. 4 are shown, for different modes of operation, the variation

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

Sample no.	Treatment temperature, °C	Treatment time, min	Weight-loss α (%)	\bar{M}_w (GPC) $\times 10^{-4}$	\bar{M}_n (GPC) $\times 10^{-4}$	\bar{M}_w/\bar{M}_n
PpBrS-0	Undecomposed	-	-	182	12.6	14.4
PpBrS-1	200	50	0.9	97.2	14.5	6.7
PpBrS-2	250	50	1.0	81.3	12.6	6.5
PpBrS-3	300	50	2.2	16.9	3.5	4.8
PpBrS-4	315	50	3.7	10.1	2.2	4.6
PpBrS-5	320	50	3.1	8.7	1.9	4.5
PpBrS-6	330	50	5.7	5.7	1.4	4.1
PpBrS-7	340	50	17.2	2.8	0.5	5.6
PpBrS-8	345	50	27.8	1.7	0.4	4.3
PpBrS-9	350	50	38.0	1.3	0.3	4.3
PpBrS-10	350	50	44.2	1.1	0.3	3.7
PpBrS-11	355	50	50.6	1.2	0.3	4.0
PpBrS-12	320	10	1.7	31.6	7.4	4.3
PpBrS-13	320	20	1.9	21.3	4.5	4.8
PpBrS-14	320	30	2.0	13.4	3.0	4.5
PpBrS-15	320	90	5.5	6.5	1.5	4.3
PpBrS-16	320	120	7.4	6.0	1.2	5.0
PpBrS-17	320	180	11.2	5.2	1.1	4.7

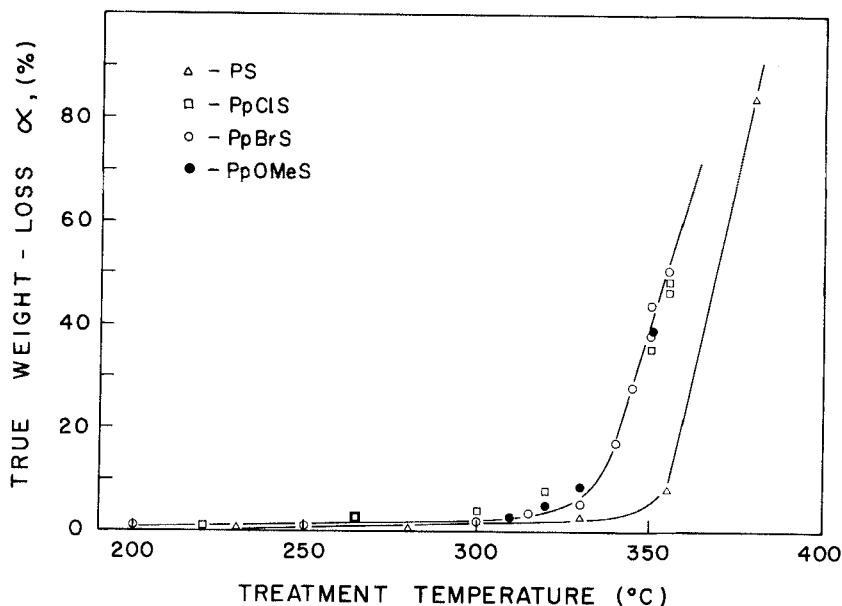


FIG. 1. Variation of weight-loss α (%) with treatment temperature T ($^{\circ}\text{C}$) for PS ($\overline{M}_w = 1.8 \times 10^5$ [2]), PpBrS ($\overline{M}_w = 1.82 \times 10^6$), PpOMeS ($\overline{M}_w = 6.7 \times 10^5$ [10]), and PpClS ($\overline{M}_w = 2.52 \times 10^5$ [11]). See Table 1 for other data on PpBrS.

in molecular weight as a function of α . Initially, the molecular weight decreases drastically with increasing values of α , and for identical values, obtained following 50-min isothermal treatments at various temperatures or at 320°C using different decomposition periods, the decrease in molecular weight is the same. This behavior in the decomposition of PpBrS is similar to that observed with PS [2].

Based on the data presented in Table 1 and on an analysis of Figs. 1 to 4, it is evident that the presence of Br groups in the aromatic rings of PS greatly enhances the formation of radicals which bring about random scission and depolymerization of the polymer chains.

To better understand the decomposition of PpBrS, 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 PpBrS, these changes are shown in Figs. 5 and 6, where the distributions

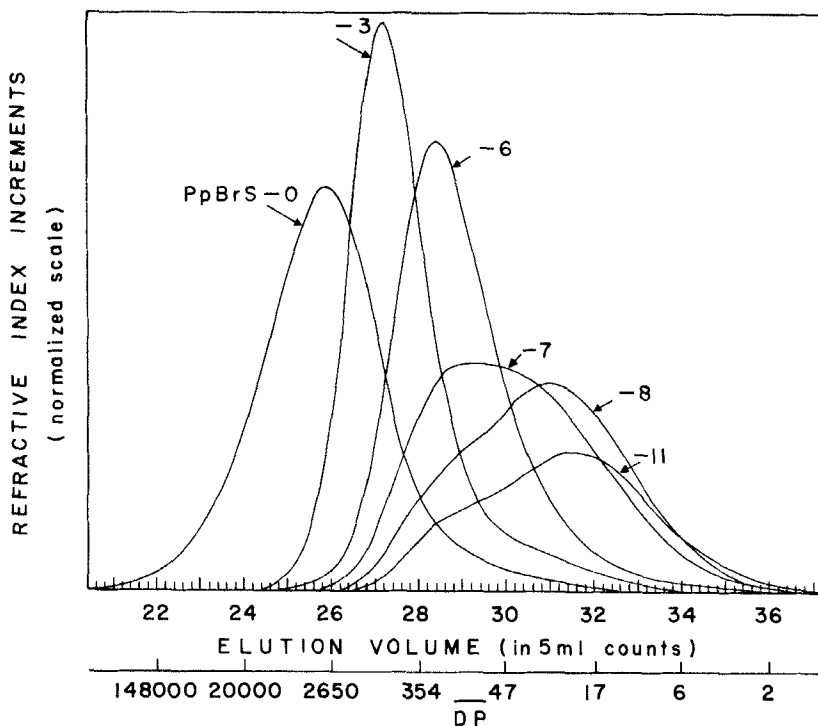


FIG. 2. Normalized GPC molecular weight distributions of PpBrS samples subjected to 50-min decomposition periods at various temperatures. See Table 1 for other data.

over the negative sign (-) (between elution counts 21 and 29) represent the volatilized fraction due to decomposition and those over the positive sign (+) (between elution counts 24 and 34) represent the newly formed products.

The characteristics of the various negative (-) and positive (+) GPC molecular weight distributions shown in Figs. 5 and 6 are summarized in Table 2 which includes α , \bar{M}_w , \bar{M}_n , and \bar{M}_w/\bar{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 (located between elution counts 21 and 29 on the GPC curve) having \bar{M}_w 's of $(97.3 \text{ to } 20.0) \times 10^5$ and \bar{M}_w/\bar{M}_n 's of 3.2 to 5.7 decompose to yield products (located between elution counts 24 and 34) having \bar{M}_w values of $(33.6 \text{ to } 0.35) \times 10^4$ and \bar{M}_w/\bar{M}_n 's of 1.5 to 4.8.

In Fig. 7 are shown the normalized GPC molecular weight distributions of five PpBrS samples subjected to thermal decomposition at

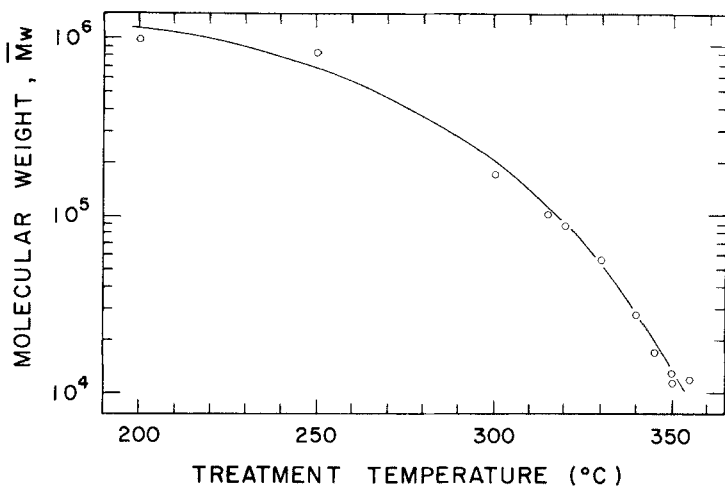


FIG. 3. Variation of molecular weight with treatment temperature for PpBrS samples subjected to 50-min decomposition periods. See Table 1 for other data.

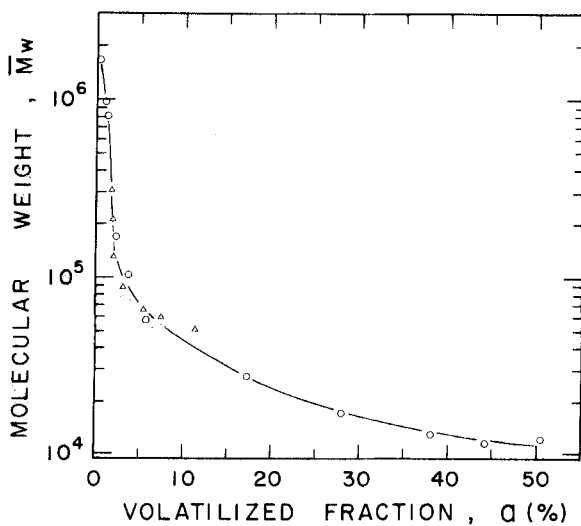


FIG. 4. Variation of molecular weight as a function of α , the percent weight-loss: (\circ) for 50-min decomposition periods at different temperatures and (\triangle) for different periods at 320°C.

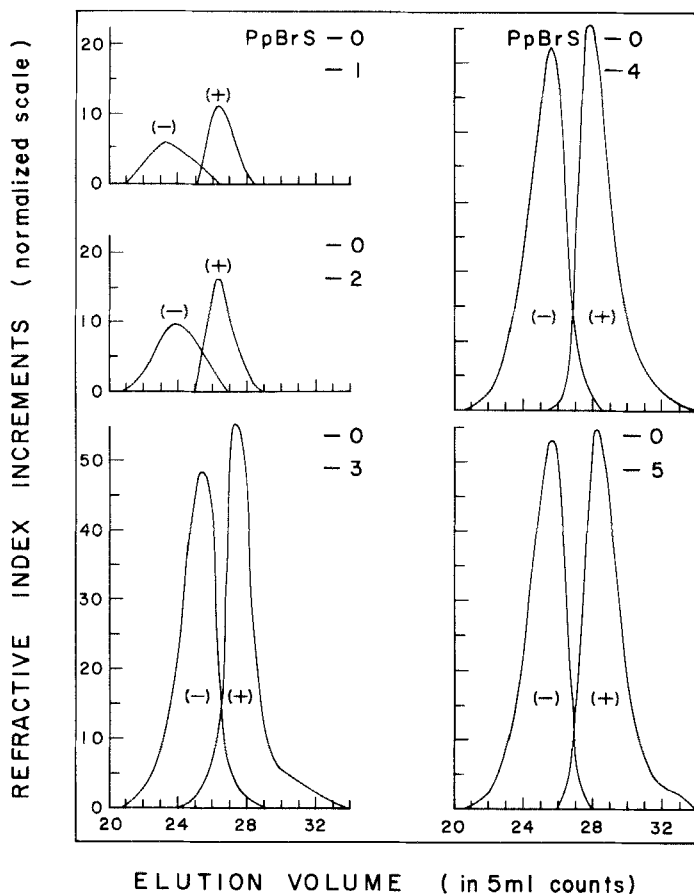


FIG. 5. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: the case of PpBrS samples subjected to 50-min decomposition periods in the temperature range of 200 to 320°C. See Table 2 for other data.

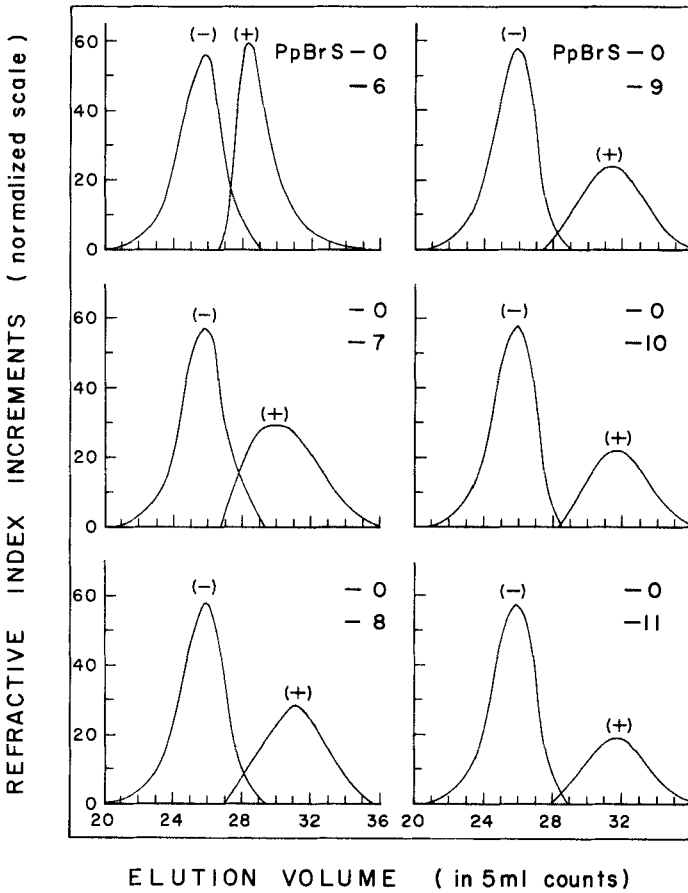


FIG. 6. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: the case of PpBrS samples subjected to 50-min decomposition periods in the temperature range of 330 to 355°C. See Table 2 for other data.

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

Polymer-pairs analyzed	Elution count range							
	21-29, (-)			24-34, (+)				
	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
PpBrS-0 - PpBrS-1	8.5	97.3	30.0	3.2	9.3	33.6	22.6	1.5
PpBrS-0 - PpBrS-2	15.2	69.3	19.2	3.6	14.6	36.5	21.1	1.7
PpBrS-0 - PpBrS-3	61.8	28.5	7.0	4.1	56.1	13.5	2.8	4.8
PpBrS-0 - PpBrS-4	69.1	25.2	6.0	4.2	64.8	6.3	2.0	3.1
PpBrS-0 - PpBrS-5	69.7	24.5	6.9	3.6	68.8	5.0	1.6	3.1
PpBrS-0 - PpBrS-6	79.9	24.6	4.4	5.5	78.9	4.2	1.3	3.2

PpBrS-0 - PpBrS-7	92.7	17.8	4.0	4.4	75.0	2.0	0.45	4.6
PpBrS-0 - PpBrS-8	90.8	20.0	3.6	5.6	62.8	1.1	0.35	3.2
PpBrS-0 - PpBrS-9	89.8	20.0	3.8	5.3	53.2	0.80	0.30	2.7
PpBrS-0 - PpBrS-10	90.1	19.4	4.0	4.9	45.8	0.50	0.25	2.0
PpBrS-0 - PpBrS-11	91.6	21.3	3.7	5.7	39.1	0.35	0.20	1.8
PpBrS-0 - PpBrS-12	44.7	40.7	12.2	3.3	43.9	19.1	7.6	2.5
PpBrS-12 - PpBrS-13	24.8	5.2	2.9	1.8	25.8	14.3	3.1	4.6
PpBrS-13 - PpBrS-14	20.6	4.6	2.1	2.2	20.4	9.7	2.1	4.6
PpBrS-14 PpBrS-5	33.3	2.1	1.1	1.9	27.9	5.6	1.4	4.1
PpBrS-5 PpBrS-15	11.8	2.0	0.80	2.5	8.1	1.3	0.70	1.9
PpBrS-15 PpBrS-16	12.0	0.70	0.40	1.8	9.8	1.35	0.45	3.0
PpBrS-16 PpBrS-17	5.8	2.0	0.80	2.5	0.80	0.35	0.35	1.0

^aSee Table 1 for decomposition reaction conditions.

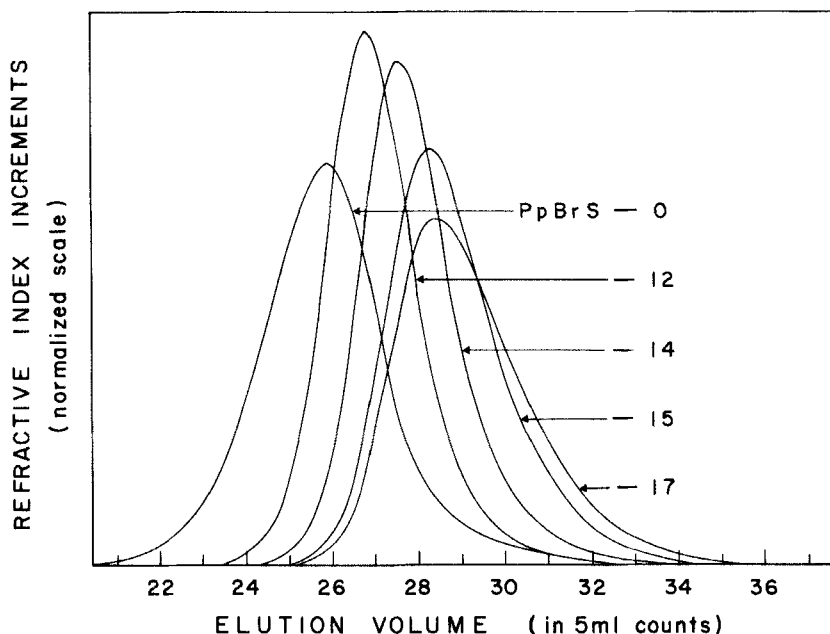


FIG. 7. Normalized GPC molecular weight distributions of PpBrS samples subjected to isothermal treatments at 320°C for different periods. See Table 1 for other data.

a fixed temperature (320°C) for different periods ranging from 10 to 180 min. Their α , \bar{M}_w , \bar{M}_n , and \bar{M}_w/\bar{M}_n values are listed in Table 1. As α increases with time of decomposition, \bar{M}_w and \bar{M}_n decrease regularly while \bar{M}_w/\bar{M}_n stays within ± 0.3 of 4.7.

In Fig. 8 are shown the changes that occur in the GPC molecular weight distributions of seven PpBrS 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 and \bar{M}_w/\bar{M}_n , associated with both the (-) and (+) distributions shown in Fig. 8, are summarized in Table 2. These data show that the isothermal treatment of PpBrS during the initial 10-min period results in the decomposition of 44.7% of the polymer having an \bar{M}_w of 40.7×10^5 and an \bar{M}_n of 12.2×10^5 ($\bar{M}_w/\bar{M}_n = 3.3$) and yielding a product (43.9%) with an \bar{M}_w of 19.1×10^4 and an \bar{M}_n of 7.6×10^4 ($\bar{M}_w/\bar{M}_n = 2.5$). In the intervals of 10 to 20, 20 to 30, 30 to 50, 50 to 90, 90 to 120, and 120 to 180 min,

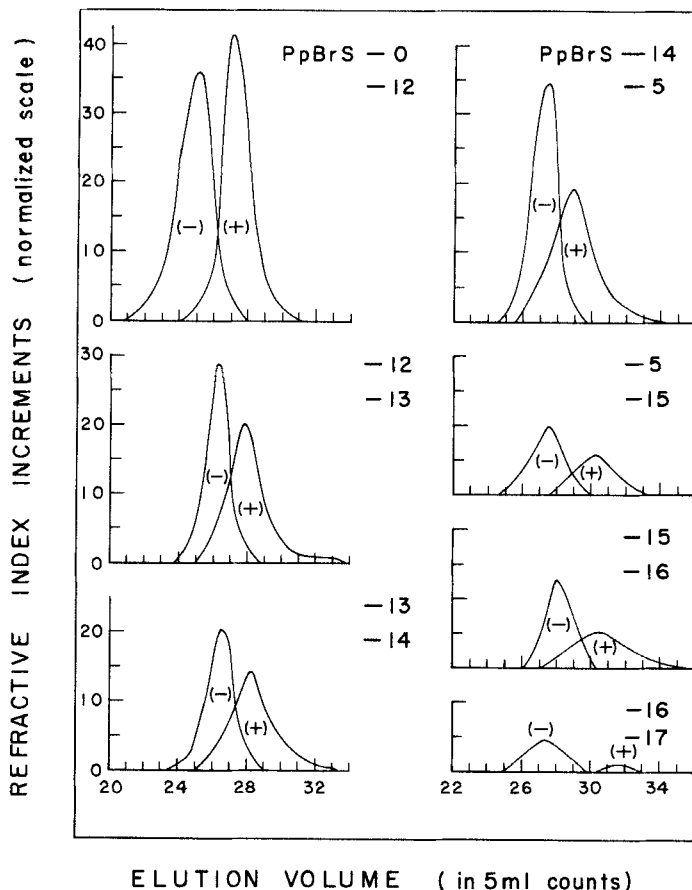


FIG. 8. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: the case of PpBrS samples subjected to isothermal treatments at 320°C for different periods. See Table 2 for other data.

24.8, 20.6, 33.3, 11.8, 12.0, and 5.8% of the polymer with \bar{M}_w 's of $(5.2 \text{ to } 2.0) \times 10^5$ and \bar{M}_n 's of $(2.9 \text{ to } 0.4) \times 10^5$ volatilize yielding 25.8, 20.4, 27.9, 8.1, 9.8, and 0.8%, respectively, of lower molecular weight products with \bar{M}_w 's of $(14.3 \text{ to } 0.35) \times 10^4$ and \bar{M}_n 's of $(3.1 \text{ to } 0.35) \times 10^4$.

Based on these GPC molecular weight distribution results derived from both undecomposed and decomposed PpBrS samples, the following conclusions are drawn.

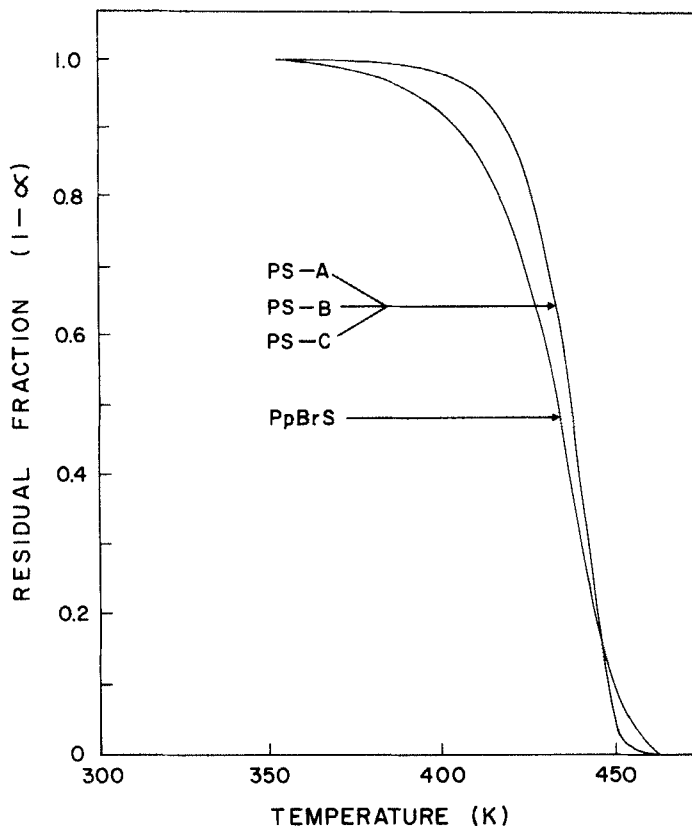


FIG. 9. Dynamic thermogravimetric decomposition of PS and PpBrS samples at a heating rate of 20 K/min. See Table 3 for other data.

1. In the 50-min isothermal treatment of PpBrS at various temperatures or in decompositions carried out at 320°C during various intervals, the mechanism of decomposition involves random scissions of the polymer chains which then volatilize via depolymerization. Because of the presence of Br groups in the PS aromatic rings, the thermal decomposition of PpBrS is facilitated; however, the changes in the \bar{M}_w/\bar{M}_n values as a function of temperature or time are not as regular as those for the thermal decomposition of PS [2] where \bar{M}_w/\bar{M}_n ratios of the decomposed products were either 2.0 or some value approaching this. This may be explained on the grounds that the PS samples used in the earlier study [2] were quasi-monodisperse

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/mol)	
			n = 0	n ^a = 1
PS-A	165.0	1.1	70.0	117.0
PS-B	78.0	1.1	91.0	111.0
PS-C	14.0	1.1	-	102.0
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
PpBrS	12.6	14.4	-	118.0

^an is the order of reaction.

whereas the PpBrS sample used in this work has an initial \bar{M}_w/\bar{M}_n value of 14.4!

2. The results of the present study agree with those reported by Inagaki et al. [16] who showed that PS is thermally more stable than PpBrS.

In Fig. 9 are shown curves representing the dynamic thermogravimetric decomposition, at a heating rate of 20 K/min, of PS and PpBrS samples. Using the method of Coats and Redfern [21], the activation energy for the decomposition of PpBrS was calculated assuming an order of reaction of one. The value obtained is presented in Table 3 along with other values for PpMeS [7] and PpClS [11]. The activation energies for the decomposition of substituted polystyrenes appear in the following descending order: $E_{PS} = E_{PpBrS} > E_{PpMeS} \approx E_{PpClS} \approx E_{PpOMeS}$

Glass Transition of PpBrS

The glass transition temperature (T_g) of a polymer is heating-rate dependent [7-15] as well as cooling-rate dependent [22, 23]. Although recent work [7-11] on PpMeS, PpiPrS, PptBuS, PpOMeS, and PpClS 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 effect that the cooling rate might have on the T_g of PpBrS.

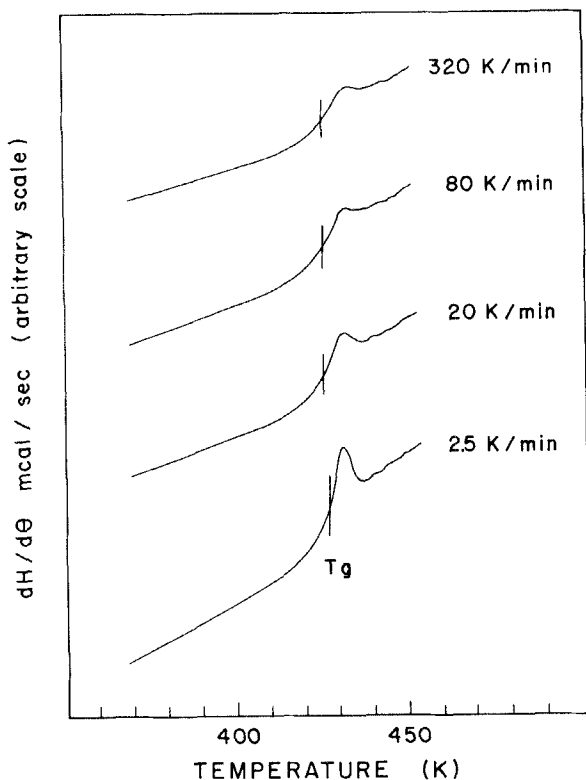


FIG. 10. Typical DSC thermograms of an undecomposed polymer sample of PpBrS recorded in the glass transition region at a heating rate of 40 K/min following cooling at various rates. See Table 4 for other data.

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 $\Delta C_p/2$ point [7-15], remained constant as the cooling rate was increased. T_g values of the undecomposed polymer subjected to four cooling rates are presented in Table 4. T_{g_e} values (extrapolated to a heating rate of 1K/min) are likewise listed. These remain constant at 415 ± 1.0 K. Subsequent T_g measurements on the decomposed polymer sample

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

Sample cooling rate (K/min)	T_g at various heating rates				$T_{g_e}^a$ (1 K/min)
	80 K/min	40 K/min	20 K/min	10 K/min	
320	426.0	424.0	422.5	421.0	415.0
80	427.0	424.0	422.0	420.0	414.0
20	427.0	423.5	422.0	420.5	416.0
2.5	430.0	425.0	423.0	421.0	414.5

^a Extrapolated value at a heating rate (q) of 1 K/min using the equation: $\log q = a - b/T_g$ [12].

were made after they had been cooled below T_g at a rate of 320 K/min.

In Fig. 11 are shown typical DSC thermograms of an undecomposed PpBrS sample recorded in the glass transition region at various heating rates. 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 PpBrS samples are summarized in Table 5. The values of T_{g_e} are found to increase with increasing \bar{M}_n .

In Fig. 12 is shown a plot of T_{g_e} as a function of \bar{M}_n . T_{g_e} increases up to a point beyond which it remains constant. The critical value is located at an \bar{M}_n value of 5.0×10^4 . A plot of T_{g_e} as a function of $1/\bar{M}_n$ shown in Fig. 13 yields a straight line described by

$$T_{g_e}(\text{K}) = 414 - 1.5 \times 10^5 / \bar{M}_n \quad (1)$$

The value of 414 K for the T_g (i.e., the T_g of polymer of infinite molecular weight) of PpBrS is higher than the value (391 K) reported in the literature [17-19].

In earlier work from this laboratory [7, 10, 11, 12], the T_{g_e} of PS (Eq. 2 [12]), PpMeS (Eq. 3 [7]), PpOMeS (Eq. 3 [10]) and PpClS (Eq. 5 [11]) were related to \bar{M}_n as follows:

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

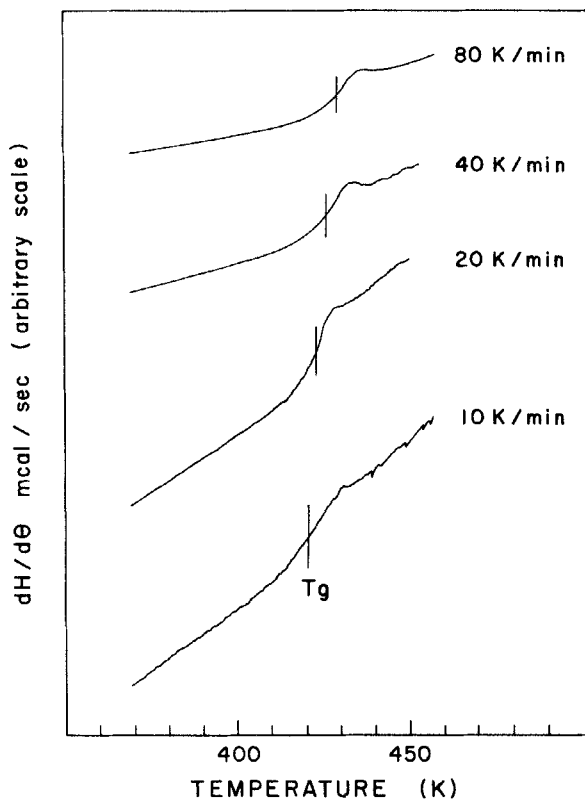


FIG. 11. Typical DSC thermograms of an undecomposed polymer sample of PpBrS recorded in the glass transition region at various heating rates (cooling rate = 320 K/min). See Table 4 for other data.

$$T_{g_e}(\text{K}) = 384 - 2.65 \times 10^5 / \bar{M}_n \quad (3)$$

$$T_{g_e}(\text{K}) = 386 - 4.67 \times 10^5 / \bar{M}_n \quad (4)$$

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

A comparison of T_{g_∞} for PS (379 K), PpMeS (384 K), PpOMeS (386 K), PpClS (398 K), and PpBrS (414 K) shows that while the electron-repelling *p*-Me and *p*-OMe substituents do not influence the T_{g_∞} for PS, the electron-withdrawing substituents *p*-Cl and *p*-Br

TABLE 5. Variation of T_g as a Function of Heating Rate for Undecomposed and Decomposed Samples of PpBrS^a

Sample no.	\bar{M}_n (GPC) $\times 10^{-3}$	\bar{M}_w/\bar{M}_n	T_g at various heating rates				T_{ge} (1 K/min)
			80 K/min	40 K/min	20 K/min	10 K/min	
PpBrS-0	126.0	14.4	426.0	424.0	422.5	421.0	415.0
PpBrS-18	128.5	3.9	428.0	426.0	423.5	421.5	414.0
PpBrS-19	53.0	3.4	425.0	423.0	420.0	418.0	410.0
PpBrS-20	51.5	3.3	424.5	422.0	419.5	417.5	409.5
PpBrS-21	45.0	4.4	423.0	419.5	417.5	415.0	406.5
PpBrS-22	23.0	3.3	419.0	416.5	414.0	411.5	403.0
PpBrS-23	20.5	3.6	420.0	417.5	414.5	412.5	404.0
PpBrS-24	12.5	3.3	415.0	412.0	410.0	407.5	399.5
PpBrS-25	10.5	3.3	412.5	412.0	409.0	407.0	399.0
PpBrS-26	10.3	3.0	411.0	409.0	407.0	405.5	399.5
PpBrS-27	9.5	3.5	409.5	407.0	404.5	402.5	395.0
PpBrS-28	6.9	3.0	399.5	398.0	396.0	395.0	390.0
PpBrS-29	6.6	3.1	401.0	400.0	399.0	-	395.0
PpBrS-30	5.4	3.4	397.0	395.0	392.0	391.0	380.0
PpBrS-31	5.0	3.3	395.0	392.5	391.0	388.5	382.0

(continued)

TABLE 5 (continued)

Sample no.	\bar{M}_n (GPC) $\times 10^{-3}$	\bar{M}_w/\bar{M}_n	T_g at various heating rates				T_{ge} (1 K/min)
			80 K/min	40 K/min	20 K/min	10 K/min	
PpBrS-32	4.9	3.2	395.0	392.5	391.0	389.0	382.5
PpBrS-33	4.8	3.2	392.5	391.5	390.5	389.5	386.0
PpBrS-34	3.9	3.4	381.0	378.0	373.5	372.5	363.5
PpBrS-35	3.8	3.3	381.0	378.0	375.0	373.0	363.5
PpBrS-36	3.1	3.3	372.0	367.0	365.5	364.0	359.0
PpBrS-37	2.9	3.2	372.5	370.5	368.0	367.0	360.5
PpBrS-38	2.4	2.7	368.0	365.5	362.5	361.0	353.0
PpBrS-39	1.8	2.3	362.5	359.0	358.0	354.5	346.0

^a PpBrS-18 to PpBrS-39 polymers were obtained by the thermal decomposition of PpBrS-0 for different periods at a few selected temperatures in order to collect samples of varying \bar{M}_n .

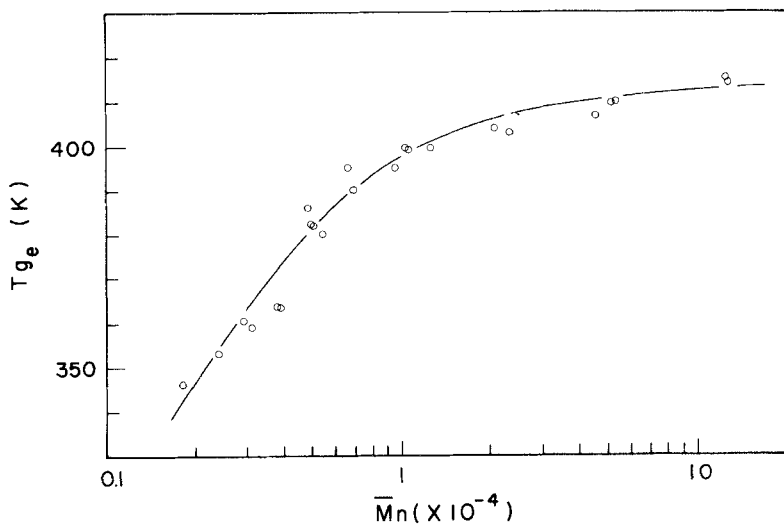


FIG. 12. Extrapolated T_{ge} values (to $q = 1$ K/min) of PpBrS as a function of \bar{M}_n . See Table 5 for other data.

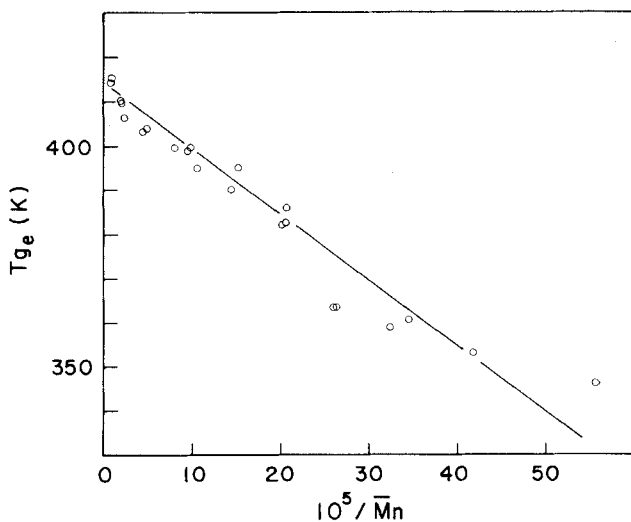


FIG. 13. Extrapolated T_{ge} values (to $q = 1$ K/min) of PpBrS as a function of $1/\bar{M}_n$. See Table 5 for other data.

do indeed increase this value. The various *p*-substituents, in polystyrene homologs, causing increased steric hindrance and decreased chain flexibility follow the order $-\text{Br} > -\text{Cl} > -\text{OMe} = -\text{Me} \cong -\text{H}$.

In earlier work [9] on the T_g of PptBuS, a comparison of T_{g_e} values for PS (363 K), PpMeS (364 K), PpiPrS (335.5 K), and PptBuS (399 K), all having \bar{M}_n 's of 1.4×10^4 , revealed that increased steric hindrance and decreased chain-flexibility-causing groups follow the order $p\text{-tBu} > p\text{-Me} \cong -\text{H} > p\text{-iPr}$.

It may be noted that replacing *p*-Me with *P*-iPr in PS lowers its T_{g_e} from 364 K (PpMeS) to 335.5 K (PpiPrS) whereas replacing, the H in *P*-iPr with a third Me group in PS increases its T_{g_e} from 335.5 (PpiPrS) to 399 K (PptBuS). It would appear that the effective bulk size of a substituent, i.e., its ability to pack in polymer layers, is more significant than its apparent bulk size. This is further supported by the fact that the T_{g_∞} of P α MeS (453 K [13]) is 69 K higher than that of PpMeS (384 K [7]) although the apparent bulk size of the Me groups in the two polymers is the same.

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

1. In the isothermal decomposition of PpBrS, random scissions reduce the chain length of the polymer in the earlier stages of the reaction while depolymerization reactions account for the polymer weight-loss. This behavior is similar to that noted for PS [2].

2. The activation energies for the decomposition of PS and its homologs (with $\bar{M}_w > 10^3$) obey the following descending order:

$$E_{\text{PS}} = E_{\text{PpBrS}} > E_{\text{PpMeS}} \cong E_{\text{PpClS}} \cong E_{\text{PpOMeS}}$$

3. The descending order of steric hindrance causing substituents in PS homologs is as follows: $\alpha\text{-Me} > p\text{-t-Bu} > p\text{-Br} > p\text{-Cl} > p\text{-OMe} = p\text{-Me} \cong \text{H} > p\text{-iPr}$.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial assistance received from the Natural Sciences and Engineering Research Council of Canada, the Department of Education (FCAC) of the Government of Quebec, and Laval University. One of us (P.L.) likewise acknowledges the financial help received in the form of a fellowship from the Aluminum Company of Canada.

REFERENCES

- [1] L. P. Blanchard, V. Hornof, H. H. Lam, and S. L. Malhotra, Eur. Polym. J., 10, 1057 (1974).

- [2] S. L. Malhotra, J. Hesse, and L. P. Blanchard, Polymer, **16**, 81 (1975).
- [3] S. L. Malhotra, C. Baillet, Ly Minh, and L. P. Blanchard, J. Macromol. Sci.-Chem., **A12**, 129 (1978).
- [4] S. L. Malhotra, C. Baillet, and L. P. Blanchard, Ibid., **A12**, 909 (1978).
- [5] S. L. Malhotra, C. Baillet, H. H. Lam-Tran, and L. P. Blanchard, Ibid., **A12**, 103 (1978).
- [6] S. L. Malhotra, C. Baillet, and L. P. Blanchard, Ibid., **A12**, 1427 (1978).
- [7] S. L. Malhotra, P. Lessard, Ly Minh, and L. P. Blanchard, Ibid., **A14**, 517 (1980).
- [8] S. L. Malhotra, P. Lessard, Ly Minh, and L. P. Blanchard, Ibid., **A14**, 915 (1980).
- [9] S. L. Malhotra, P. Lessard, and L. P. Blanchard, Ibid., **A15**, 121 (1981).
- [10] S. L. Malhotra, P. Lessard, and L. P. Blanchard, Ibid., **A15**, 301 (1981).
- [11] S. L. Malhotra, P. Lessard, and L. P. Blanchard, Ibid., **A15**, 279 (1981).
- [12] L. P. Blanchard, J. Hesse, and S. L. Malhotra, Can. J. Chem., **52**, 3170 (1974).
- [13] S. L. Malhotra, Ly Minh, and L. P. Blanchard, J. Macromol. Sci.-Chem., **A12**, 167 (1978).
- [14] S. L. Malhotra, Ly Minh, and L. P. Blanchard, Ibid., **A13**, 51 (1979).
- [15] S. L. Malhotra, Ly Minh, and L. P. Blanchard, Ibid., **A12**, 149 (1978).
- [16] N. Inagaki, Y. Takagi, and K. Katsuura, Eur. Polym. J., **13**, 433 (1977).
- [17] R. Kosfeld, Kolloid-Z., **172**, 182 (1960).
- [18] K. H. Illers, Z. Electrochem., **65**, 679 (1961).
- [19] K. R. Dunham, J. W. H. Faber, J. Vanderberghe, and W. F. Fowler, J. Appl. Polym. Sci., **7**, 897 (1963).
- [20] Y. Noguchi, A. Aoki, G. Tanaka, and H. Yamakawa, J. Chem. Phys., **52**, 2651 (1970).
- [21] A. W. Coats and J. P. Redfern, J. Polym. Sci., Part B, **3**, 917 (1965).
- [22] B. Wunderlich and D. M. Bodily, J. Polym. Sci., Part C, **6**, 137 (1964).
- [23] J. Bourdariat, A. Berton, J. Chaussy, R. Isnard, and J. Odin, Polymer, **14**, 167 (1973).

Accepted by editor February 13, 1980

Received for publication March 5, 1980