The Thermal Decomposition and Glass Transition Temperature of Poly(p-tert-butyistyrene)

S. L. Malhotra[a]; P. Lessard[b]; L. P. Blanchard[c]

[a] Xerox Research Centre of Canada, Ontario, Canada [b] Centre de Recherche pour la Défense, Division de la propulsion, Québec, Canada [c] Groupe de Recherches en Sciences Macromoléculaires Départment de Génie chimique Faculté des Sciences et de Génie, Université Laval Québec, Canada

PLEASE SCROLL DOWN FOR ARTICLE

The Thermal Decomposition and Glass Transition Temperature of Poly(p-tert-butylstyrene)

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, Canada G1K 7P4

ABSTRACT

The thermal decomposition and the glass transition temperature of poly-p-tert-butylstyrene (PptBuS) were studied with a (DSC-2) differential scanning calorimeter. The undecomposed and decomposed polymers were analyzed by gel permeation chromatography for molecular weight distributions and by DSC-2 for changes in the polymer glass transition temperatures. Decomposition of PptBuS under isothermal conditions during 50 min periods in the 25 to 360°C region led increasing quantities of high molecular weight polymer with $\overline{M}_w$ = (12 to 19) × 10⁴ to yield lower molecular weight products with $\overline{M}_w$ = (6 to 14) × 10³, suggesting the involvement of partial depolymerization reactions. Decompositions at fixed temperature (320°C) for different periods– 10 to 180 min–showed that in the early stages of the reaction (< 10 min) random scissions occur in some of the chains which

*Present address: Xerox Research Centre of Canada, Mississauga, Ontario, Canada L5L 1J9.
†Present address: Centre de Recherche pour la Défense, Division de la propulsion, Valcartier, C.P. 880, Courcelette, Québec, Canada G0A 1R0.

later undergo partial or total depolymerization. Activation energies for the decomposition of PS and its homologs follow the order $E_{PS} > E_{PpMeS} > E_{PpiPrS} > E_{PptBuS}$. Variation of T_{g_e} (at q = 1°K/min) with $\overline{M}_n$ obeys the following relation: T_{g_e} (°K) = 446 - 7.33 $\times 10^5/\overline{M}_n$. The T_{g_∞} value of 446°K for PptBuS is far removed from that of PpMeS (384°K) and PS (379°K) due primarily to increased steric hindrance and decreased chain flexibility which arise because the effective bulk size (packing ability) of the tert-butyl group in PptBuS is lower than its apparent bulk size.

INTRODUCTION

Thermal decomposition [1-8] and glass transition temperature studies [7-12] of polystyrene (PS) [1, 2, 9], poly α-methylstyrene (PαMeS) [3, 4, 10, 11], poly-p-isopropyl α-methylstyrene (PpiPrαMeS) [5, 6, 12], poly p-methylstyrene (PpMeS) [7] and poly p-iospropylstyrene (PpiPrS) [8] have been reported on earlier from this laboratory. The results of the isothermal treatments showed that in the initial stages of the reaction (weight loss $\alpha < 3\%$), the respective decomposition temperatures for identical values of α of PpMeS and PS were the same. For α values greater than 3%, however, the corresponding decomposition temperatures of PpMeS were about 15 to 22°K lower than those of PS. A similar comparison of the decomposition temperatures, for identical values of α, of PS and PpiPrS revealed that for α less than 10% the latter polymer required lower temperatures than those for the former. For values of α greater than 10%, however, the decomposition temperatures of PpiPrS were either the same or about 10°K higher than those of PS.

These observations suggest that, in general, for a weight loss of less than 3%, the presence of p-methyl groups in the aromatic ring of PS has no significant effect on the decomposition reaction whereas that of the p-isopropyl groups facilitates the process. For values of α greater than 10%, the presence of the p-methyl group in the aromatic ring of PS facilitates the reaction whereas that of the p-isopropyl group is of no help or even hinders the decomposition reaction.

In the glass transition range, the values of T_g for PS, PpMeS, and PpiPrS samples of identical molecular weight ($\overline{M}_n = 1.4 \times 10^4$) were found to be 363, 364 and 335.5°K, respectively. This shows that although the presence of the p-methyl group in the aromatic ring of PS has no visible effect on T_g, that of the p-isopropyl group lowers the T_g of PS by about 30°K.

Keeping this in mind, a study of the thermal decomposition and the glass transition temperature of yet another homolog of polystyrene, namely poly p-tert-butylstyrene (PptBuS), was carried out and the

data obtained were compared with those recorded for PS incorporat-
ing other substituents as well as with those reported on the photolysis
[13] and T_g [14, 15] of PptBuS. The results of this work are out-
lined in the present article.

EXPERIMENTAL

Poly p-tert-butylstyrene (PptBuS) (Aldrich Chemical Co.) was
used as received. The weight-average molecular weight $\overline{M}_w$ of the
polymer was calculated from the intrinsic viscosity data obtained
with benzene at 35°C using the relation reported in the literature [16].
Molecular weight distributions of PptBuS samples were obtained with
a Waters Associates (Model 200) gel permeation chromatograph [1-
8] calibrated with standard PS and PptBuS samples.

A Perkin-Elmer (Model DSC-2) differential scanning calorimeter
operating with pure dry helium was used for the isothermal decom-
position of PptBuS whereas a Perkin-Elmer (Model TGS-1) thermo-
gravimetric scanning balance operating in pure dry nitrogen was used
for the dynamic decomposition of PptBuS. The T_g values of the un-
decomposed and decomposed samples of PptBuS were determined with
the DSC-2 apparatus [9-12].

RESULTS AND DISCUSSION

Thermal Decomposition of PptBuS

In Table 1 are summarized values of the weight loss α (in %), the
molecular weights ($\overline{M}_w$ and $\overline{M}_n$), and the polydispersities ($\overline{M}_w/\overline{M}_n$
ratios) obtained with PptBuS both before and after its isothermal treat-
ment at various temperatures for different periods. Using the 50-min
isothermal treatment data, a curve showing the variation of α with
temperature is given in Fig. 1. For comparison purposes, data for
50 min isothermal treatments of PS [2], PpMeS [7], and PpiPrS [8]
samples are also plotted in this figure. For α values less than 10%,
the thermal stability of various PS homologs obey the following order:
PS > PpMeS > PptBuS > PpiPrS.

For α values greater than 10%, however, the order of thermal
stability changes to PpiPrS > PS > PptBuS > PpMeS. This indicates
that in the earlier stages of decomposition ($\alpha < 10\%$), the presence of
substituents on the aromatic ring of PS facilitates the formation of
radicals which bring about the random scissions or depolymerization
of the polymer chains. Once the decomposition reactions have started
($\alpha > 10\%$), however, the role of the substituent becomes less promi-
nent.

For identical values of α, the respective decomposition tempera-
tures for PptBuS and PpMeS are 10 and 14 to 22°K lower than those

MALHOTRA, LESSARD, AND BLANCHARD

TABLE 1. Data on PptBuS Samples Subjected to Isothermal Treatment at Various Temperatures for Different Periods

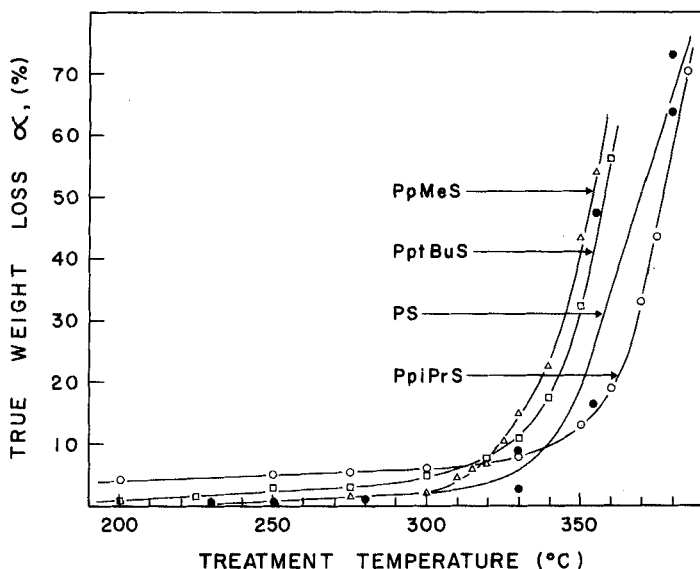| Sample no.	Treatment temperature (°C)	Treatment time (min)	Weight loss α (%)	$\overline{M}_w$ (GPC) $\times 10^{-4}$	$\overline{M}_n$ (GPC) $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PptBuS-0	Undecomposed	-	-	8.7	3.1	2.8
PptBuS-1	200	50	0.9	8.3	2.6	3.2
PptBuS-2	230	50	1.4	8.3	2.6	3.2
PptBuS-3	250	50	2.8	-	-	-
PptBuS-4	275	50	2.5	7.8	2.7	2.9
PptBuS-5	300	50	4.8	8.1	2.7	3.0
PptBuS-6	320	50	7.6	6.8	2.5	2.7
PptBuS-7	330	50	10.8	6.5	2.3	2.8
PptBuS-8	340	50	17.3	6.2	2.2	2.8
PptBuS-9	350	50	32.7	5.0	1.7	2.9
PptBus-10	360	50	56.4	3.6	1.4	2.6
PptBuS-11	320	10	6.2	5.5	1.8	3.0
PptBuS-12	320	20	6.8	6.0	1.9	3.2
PptBuS-13	320	30	8.2	5.9	1.8	3.3
PptBuS-14	320	50	10.0	5.3	1.8	2.9
PptBuS-15	320	90	14.0	5.3	1.8	2.9
PptBuS-16	320	120	17.5	5.2	1.7	3.1
PptBuS-17	320	180	25.5	4.8	1.5	3.2

FIG. 1. Variation of weight-loss α (%) with treatment tempera-
ture T (°C) for PS ($\overline{M}_w$ = 1.0 × 10⁴ to 1.6 × 10⁵ [2]), PpMeS ($\overline{M}_w$ =
1.35 × 10⁵ [7]), PpiPrS ($\overline{M}_w$ = 5.5 × 10⁴ [8]), and PptBuS ($\overline{M}_w$ = 8.7
× 10⁴) samples. See Table 1 for other data.

for PS. Under similar conditions the decomposition temperatures
for PαMeS [3, 4] are about 70°K lower than those for PS. It would
appear that the position of the substituent is more than its bulk size
in bringing about the decomposition reaction.

In Fig. 2 are shown the normalized GPC molecular weight distri-
butions of four PptBuS samples subjected to 50 min isothermal treat-
ment at various temperatures. The peak maxima in the GPC dis-
tributions of the decomposed polymers move toward higher elution
counts (i.e., lower molecular weights). Furthermore, as the treat-
ment temperature is raised, an increase is noted in the quantity of
low molecular weight polymer between elution counts 30 and 34.
This behavior is similar to that observed in the case of PS [2] where
random scission and depolymerization reactions operate.

In Fig. 3 is shown the variation of molecular weight with treatment
temperature for PptBuS samples subjected to 50 min decomposition
periods. Between 200 and 300°C, the $\overline{M}_w$ values remain constant at

8.0 × 10⁴ in spite of weight losses as high as 5%. Beyond 300°C,
molecular weights decrease regularly with increasing temperature.

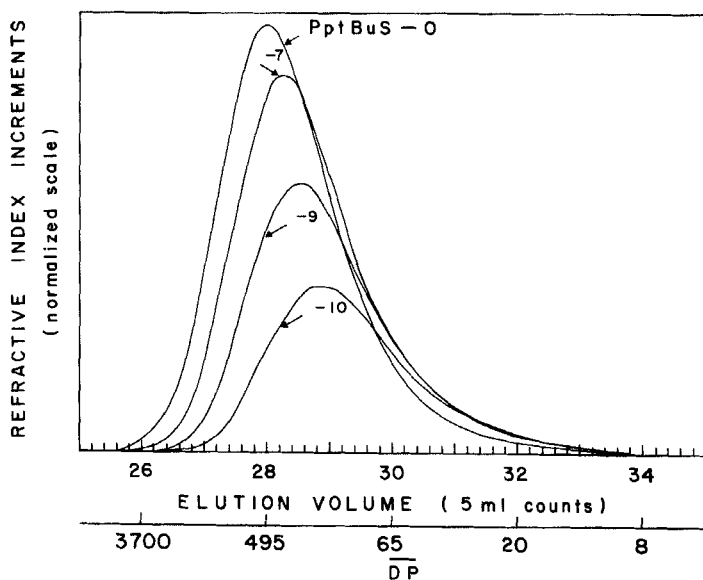In Fig. 4 are shown, for different modes of operation, curves of

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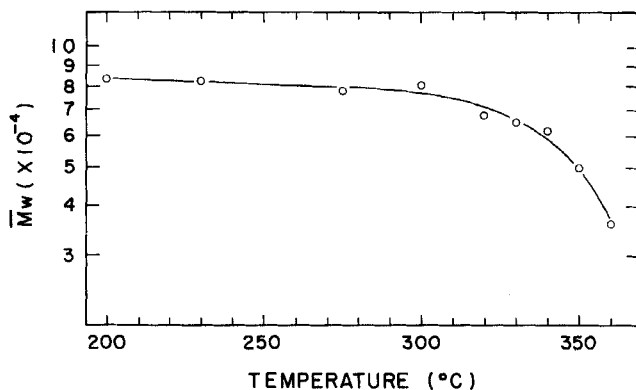

FIG. 3. Variation of molecular weight with treatment temperature for PptBuS samples subjected to 50 min decomposition periods. See Table 1 for other data.
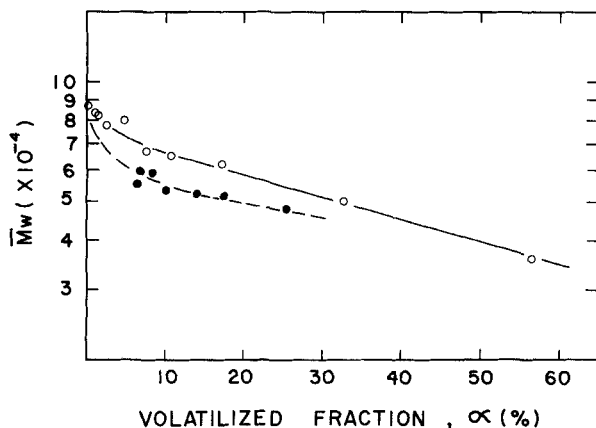
FIG. 4. Variation of molecular weight as a function of the weight loss: ($\circ$) α (%) for 50 min decomposition periods at different temperatures and ($\bullet$) α (%) for different periods at 320°C.

the variation in molecular weight as a function of α. It may be noted that, in general, molecular weights decrease with increasing values of α. For identical α values obtained with 50 min isothermal treatment at various temperatures or at 320°C using different decomposition periods, the decreases in molecular weight are not the same. In the case of the decomposition of PS [2] where random scission as well as depolymerization reactions take part, for identical values of α obtained as a function of temperature or time, the decreases in molecular weight were the same. Furthermore, for α values as high as 5%, the decrease in $\overline{M}_w$ due to random scissions was very significant. This would suggest that in the decomposition of PptBuS, random scissions of the polymer chains are not frequent.

To better understand the decomposition of PptBuS, 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 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 PptBuS samples studied, these changes are shown in Fig. 5, where the distributions over the negative sign (-) (between elution counts 26 and 29) represent the volatilized fraction due to decomposition and those over the positive sign (+) (between elution counts 29 and 32) represent the newly formed products.

The characteristics of the various (-) and (+) GPC molecular weight distributions shown in Fig. 5 are summarized in Table 2
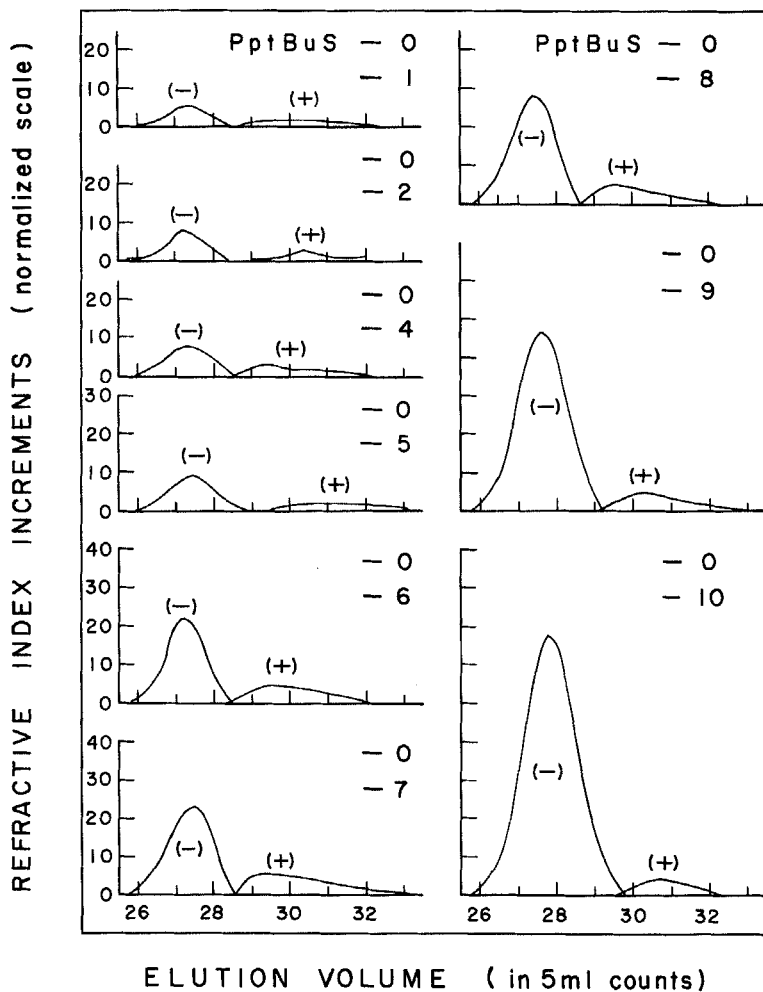
FIG. 5. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of a PptBuS sample subjected to 50 min decomposition periods. See Table 2 for other data.

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

Polymer-pairs analyzed	Elution volume range (in 5 mL counts)							
	26 to 30 (-)				28 to 34 (+)			
	α (%)	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	α (%)	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PptBuS-0 → PptBuS-1	3.5	18.7	14.2	1.3	1.9	11.4	7.8	1.4
PptBuS-0 → PptBuS-2	4.5	19.0	14.8	1.3	1.9	8.3	6.8	1.2
PptBuS-0 → PptBuS-4	5.5	18.4	13.7	1.3	2.7	15.0	9.7	1.5
PptBuS-0 → PptBus-5	6.3	16.5	12.3	1.3	2.1	5.7	4.5	1.2
PptBuS-0 → PptBuS-6	14.0	19.2	15.0	1.3	4.8	14.1	9.3	1.5
PptBuS-0 → PptBuS-7	16.5	17.9	13.5	1.3	6.4	13.3	8.3	1.6
PptBuS-0 → PptBuS-8	19.5	17.2	13.0	1.3	4.7	13.3	9.2	1.4
PptBuS-0 → PptBuS-9	37.5	14.1	9.6	1.5	4.9	8.2	6.3	1.3
PptBuS-0 → PptBuS-10	59.5	11.8	7.5	1.6	3.1	6.4	5.8	1.1
PptBuS-0 → PptBuS-11	28.8	14.8	10.6	1.4	22.5	34.8	10.0	3.5
PptBuS-11 → PptBuS-12	3.0	1.6	1.0	1.6	3.0	135.0	107.0	1.3
PptBuS-12 → PptBuS-13	2.8	5.3	4.2	1.3	-	-	-	-
PptBuS-13 → PptBuS-14	5.6	14.5	9.7	1.5	4.4	32.9	17.9	1.8

(continued)

TABLE 2 (continued)

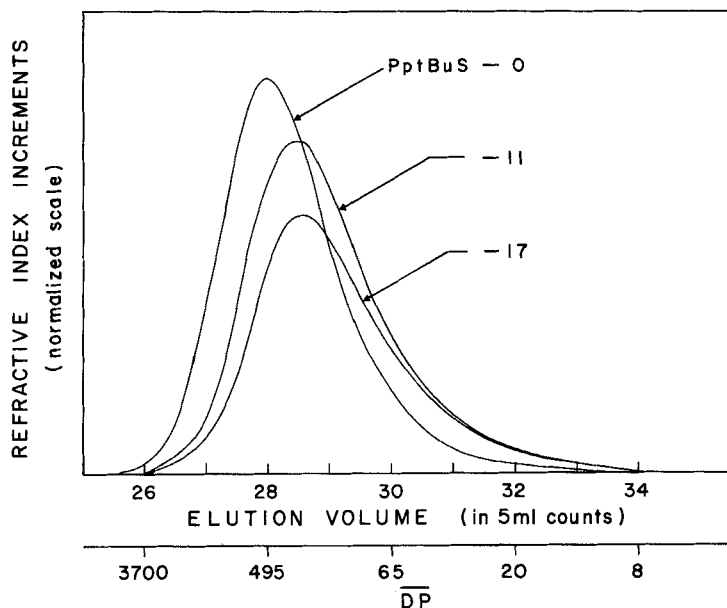| Polymer-pairs analyzed | Elution volume range (in 5 mL counts) | | | | | | | |
| | 26 to 30 (−) | | | | 28 to 34 (+) | | | |
	α (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	α (%)	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
PptBuS-14 → PptBuS-15	7.7	7.9	1.6	4.9	−	−	−	−
PptBuS-15 → PptBuS-16	{ 2.9 { 1.6	12.1 3.0	10.2 2.5	1.2 1.2	− −	− −	− −	− −
PptBuS-16 → PptBuS-17	10.5	7.4	4.7	1.6	1.9	4.3	3.6	1.2

[a]See Table 1 for decomposition reaction conditions.

FIG. 6. Normalized GPC molecular weight distributions of PptBuS subjected to isothermal treatment at 320°C for different periods. See Table 1 for other data.

which includes α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values. For 50 min isothermal decompositions, as the temperature is raised from 25 to 360°C, increasing quantities of high molecular weight material with $\overline{M}_w$ of (12 to 19) $\times 10^4$ and $\overline{M}_w/\overline{M}_n$ of 1.3 to 1.6 (located between elution counts 26 and 29) on the GPC curves decompose to yield products (appearing on the GPC curves between elution counts 29 and 32) having M_w values of (6 to 14) $\times 10^3$ and $\overline{M}_w/\overline{M}_n$ ratios varying from 1.1 to 1.6.

In Fig. 6 are shown the normalized GPC molecular weight distributions of three PptBuS samples subjected to thermal decomposition at a fixed temperature (320°C) for different periods ranging from 10 to 180 min. Their α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values are listed in Table 1. Between zero and 10 min, $\overline{M}_w$ and $\overline{M}_n$ decrease, respectively, from 8.7×10^4 to 5.5×10^4 and from 3.1×10^4 to 1.8×10^4. Between 10 and 180 min, $\overline{M}_w$ and $\overline{M}_n$ remain constant.

In Fig. 7 are shown changes that occur in the GPC molecular weight distributions of seven PptBuS samples subjected to thermal decomposition at 320°C where the decomposition time is varied from zero to 10,
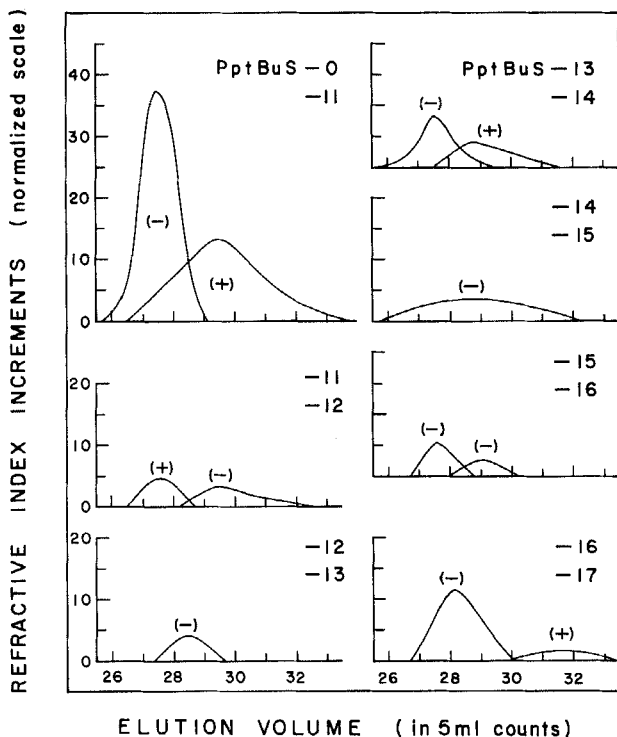
FIG. 7. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into various components: The case of PptBuS subjected to isothermal treatments at 320°C for different periods. See Table 2 for other data.

10 to 20, 20 to 30, 30 to 50, 50 to 90, 90 to 120, and 120 to 180 min, respectively. The values of α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$, associated with both the (-) and the (+) distributions shown in Fig. 7 are summarized in Table 2. These data show that isothermal treatment of PptBuS during the initial 10 min period results in the decomposition of 28.8% of the polymer having an $\overline{M}_w$ of 14.8×10^4 and an $\overline{M}_n$ of 10.6×10^4 and yielding a product (22.5%) with an $\overline{M}_w$ of 3.5×10^4 and an $\overline{M}_n$ of 1.0×10^4. In the intervals of 10 to 20, 20 to 30, 30 to 50, 50 to 90, 90 to 120, and 120 to 180 min, 3.0, 2.8, 5.6, 7.7, 4.5, and 10.5% of the polymer, respectively, volatilize yielding little or no product of decomposition.

Based on these GPC molecular weight distribution results derived from both undecomposed and decomposed PptBuS samples, one may note the following:
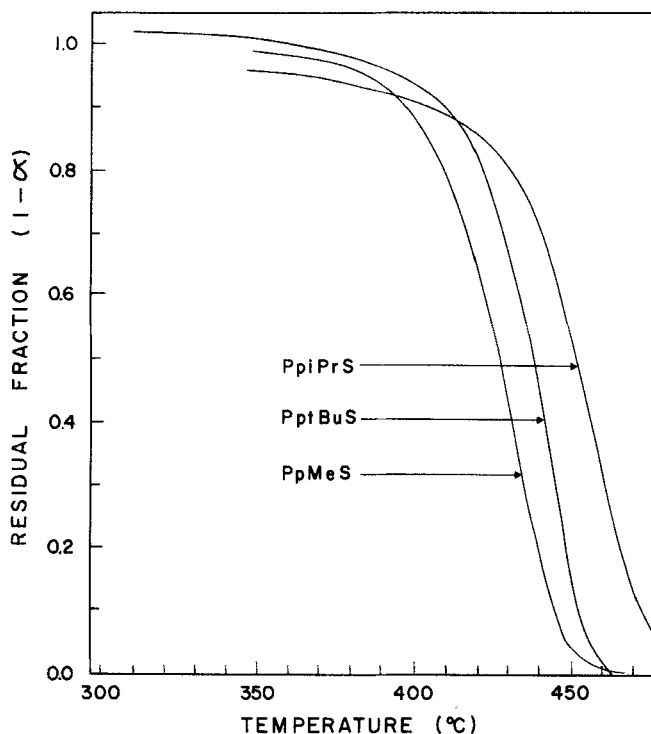
FIG. 8. Dynamic thermogravimetric decomposition of PS and PptBuS samples at a heating rate of 20°K/min. See Table 3 for other data.

1. In the 50-min isothermal treatment of PptBuS at various temperatures, the mechanism of decomposition is in all appearance that of a partial depolymerization which yields low molecular weight products rather than oligomers (tetramer, trimer, or dimers) which are usually obtained on total depolymerization as was the case with PS [2].

2. In decompositions carried out at 320°C during various time intervals, random scissions would appear to break the polymer chains during the first 10 min and then depolymerization (both partial as well as total) takes over.

3. The isothermal decomposition of PptBuS follows in general the same pattern as that in the photolysis of this polymer [13]. Unlike the isothermal decomposition and photolysis of PpMeS [13] and PpiPrS [13] where cross-linked products are formed, no such reactions were noted in the case of the isothermal decomposition of PptBuS and very little cross-linking is observed in the photolysis of this polymer [13].

TABLE 3. Activation Energy Values Calculated by the Method of
Coats and Redfern [17, 18] for the Thermal Decomposition of Styrene
and Its Homologs

| Sample | $M_n \times 10^{-4}$ | M_w/M_n | Activation energy (kcal/mole)[a] | |
			With n = 0	With n = 1
PS	1.8	1.1	51.4	88.5
PpMeS	5.1	2.7	45.7	62.2
PpiPrS	1.4	3.9	44.0	65.1
PptBuS	3.1	2.8	36.2	–

[a]n is the order of reaction.

In Fig. 8 are shown curves representing the dynamic thermo-
gravimetric decomposition at a heating rate of 20°K/min of PS and
PptBuS samples of similar M_n Using the method of Coats and Red-
fern [17, 18], activation energies were calculated assuming succes-
sively orders of reaction of zero and one. These values, along with
those for PpMeS and PpiPrS, are presented in Table 3. The activa-
tion energies for the decompositions follow the order $E_{PS} > E_{PpMeS}$
$\simeq E_{PpiPrS} > E_{PptBuS}$.

Glass Transition of PptBuS

The glass transition temperature (T_g) of a polymer is heating-rate
dependent [7-12] as well as cooling-rate dependent [19, 20]. Al-
though recent work [7, 8] on PpMeS and PpiPrS has shown that in the
case of substituted polystyrenes the cooling rate has no effect on T_g,
it was thought pertinent to study the effects that the cooling rate might
have on the T_g of PptBuS.
    In Fig. 9 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 [7-12], increased
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}
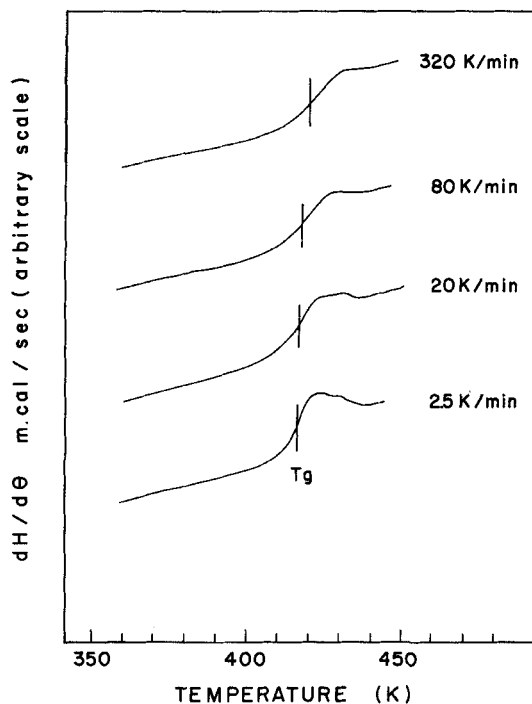
FIG. 9. Typical DSC thermograms of an undecomposed polymer sample of PptBuS recorded in the glass transition region at a heating rate of $40°K/min$ following cooling at various rates. See Table 4 for other data.

(values extrapolated to a heating rate of $1°K/min$) are likewise listed. The T_{g_e} values are found to increase from $399.0°K$ for a sample initially cooled at $2.5°K/min$ to 404.0 when the initial cooling rate was $320°K/min$. Normally, one would expect the value at $320°K/min$ to be lower than that for a cooling rate of $2.5°K/min$ because of the lack of time available on fast cooling for the polymer to reach its equilibrium state [19]. The difference of $5°K$ in the values of T_{g_e} at the two extreme cooling rates is not large enough, however, to warrant modifications in the hole theory [19] and may simply be considered as the margin of error in T_g measurements for PptBuS. Therefore, subsequent T_g measurements on the decomposed polymer samples were made after they had been cooled below T_g at a rate of $320°K/$ min.

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

Sample cooling rate prior to T_g determination ($°K/min$)	T_g at various heating rates				T_{g_e} a ($1°K/min$)
	$80°K/min$	$40°K/min$	$20°K/min$	$10°K/min$	
2.5	414.0	412.0	409.5	407.0	399.0
20	415.0	412.5	410.5	408.0	400.5
80	416.5	414.0	412.5	410.0	403.0
320	417.5	415.5	413.5	411.0	404.0

[a]Extrapolated value at a heating rate (q) of $1°K/min$ using the
equation: $\log q = a - b/T_g$ [9].

In Fig. 10 are shown typical DSC thermograms of an undecomposed
PptBuS polymer sample recorded in the glass transition region at
various heating rates. T_g was found to increase with increasing rate
of heating. 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 undecom-
posed and a number of decomposed PptBuS samples are summarized
in Table 5. The values of T_{g_e} are found to increase with increasing
$\overline{M}_n$.
In Fig. 11 is shown a plot of T_{g_e} as a function of $\overline{M}_n$. T_{g_e} in-
creases up to a point beyond which it remains constant. The critical
value is located at $\overline{M}_n = 2 \times 10^4$. A plot of T_{g_e} as a function of $1/\overline{M}_n$
shown in Fig. 12 yields a straight line best described by

$$T_{g_e} = 446 - 7.33 \times 10^5/\overline{M}_n \qquad (1)$$

The value of $446°K$ for the T_{g_∞} of PptBuS is far greater than the
value $403°K$ reported in the literature [14, 15].
In earlier work from this laboratory [7-9] the T_{g_e} of PS (Eq. 2)
and PpMeS (Eq. 3) were related to $\overline{M}_n$ as follows:

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

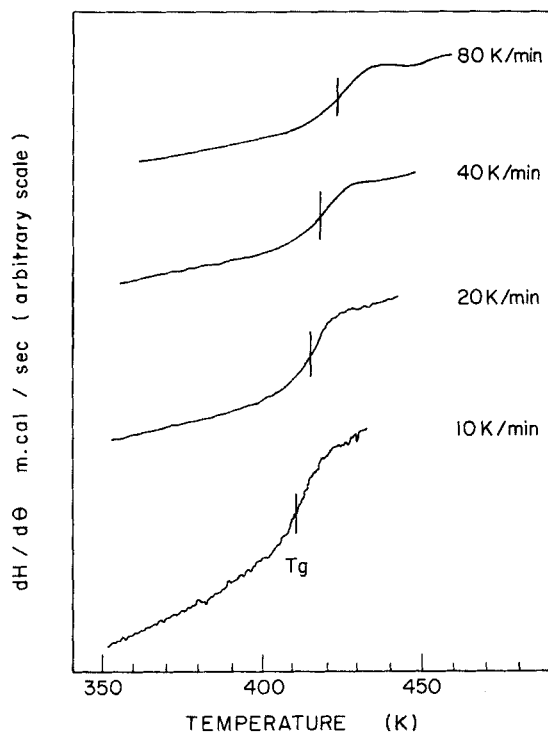$$T_{g_e}(°K) = 384 - 2.65 \times 10^5/\overline{M}_n \qquad (3)$$

FIG. 10. Typical DSC thermograms of an undecomposed polymer sample of PptBuS recorded in the glass transition region at various heating rates; (cooling rate = $320°K/min$). See Table 5 for other data.

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); the addition of a p-tertiary butyl group, however, increases the T_{g_∞} from 379 (for PS) to 446 (for PptBuS). This would indicate that the presence of a bulkier substituent, e.g., p-tert-butyl group in the aromatic ring of PS, results in increased steric hindrance and decreased chain flexibility, thereby increasing its T_{g_∞}. This is contrary to what was noted in earlier work from this laboratory on PpiPrS [8] and PpiPraMeS [12] where the presence of a p-isopropyl group lowered the values of T_{g_∞} due to increased chain flexibility and lower steric hindrance.

A comparison of the T_g values for PS ($363°K$), PpMeS ($364°K$), PpiPrS ($335.5°K$), and PptBuS ($399°K$), all having $\overline{M}_n$ values of

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

Sample no.	Weight loss (α), (%)	$\bar{M}_n$ (GPC) $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	T_g at various heating rates				T_{ge} (1°K/min)
				80°K/min	40°K/min	20°K/min	10°K/min	
PptBuS-0	Undecomposed	3.1	2.8	417.5	415.5	413.5	411.0	404.0
PptBuS-11	6.2	1.8	3.1	419.0	416.5	414.0	413.0	404.5
PptBuS-12	6.8	1.9	3.2	419.5	417.0	414.0	412.5	403.5
PptBuS-13	8.2	1.8	3.3	418.0	415.5	413.0	412.0	404.0
PptBuS-18	9.2	1.8	3.2	414.5	412.0	410.5	408.5	402.0
PptBuS-14	10.0	1.8	3.0	420.0	417.0	415.5	414.0	407.0
PptBuS-15	14.0	1.8	2.9	419.5	417.0	414.0	412.5	403.5
PptBuS-16	17.5	1.7	3.0	419.0	416.0	415.0	413.0	406.0
PptBuS-19	20.0	1.6	3.2	415.0	413.5	410.0	407.0	398.5
PptBuS-17	25.5	1.5	3.3	417.0	414.0	412.5	410.5	403.0
PptBus-20	30.2	1.2	3.4	400.0	396.0	392.5	390.5	379.0
PptBuS-21	34.1	1.2	3.2	399.5	396.5	392.0	390.5	379.0
PptBuS-22	40.7	1.0	3.7	391.0	389.0	388.0	386.0	380.5
PptBuS-23	51.5	6.9	3.3	385.0	381.5	378.0	377.0	367.5

[a]As in Table 4.
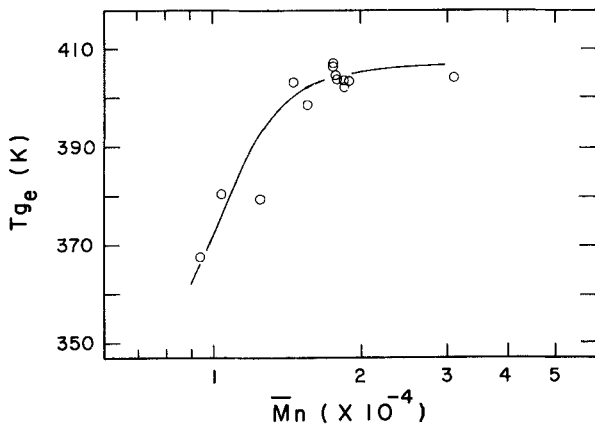
FIG. 11. Extrapolated T_{g_e} values (to q = $1°$K/min) of PptBuS as a function of $\overline{M}_n$. See Table 5 for other data.
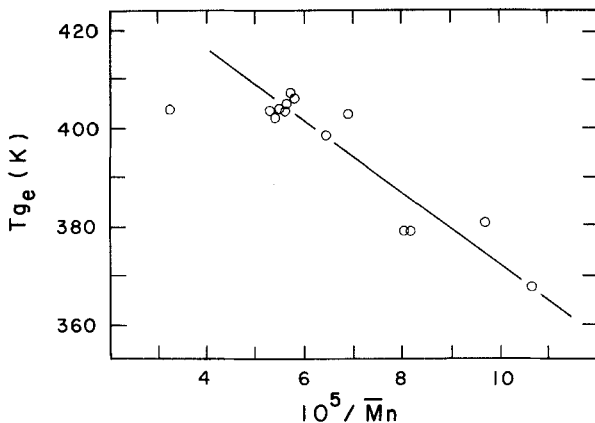
FIG. 12. Extrapolated T_{g_e} values (to q = $1°$K/min) of PptBuS as a function of $1/\overline{M}_n$. See Table 5 for other data.

1.4×10^4, shows that the increased chain flexibility and lower steric hindrance do not necessarily arise from the apparent bulkier size of the substituent. A comparison of T_{g_e} values of PS and its p-substituted homologs reveals the following order of steric hindrance causing groups: ptBu > pMe ≥ H > piPr. It may be noted that on replacing p-CH₃ with p-CH(CH₃)₂ in PS lowers its T_{g_e} from $364°$K

(PpMeS) to 335.5°K (PpiPrS) whereas replacing H on p-CH(CH₃) with another methyl, i.e., $-C(CH_3)_3$, increases its T_{g_e} from 335.5 (PpiPrS) to 399°K (PptBuS). It appears that the effective bulk size of a substituent (i.e., its ability to pack in polymer layers) is more significant in affecting T_g than its apparent bulk size.

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

1. In the isothermal decomposition of PptBuS, random scissions reduce the chain length of the polymer in the earlier stages of the reaction ($\alpha < 10\%$) while partial as well as total depolymerization accounts for the polymer weight loss.

2. The activation energies for decomposition of PS and its homologs follow the order $E_{PS} > E_{PpMeS} \simeq E_{PpiPrS} > E_{PptBuS}$.

3. A comparison of T_{g_e} values for PS (363°K), PpMeS (364°K), PpiPrS (335.5°K), and PptBuS (399°K), all having $\overline{M}_n$ values of 1.4×10^4, reveals that increased chain flexibility and lower steric hindrance are related to effective bulk size (packing ability) rather than apparent bulk size. This conclusion is based on the fact that although the apparent bulk size of various groups follows the order $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_3 > H$, the effective bulk size determined from the T_{g_e} data where these groups are involved follows the order p-t-$C(CH_3)_3 > $ p-$CH_3 \geq -H > $ p-i$CH(CH_3)_2$.

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 in due course.

ACKNOWLEDGMENTS

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, L. 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, L. Minh, and L. P. Blanchard, Ibid., A14, 517 (1980).

[8] S. L. Malhotra, P. Lessard, L. Minh, and L. P. Blanchard, Ibid., A14, 915 (1980).

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

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

[11] S. L. Malhotra, L. Minh, and L. P. Blanchard, Ibid., A13, 51 (1979).

[12] S. L. Malhotra, L. Minh, and L. P. Blanchard, Ibid., A12, 149 (1978).

[13] N. A. Weir, T. H. Milkie, and D. Nicholas, J. Appl. Polym. Sci., 23, 609 (1979).

[14] W. G. Barb, J. Polym. Sci., 37, 515 (1959).

[15] T. E. Davies, Br. Plast., 32, 283 (1959).

[16] Z. Kucukyavuz and S. Kucukyavuz, Eur. Polym. J., 14, 867 (1978).

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

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

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

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