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

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ABSTRACT

Thermal decomposition and glass transition temperature
studies have been carried out on poly-p-isopropylstyrene
(PpiPrS) with a differential scanning calorimeter. The un-
decomposed polymer as well as its decomposition products were
analyzed by gel permeation chromatography (GPC), infrared spec-
troscopy (IR) and nuclear magnetic resonance (NMR). During iso-
thermal treatments in the 25-150°C temperature range ($\alpha < 3\%$),
the observed increase in M_w arose primarily from interchain
linking between the longer radical-bearing chains. Beyond 315°C
($\alpha > 6\%$), the molecular weight increases result from crosslinking
reactions between decomposed polymer and longer undecomposed
chains. During interchain linking, the number of isomethyl
groups (iso-CH_3) increase. In the crosslinking reactions that take
place at temperatures beyond 315°C, the number of iso-CH_3 and
terminal or α-methyl groups (α-CH_3) both increase while the
number of methylene groups (CH_2) decreases. Activation ener-
gies of decomposition for various homologs of polystyrene (PS)
obey the following order: $E_{PS} > E_{PpiPrS} > E_{PpiPr\alpha MeS} \geq$
$E_{P\alpha MeS}$. A comparison of the T_{g_e} values of PS with those of
PpiPrS, poly-α-methylstyrene (PαMeS) and poly-p-isopropyl-α-

methylstyrene (PpiPrαMeS) shows that the presence of the p-isopropyl groups lowers the T_g of PS as well as that of PαMeS by about 30-35°K.

INTRODUCTION

Thermal decomposition [1-7] and glass transition temperature studies [7-11] of polystyrene (PS) [1, 2, 8], poly-α-methylstyrene (PαMeS) [3, 4, 9, 10], poly-p-isopropyl-α-methylstyrene (PpiPrαMeS) [5, 6, 11], and poly-p-methylstyrene (PpMeS) [7] have been reported on earlier from this laboratory. From the results of the isothermal decompositions, it was observed that for identical values of weight loss α, the respective decomposition temperatures of PpMeS and PαMeS were about 22 and 72°K lower than those of PS. Similarly, for identical values of α, the decomposition temperatures of PpiPrαMeS were about 10-20°K lower than those of PαMeS. In the glass transition range, the values of $T_{g\infty}$ (the glass transition at infinite molecular weight) for PS, PpMeS, PαMeS, and PpiPrαMeS were found to be 379, 384, 453, and 422°K, respectively.

These results clearly suggest that the presence of substituents in PS, e. g., methyl and isopropyl groups, on the vinyl chains or on the aromatic rings, plays an important role in its decomposition as well as in its glass transition behavior. Keeping this in mind, a study of the thermal decomposition and the glass transition temperature of another homolog of polystyrene, namely poly-p-isopropylstyrene (PpiPrS), was carried out and the data recorded was compared with those obtained with PS incorporating other substituents as well as with those, previously reported, on the T_g of PpiPrS [12]. The principal results obtained are summarized in the present article.

EXPERIMENTAL

Poly-p-isopropylstyrene (PpiPrS) (Aldrich Chemical Co.) was used as received. The weight-average molecular weight $\overline{M}_w$ of the polymer was calculated from the intrinsic viscosity data obtained with toluene as solvent at 25°C, using the relation reported in the literature [13]. Molecular weight distributions of PpiPrS samples both before and after thermal decomposition were obtained with a Waters Associates (model 200) gel permeation chromatograph [1-7]. Calibration of the instrument was performed with standard PS and PpiPrS samples. Molecular weights were calculated by the summation method suggested by the supplier [14].

A Perkin-Elmer (Model DSC-2) differential scanning calorimeter

operating with pure dry helium in the cell area was used to decompose 10 mg samples of PpiPrS. A Perkin-Elmer (Model TGS-1) thermogravimetric scanning balance operating in a pure dry nitrogen atmosphere with a heating rate of $20°K/min$ was also used to follow the dynamic decomposition of 2 mg samples of the polymer.

IR spectra of the undecomposed and the decomposed samples of PpiPrS deposited on KBr pellets were recorded with a Perkin-Elmer 521 grating spectrometer. A series of experiments was carried out in which the total weight of KBr and undecomposed PpiPrS was kept constant at 50 mg but where the content of PpiPrS in the mixture was varied from 2 to 4%. The ratios of aromatic to aliphatic ν_{CH} bands increased with increasing concentration of PpiPrS. This increase resulted from the enhanced intensity of the aromatic ν_{CH} band rather than that of the aliphatic ν_{CH} band. Best results were obtained with KBr pellets containing 4% (2 mg polymer + 48 mg KBr) of PpiPrS.

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

The T_g values of the undecomposed as well as the decomposed samples of PpiPrS were determined with the Perkin-Elmer DSC-2 apparatus [9-11].

RESULTS AND DISCUSSION

Thermal Decomposition of PpiPrS

In Table 1 are summarized values of the percent weight loss α, the molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and the polydispersity ratios ($\overline{M}_w/\overline{M}_n$) obtained with PpiPrS both before and after its isothermal treatment at various temperatures for different periods. From 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], PαMeS [3], and PpiPrαMeS [5] samples of similar $\overline{M}_w$ are also plotted in Fig. 1. For identical values of α, the decomposition temperatures for PpiPrαMeS are always 20-30°K lower than those for PαMeS. For $\alpha < 10\%$, the decomposition temperatures for PpiPrS are also lower (from 140°K when $\alpha = 4\%$ to 5°K when $\alpha = 10\%$) than those for PS. For $\alpha > 10\%$, the presence of p-isopropyl groups seems to have no influence on the decomposition process.

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

Sample	Treatment temperature (°C)	Treatment time (min)	Weight loss α (%)	$\bar{M}_w$ (GPC) $\times 10^{-4}$	$\bar{M}_n$ (GPC) $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
PpiPrS-0	(undecomposed)	–	0	5.5	1.4	3.9
PpiPrS-1	50	50	0.6	5.9	1.5	3.9
PpiPrS-2	100	50	2.0	6.4	1.5	4.3
PpiPrS-3	125	50	2.1	7.6	1.5	5.1
PpiPrS-4	150	50	2.4	11.0	1.8	6.1
PpiPrS-5	175	50	3.5	8.0	1.6	5.0
PpiPrS-6	200	50	3.9	7.7	1.5	5.1
PpiPrS-7	250	50	4.6	6.7	1.3	5.1
PpiPrS-8	275	50	4.8	6.2	1.4	4.4
PpiPrS-9	300	50	5.9	5.7	1.3	4.4
PpiPrS-10	315	50	6.2	5.6	1.5	3.9
PpiPrS-11	330	50	7.7	6.3	1.3	4.8
PpiPrS-12	350	50	13.0	6.2	1.3	4.7
PpiPrS-13	360	50	19.1	8.1	1.3	6.2
PpiPrS-14	370	50	32.8	11.1	1.2	9.2
PpiPrS-15	375	50	43.5	30.3	1.2	25.8

PpiPrS-16	385	50	70.5	-	-	-
PpiPrS-17	375	5	14.5	4.8	1.2	4.0
PpiPrS-18	375	10	20.0	4.9	1.2	4.2
PpiPrS-19	375	20	28.8	5.7	1.2	4.8
PpiPrS-20	375	30	37.8	6.9	1.2	5.8
PpiPrS-21	375	35	38.0	8.6	1.1	8.1
PpiPrS-22	375	40	42.6	12.2	1.2	10.3
PpiPrS-23	375	45	44.7	17.4	1.2	14.8
PpiPrS-24[a]	375	60	57.6	7.1	0.3	23.7
PpiPrS-25[a]	375	70	60.5	7.1	0.5	14.2
PpiPrS-26[a]	375	90	65.3	4.8	0.4	12.0

[a]Limited solubility in THF.
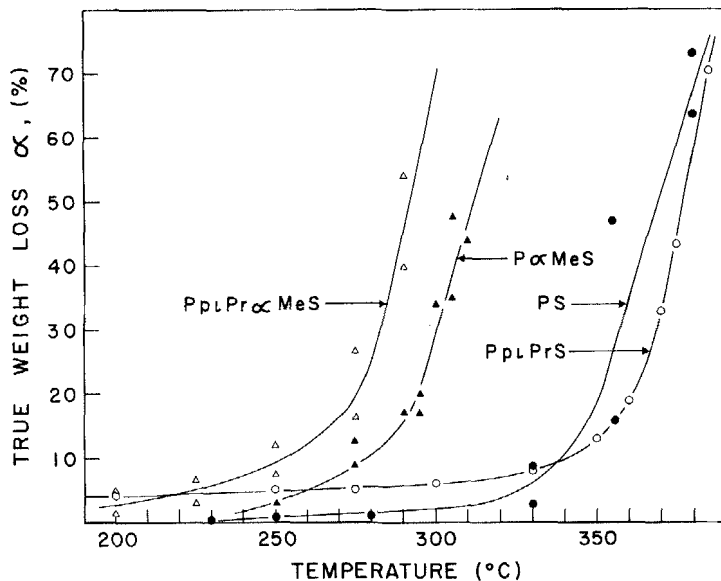
FIG. 1. Variation of weight loss α (%) with treatment temperature T (°C) for PS ($\overline{M}_w$ = 1.0 × 10^4 to 1.6 × 10^5 [2]), PαMeS ($\overline{M}_w$ = 4.0 × 10^4 to 6.0 × 10^4 [3]), PpiPrαMeS ($\overline{M}_w$ = 3.8 × 10^4 to 7.5 × 10^4 [5]), and PpiPrS ($\overline{M}_w$ = 5.5 × 10^4) samples. See Table 1 for other data.

In Fig. 2 are shown the normalized GPC molecular weight distributions of some of the PpiPrS samples subjected to 50 min isothermal treatments at various temperatures. It may be noted that the maxima in the GPC distributions of the decomposed polymers move towards lower elution counts (higher molecular weights). Furthermore, the quantity of polymer appearing below an elution count of 26 (high molecular weight region) keeps on increasing with increasing temperature of decomposition, suggesting the presence of crosslinking reactions which result in an increase in molecular weight. It may be added here that, during the thermal decomposition of PpiPrαMeS [5], the extent of cross linking was found to be negligible. This indicates that the presence of α-methyl groups on the vinyl chains of PpiPrαMeS prevents crosslinking reactions from taking place.

In Fig. 3 are shown the variations in $\overline{M}_w$ and $\overline{M}_n$ with temperature of decomposition for PpiPrS samples subjected to 50 min isothermal treatments. In the temperature range 25-150°C (α < 3%), the $\overline{M}_w$ values increase regularly, whereas the $\overline{M}_n$ values remain constant at
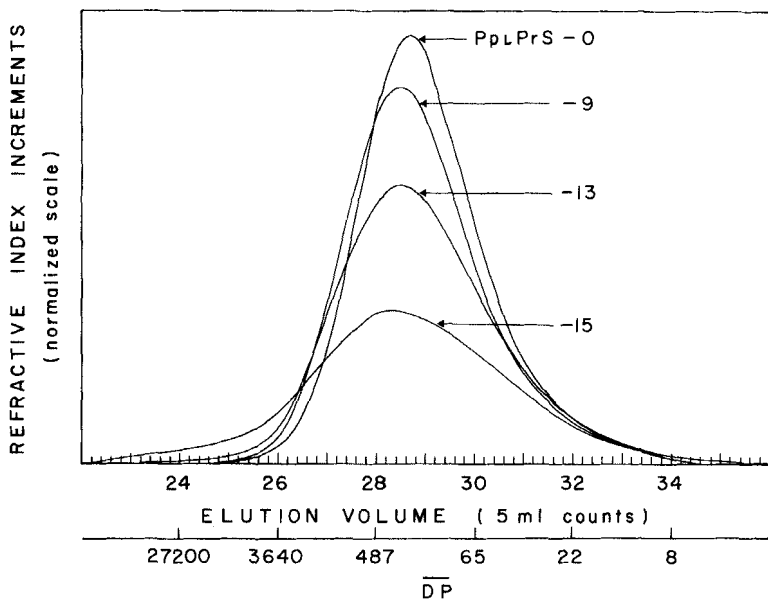
FIG. 2. GPC molecular weight distributions of PpiPrS samples subjected to 50 min decomposition periods at various temperatures. See Table 1 for other data.

$1.6 \pm 0.2 \times 10^4$. Between 150 and 315°C ($3 < \alpha < 6\%$), $\overline{M}_w$ decreases while $\overline{M}_n$ remains stable at $1.4 \pm 0.2 \times 10^4$. Beyond 315°C, $\overline{M}_w$ increases again but $\overline{M}_n$ continues to remain constant. The $\overline{M}_w$ increases, obtained when the polymer is decomposed in the 25-150°C temperature range ($\alpha < 3\%$) and above 315°C ($\alpha > 6\%$), suggest the presence of crosslinking reactions which in both cases may or may not follow the same mechanism. Polymers decomposed at temperatures higher than 375°C were only partly soluble in THF.

To understand the decomposition of PpiPrS better, the normalized GPC distribution of the undecomposed sample (PpiPrS-0) was compared successively with the distributions of other samples which had been decomposed during 50 min periods at different temperatures. On subtracting from the initial distribution curve of the undecomposed polymer the distribution of any subsequently decomposed polymer, the changes that take place resulting from the decomposition or cross-linking of the higher molecular weight species can readily be visualized. For PpiPrS samples, these changes are shown in Figs. 4, 5, and 6, where all the (+) distributions appearing between elution counts 22 and 30 represent inter-chain-linked or crosslinked polymer and all the (-) distributions between elution counts 26 and 34 (such as those
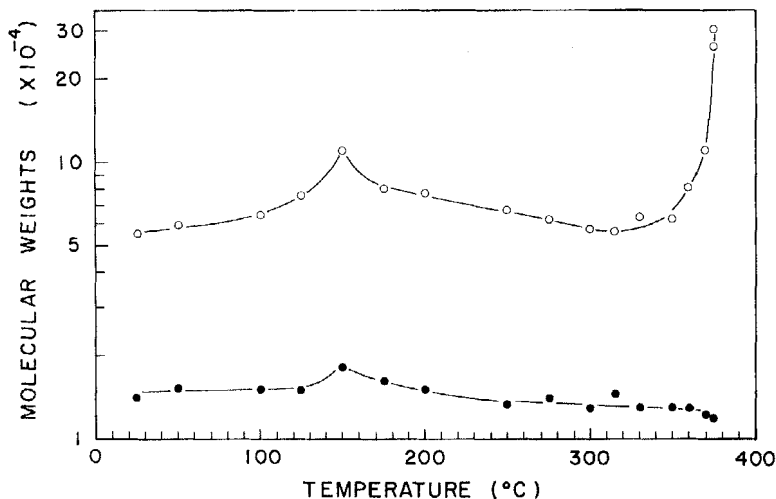
FIG. 3. Variation of molecular weight with treatment temperature for PpiPrS samples subjected to 50 min decomposition periods: (o) $\overline{M}_w$; (•) $\overline{M}_n$. See Table 1 for other data.

between 27 and 31 and those between 30 and 34) represent the fraction of the polymer which is involved in inter-chain linking or crosslinking reactions yielding high molecular weight polymers (between elution counts 26 and 34) or which simply depolymerizes to low molecular weight (1000) polymers (appearing as a (+) distribution between elution counts 33 and 36) in combination with still lower molecular weight depolymerized oligomers which volatilize completely.

The characteristics of the various (-) and (+) distributions shown in Figs. 4, 5 and 6 are summarized in Table 2, which lists their α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values. For isothermal decompositions at temperatures of 50, 100, 125, and 150°C, 3.1, 7.1, 9.7, and 18.2% of the polymer chains respectively, eluting between counts 26 and 32 ($\overline{M}_w$ = 1.4×10^4 to 3.4×10^4 and $\overline{M}_n$ = 1.05×10^4 to 1.9×10^4), participate in the formation of 4.1 to 16.5% of higher molecular weight polymers ($\overline{M}_w$ = 1.4×10^5 to 3.5×10^5 and $\overline{M}_n$ = 1.0×10^5 to 1.5×10^5) which elute between counts 22 and 29. Furthermore, about 2% of the polymer ($\overline{M}_w$ of 3×10^3 to 4.8×10^3 and $\overline{M}_n$ of 2.5×10^3 to 4×10^3) appearing between elution counts of 29 and 34 depolymerize and volatilize completely.

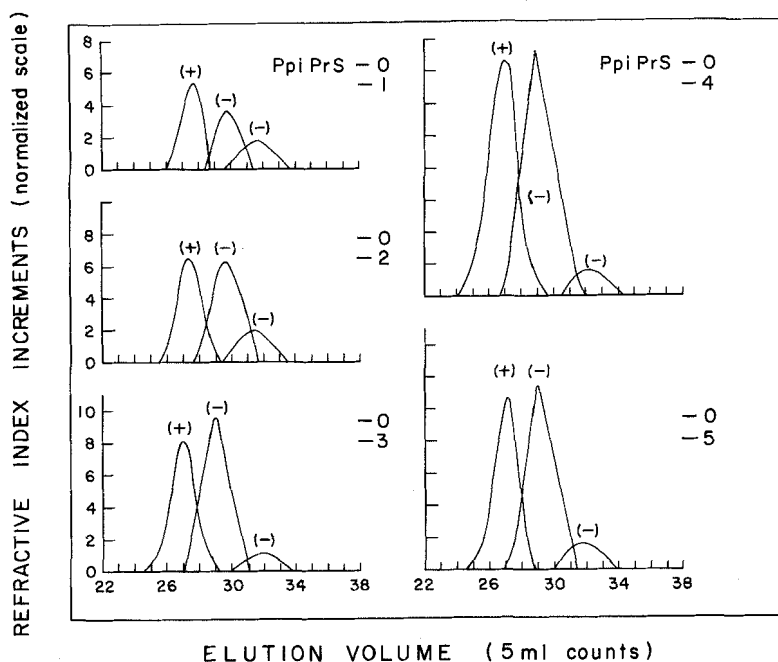For isothermal decompositions carried out at temperatures of 150,

REFRACTIVE INDEX INCREMENTS (normalized scale)

ELUTION VOLUME (5 ml counts)

FIG. 4. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into their various components. The case of PpiPrS samples subjected to 50 min decomposition periods at 50, 100, 125, 150, and 175°C. See Table 2 for other data.

175, 200, 250, 275, 300, and 315°C, the quantity of polymer eluting between counts 26 and 32 ($\overline{M}_w = 3 \times 10^4$ and $\overline{M}_n = 1.8 \times 10^4$) and participating in the formation of higher molecular weight polymer decreases from 18.2 at 150°C to 6.4 at 315°C. This results in a decrease (from 16.5% at 150°C to 1.6% at 315°C) of the high molecular weight polymer ($\overline{M}_w = 2.0 \times 10^5$ and $\overline{M}_n = 1.3 \times 10^5$) eluting between counts 22 and 29. This suggests that a part of the polymer with $\overline{M}_w$ of 3×10^4 and $\overline{M}_n$ of 1.8×10^4 decomposes to yield between 0.5 and 0.7% of low molecular weight products with $\overline{M}_w$ and $\overline{M}_n$ of 1×10^3. The quantity of completely volatilized polymer eluting between counts 29 and 34 ($\overline{M}_w$ ranging from 3×10^3 to 6×10^3 and $\overline{M}_n$ from 2.5×10^3 to 4.7×10^3) varies from 1 to 3%.

For isothermal decompositions carried out at temperatures of 315, 330, 350, 360, 370, and 375°C, 6.4-56.0% of the polymer eluting between
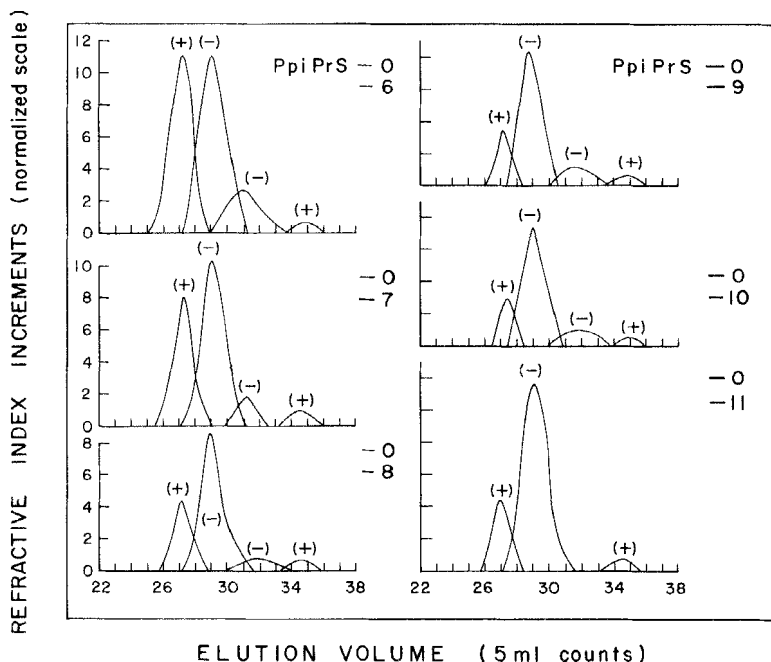
FIG. 5. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into their various components. The case of PpiPrS samples subjected to 50 min decomposition periods at 200, 250, 275, 300, 315 and 330°C. See Table 2 for other data.

counts 26 and 32 ($\overline{M}_w = 4 \times 10^4$ and $\overline{M}_n = 2 \times 10^4$) participate in the formation of 1.6 (at 315°C) to only 8.6% (at 375°C) of the higher molecular weight polymer ($\overline{M}_w = 1.7 \times 10^5$ to 13.5×10^5 and $\overline{M}_n = 1.0 \times 10^5$ to 3.0×10^5) eluting between counts 22 and 29. This would mean that a major part of the polymer ($\overline{M}_w = 4 \times 10^4$ and $\overline{M}_n = 2 \times 10^4$) depolymerizes to oligomers.

Based on these analyses of the changes in the GPC distributions after thermal treatments between 25 and 375°C, the formation of the high molecular weight polymer may be explained as follows.

For isothermal decompositions carried out at temperatures below 150°C, the weight loss is not significant, and thus it may be assumed that no drastic changes, i. e., formation of double bonds etc, have taken place in the structure of PpiPrS. The transformation of the low molecular weight polymer ($\overline{M}_w = 1.4 \times 10^4$ to 3.4×10^4) into that of a higher molecular weight polymer ($\overline{M}_w = 1.4 \times 10^5$ to 3.4×10^5) may
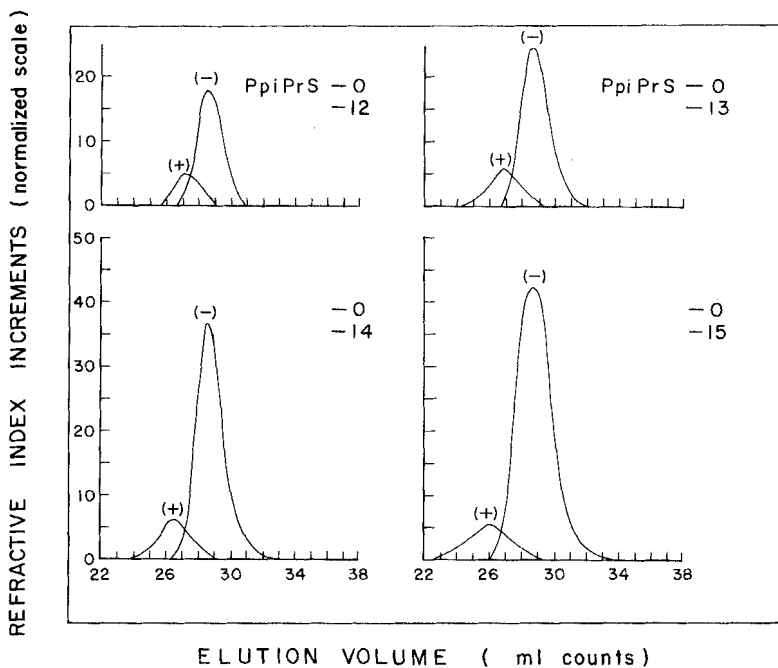
FIG. 6. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into their various components. The case of PpiPrS subjected to 50 min decomposition periods at 350, 360, 370 and 375°C. See Table 2 for other data.

now be explained on the basis that, prior to their decomposition, the longer polymer chains in the former polymer are involved in certain inter-chain linking reactions.

For isothermal decompositions carried out beyond 315°C, a major part of the polymer depolymerizes, and it is only a minor part of the polymer ($\overline{M}_w \doteq 4 \times 10^4$ and $\overline{M}_n = 2 \times 10^4$) that participates in the formation of high molecular weight polymer ($\overline{M}_w = 1.7 \times 10^5$ to 13.5 $\times 10^5$). Furthermore, decompositions carried out at temperatures above 315°C may introduce some structural changes, i. e., formation of double bonds, migration of certain protons to other active sites in the molecule, etc. and thus the resulting crosslinking reactions may be of a different nature from those noted in the lower (25-150°C) temperature range.

With a view to studying the evolution of crosslinking reactions as a function of time PpiPrS samples were decomposed isothermally at 375°C over different periods ranging from 5 min to 90 min. Their

TABLE 2. Characteristics of Polymers Appearing in Four GPC Elution Count Ranges: PpiPrS Decomposed for 50 min at Different Temperatures and for Different Periods at 375°C[a]

Polymers pairs analyzed	Elution count range															
	22-29				26-32				29-34				32-35			
	α (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	α (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	α (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	α (%)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
PpiPrS-0 → PpiPrS-1	4.1	13.6	9.8	1.4	3.1	1.4	1.05	1.35	2.1	0.43	0.35	1.2	-	-	-	-
PpiPrS-0 → PpiPrS-2	5.9	16.3	9.9	1.7	7.1	1.8	1.1	1.7	2.4	0.48	0.39	1.2	-	-	-	-
PpiPrS-0 → PpiPrS-3	7.8	26.5	14.2	1.9	9.7	3.4	1.9	1.8	1.2	0.37	0.31	1.2	-	-	-	-
PpiPrS-0 → PpiPrS-4	16.5	34.9	15.3	2.3	18.2	3.4	1.6	2.2	1.9	0.30	0.25	1.2	-	-	-	-
PpiPrS-0 → PpiPrS-5	9.7	26.2	15.2	1.8	12.1	3.0	1.6	1.9	1.9	0.38	0.32	1.2	-	-	-	-
PpiPrS-0 → PpiPrS-6	10.0	24.0	15.9	1.5	11.8	3.0	1.7	1.8	3.3	0.61	0.46	1.3	0.5	0.07	0.07	1.0
PpiPrS-0 → PpiPrS-7	6.7	17.1	10.7	1.6	9.4	2.8	1.7	1.6	1.3	0.51	0.47	1.1	0.7	0.11	0.10	1.1
PpiPrS-0 → PpiPrS-8	3.1	18.0	12.6	1.5	7.4	3.0	1.8	1.7	0.9	0.40	0.33	1.2	0.5	0.09	0.08	1.1
PpiPrS-0 → PpiPrS-9	1.9	17.0	14.0	1.2	7.0	3.5	2.4	1.5	1.2	0.39	0.33	1.2	0.5	0.08	0.08	1.0

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PpiPrS-0 → PpiPrS-10	1.6	13.7	11.7	1.2	6.4	3.0	1.9	1.6	-	-	-	-	0.4	0.07	0.07	1.0
PpiPrS-0 → PpiPrS-11	2.9	20.5	15.9	1.3	10.6	2.9	1.8	1.6	-	-	-	-	0.6	0.10	0.09	1.1
PpiPrS-0 → PpiPrS-12	4.7	16.9	10.3	1.7	17.3	4.2	2.4	1.7	-	-	-	-	-	-	-	-
PpiPrS-0 → PpiPrS-13	6.4	32.5	13.5	2.4	25.0	3.9	2.1	1.9	-	-	-	-	-	-	-	-
PpiPrS-0 → PpiPrS-14	7.4	45.2	18.5	2.4	38.5	4.1	2.0	2.1	-	-	-	-	-	-	-	-
PpiPrS-0 → PpiPrS-15	8.6	135.5	29.5	4.6	56.0	4.5	1.8	2.6	-	-	-	-	-	-	-	-
PpiPrS-0 → PpiPrS-17	-	-	-	-	16.8	8.55	2.0	4.3	-	-	-	-	0.4	0.11	0.10	1.1
PpiPrS-17 → PpiPrS-18	1.5	32.8	25.0	1.3	3.2 / 3.4	2.8 / 2.3	2.0 / 1.0	1.4 / 2.3	-	-	-	-	0.4	0.29	0.27	1.1
PpiPrS-18 → PpiPrS-19	1.8	43.2	16.4	2.6	10.4	4.9	2.3	2.1	-	-	-	-	0.6	0.15	0.14	1.1
PpiPrS-19 → PpiPrS-20	1.8	57.2	20.5	2.8	11.3	5.0	1.9	2.6	-	-	-	-	0.7	0.15	0.13	1.1
PpiPrS-20 → PpiPrS-22	2.8	72.7	35.4	2.1	6.8	4.8	1.6	3.0	-	-	-	-	0.9	0.15	0.12	1.2
PpiPrS-22 → PpiPrS-15	2.3	325.0	136.0	2.4	7.0	5.8	1.9	3.0	0.8	0.36	0.32	1.1	-	-	-	-

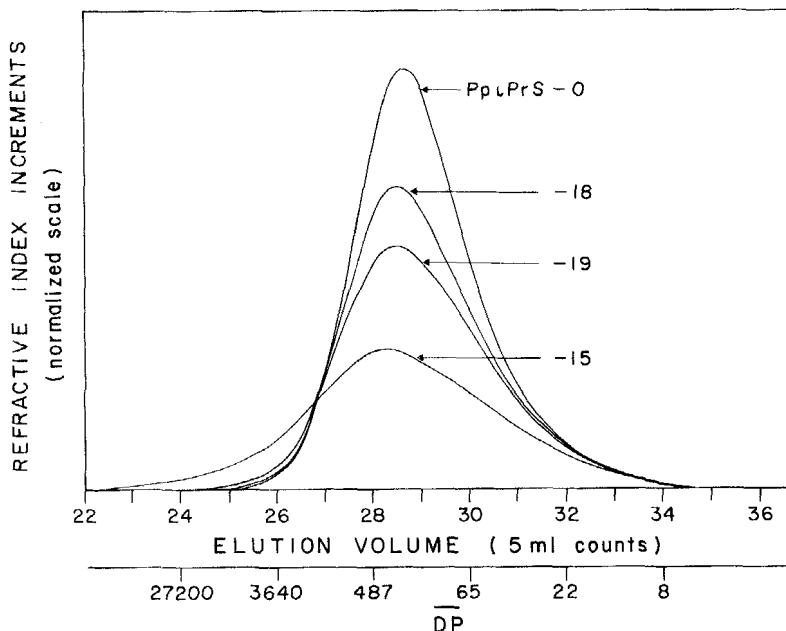[a]See Table 1 for decomposition reaction conditions.

FIG. 7. GPC molecular weight distributions of a PpiPrS sample subjected to isothermal treatments at 375°C for different periods. See Table 1 for other data.

α, $\overline{M}_w$, $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values are summarized in Table 1. In the first 5 min of decomposition, α reached a value of 14.5%, and the $\overline{M}_w$ and $\overline{M}_n$ values decreased slightly. Between decomposition periods of 5 to 50 min, α increased from 14.5 to 45.0%. $\overline{M}_n$ remained constant at 1.2×10^4, but $\overline{M}_w$ increased from 4.8×10^4 to 30.3×10^4. The polymers recovered after more than 50 min decomposition were only partly soluble (viz., 60 min $\sim$ 85% soluble, 70 min $\sim$ 65% soluble, and 90 min $\sim$ 50% soluble) which may explain their low $\overline{M}_w$ and $\overline{M}_n$ values, their high molecular weight, crosslinked components not being accounted for.

The normalized GPC molecular weight distributions of PpiPrS decomposed at 375°C for various periods are shown in Fig. 7. These distributions resemble at first sight those obtained following 50 min isothermal decompositions of the polymer at various temperatures; however, for identical values of α, obtained as a function of temperature as well as time, the overall $\overline{M}_w$ values do not agree. During the
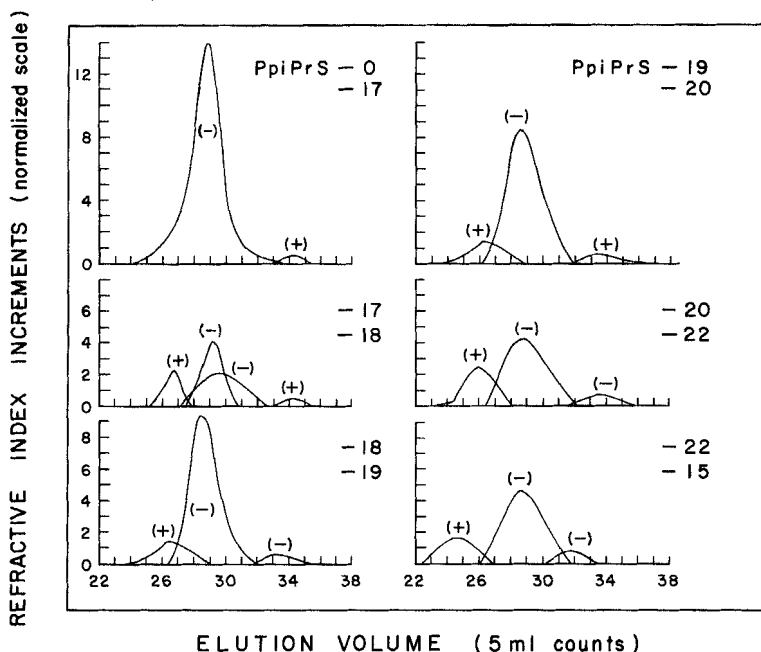
ELUTION VOLUME (5 ml counts)

FIG. 8. Graphical method of analysis whereby the GPC molecular weight distribution curves are broken down into their various components. The case of PpiPrS subjected to isothermal treatments at 375°C for different periods. See Table 2 for other data.

50 min isothermal decompositions carried out at the various temperatures, for α = 13% (PpiPrS-12), α = 19.1% (PpiPrS-13), α = 32.8% (PpiPrS-14), and α = 43.5% (PpiPrS-15) the corresponding $\overline{M}_w$ values were 6.2×10^4, 8.1×10^4, 11.1×10^4 and 30.3×10^4, respectively. For isothermal decompositions carried out at 375°C over various periods, for α = 14.5% (PpiPrS-17), α = 20% (PpiPrS-18), α = 28.8% (PpiPrS-19), and α = 42.6% (PpiPrS-22) the corresponding values of $\overline{M}_w$ were 4.8×10^4, 4.9×10^4, 5.7×10^4, and 12.2×10^4, respectively.

In Fig. 8 are shown the changes that take place in the GPC molecular weight distributions of PpiPrS when the normalized distributions of both undecomposed and decomposed samples were successively compared. After only 5 min of treatment at 375°C, 16.8% of the polymer ($\overline{M}_w$ = 8.55×10^4 and $\overline{M}_n$ = 2.0×10^4) had volatilized and 0.35% of lower molecular weight polymer ($\overline{M}_w$ and $\overline{M}_n$ = 1×10^3) had been formed. Beyond the first 5 min, a major part of the polymer ($\overline{M}_w$ =

5.0×10^4 and $\overline{M}_n = 2.0 \times 10^4$) had depolymerized to yield lower molec-
ular weight polymer ($\overline{M}_w = 1.5 \times 10^3$ and $\overline{M}_n = 1.3 \times 10^3$). A minor
part of the polymer, however, ($\overline{M}_w = 5.0 \times 10^4$ and $\overline{M}_n = 2.0 \times 10^4$)
also participated in crosslinking reactions to yield 2 to 3% of a very
high molecular weight material ($\overline{M}_w = 4.32 \times 10^5$ to 3.25×10^6 and
$\overline{M}_n = 1.64 \times 10^5$ to 1.36×10^6). The fact that the formation of very
high molecular weight polymer started only when α had reached about
15% suggests that certain structural changes in the undecomposed
polymer were needed to produce crosslinking reactions. These re-
sults agree well with those obtained for 50 min isothermal decompo-
sitions carried out at temperatures above $315°C$ where crosslinking
reactions were accompanied by significant weight losses. But they
are quite different to those obtained for 50 min isothermal decomposi-
tions carried out at temperatures between 25 and $150°C$, where weight
losses never exceeded 3% and inter-chain linking yielded high molecu-
lar weight products.

    To gain insight into the mechanism of the crosslinking reactions,
it was thought pertinent to elucidate with the help of IR and NMR
spectroscopy the structural changes that take place in the decomposed
samples of PpiPrS.

    In Fig. 9 are shown the IR spectra of an undecomposed (PpiPrS-0)
and two decomposed (PpiPrS-9, PpiPrS-16) polymer samples. The
spectrum of PpiPrS-0 shows important peaks [15] at the following
wavenumbers (cm^{-1}): 3080, 3040, 3010 (aromatic ν_{CH}), 2950, 2910
(ν_{CH_3}), 2860 (ν_{CH_2}), 2000 to 1600 (shape typical of p-substitution),
1490 (phenyl rings), 1445, 1405 (δ_{CH_3}, δ_{CH_2}), 1345, 1365 (δ_{CH_3}-gem
dimethyl), 1080, 1035, 1000 (in-plane CH bending of phenyl), and 810
(out-of-plane bending of two adjacent aromatic hydrogens on the p-
substituted phenyls). All of these peaks are present in the spectra
of the decomposed polymers (PpiPrS-9 and PpiPrS-16) though their
intensities differ. Furthermore, there are no double bonds present
in the decomposed polymers as was postulated earlier.

    In Table 3 are summarized ν_{CH} band intensity ratios obtained
with undecomposed and decomposed samples of PpiPrS. At $150°C$,
the ν_{CH} band intensity ratios, iso-CH_3/CH_2 and iso-CH_3/arom in-
crease while the CH_2/arom ratio remains constant. At 300, 360, and
$375°C$ the iso-CH_3/CH_2, iso-CH_3/arom, and CH_2/arom ratios remain
constant at 2.73 ± 0.10, 1.73 ± 0.12, and 0.63 ± 0.03, respectively.
At $385°C$, the iso-CH_3/CH_2 ratio decreases, where the iso-CH_3/arom
and CH_2/arom ratios both increase. These results indicate that at
$150°C$, the number of iso-CH_3 groups increases, whereas at $385°C$
their number remains constant while the number of CH_2 and aromatic
groups decreases.

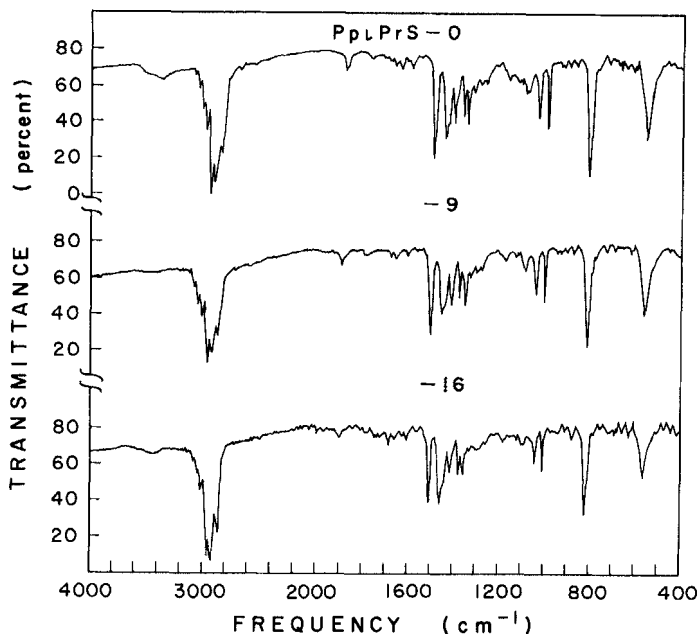   In Fig. 10 are shown the NMR spectra of an undecomposed

FIG. 9. IR spectra of undecomposed and decomposed samples of PpiPrS. See Table 3 for other data.

(PpiPrS-0) and three decomposed (PpiPrS-4, PpiPrS-9, PpiPrS-15) polymer samples. The highlights of these spectra are as follows: benzene protons (H_{arom}), $\tau = 2.8$-40; methine protons of the isopropyl group (iso-CH), $\tau = 7.0$-7.5; methine protons of the vinyl group (CH), $\tau = 7.5$-8.3; methylene protons of the vinyl group (CH_2), $\tau = 8.3$-8.7; methyl protons of the isopropyl group (iso-CH_3), $\tau = 8.7$-9.0; and terminal or α-methyls (α-CH_3), $\tau = 9.0$-9.3.

The relative abundance of the various protons in a decomposed polymer may best be explained in terms of proton ratios. In PpiPrS there are fifteen possible combinations and these are presented in Table 4 for the monomer (piPrS) and for the following polymers, PpiPrS-0, PpiPrS-4, PpiPrS-9, PpiPrs-13, and PpiPrS-15. A comparison of the proton/proton ratios of piPrS and PpiPrS-0 show that within the NMR limits these agree well suggesting that the undecomposed polymer has a regular structure. Comparisons of the various proton/proton ratios for PpiPrS-4, PpiPrS-9, PpiPrS-13, and PpiPrS-15 with those of undecomposed polymer reveal that the following changes in the structure of the undecomposed PpiPrS occur when it is subjected to isothermal decompositions at various temperatures:

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TABLE 3. IR ν_{CH} Band Intensity Ratios of Undecomposed and Decomposed Samples of PpiPrS[a]

Sample	Decomposition temperature (°C)	ν_{CH} intensity ratios		
		iso-CH_3/CH_2	iso-CH_3/arom	CH_2/arom
PpiPrS-0	undecomposed	2.79	1.85	0.66
PpiPrS-4	150	2.93	1.98	0.68
PpiPrS-9	300	2.71	1.67	0.62
PpiPrS-13	360	2.64	1.63	0.62
PpiPrS-15	375	2.77	1.78	0.64
PpiPrS-16	385	2.55	2.55	1.00

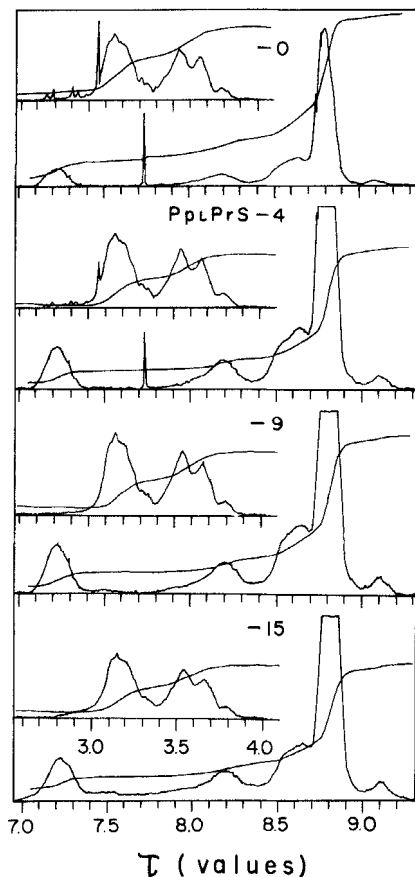[a]See Table 1 for decomposition reaction conditions.

FIG. 10. NMR spectra of undecomposed and decomposed samples of PpiPrS. See Table 4 for other data.

1. Terminal or α-CH$_3$ groups increase (see ratios 5, 7, 11, 13, and 15 in Table 4)
2. Vinyl CH$_2$ groups decrease (see ratios 4, 9, 11, and 12 in Table 4)
3. iso-CH$_3$ groups increase (see ratios 2, 4, and 8 to 10 in Table 4)
4. H$_{arom}$ protons remain constant (see ratios 1-5 in Table 4)
5. iso-CH and vinyl CH groups remain constant (see ratios 1, 3, and 14 in Table 4), except in PpiPrS-4.

These observations, based on the NMR analyses of PpiPrS samples decomposed at temperatures varying from 25 to 375°C, yield further

TABLE 4. Values of Proton-Proton Ratios Obtained from NMR Spectra of Undecomposed and Decomposed Samples

No.	Proton ratio	PiPrS* (monomer)[b]	Proton-proton ratios				
			PpiPrS-0[c]	PpiPrS-4	PpiPrS-9	PpiPrS-13	PpiPrS-15
1	H_{arom}/iso-CH	4.0	4.1 ± 0.2	4.3	4.0	3.9	3.7
2	H_{arom}/iso-CH$_3$	0.7	0.7 ± 0.05	0.6	0.6	0.6	0.6
3	H_{arom}/vinyl-CH	4.0	3.6 ± 0.4	4.1	3.8	3.9	3.7
4	H_{arom}/vinyl-CH$_2$	2.0	2.1 ± 0.2	2.2	2.4	2.5	2.6
5	H_{arom}/α-CH$_3$	-	14.5 ± 1.5	11.0	9.1	8.7	8.8
6	iso-CH$_3$/iso-CH	6.0	5.7 ± 0.35	7.1	6.6	6.4	6.1
7	iso-CH$_3$/α-CH$_3$	-	22.0 ± 5	18.0	15.0	14.0	14.0
8	iso-CH$_3$/vinyl-CH	6.0	5.0 ± 0.7	6.7	6.3	6.4	5.8
9	iso-CH$_3$/vinyl-CH$_2$	3.0	2.9 ± 0.2	3.7	3.9	4.0	4.1
10	vinyl-CH$_2$/vinyl-CH	2.0	1.8 ± 0.15	1.8	1.6	1.6	1.4
11	vinyl-CH$_2$/α-CH$_3$	-	7.8 ± 1.7	4.9	3.8	3.4	3.4
12	vinyl-CH$_2$/iso-CH	2.0	1.9 ± 0.1	< 2.0	1.7	< 1.6	1.4
13	vinyl-CH/α-CH$_3$	-	4.5 ± 1.3	2.7	2.4	2.2	2.4
14	vinyl-CH/iso-CH	1.0	1.2 ± 0.1	1.1	1.0	1.0	1.0
15	iso-CH/α-CH$_3$	-	4.0 ± 1.0	2.4	2.4	2.2	2.4

[a]See Table 1 for decomposition reaction conditions.
[b]Theoretical values.
[c]Average of values obtained from NMR spectra observed with 7, 11, 15, and 20 wt % solutions.

insight into the structural changes involved prior to or during cross-linking reactions and confirm the observations (based on the IR data) that at 150°C the number of iso-CH₃ groups increases. The polymer sample (PpiPrS-16) subjected to isothermal decomposition at 385°C was not soluble in CCl₄ and thus NMR data could not be obtained to support or refute the results of the IR analyses which showed the number of iso-CH₃ groups to be constant or increasing, the number of arom groups to be decreasing. As was reported elsewhere [7], however, in the IR spectra of the highly decomposed polymers, ν_{CH} of aromatic groups is generally low due to some artefact in the spectra and thus, because of its unreliable value, its use in elucidating the mechanism of the crosslinking reactions should be exercised with caution. For the present study, the IR data for the polymer decomposed at 385°C was not retained.

Based on the present NMR and IR data, the crosslinking reactions in PpiPrS originate at the vinyl chain protons and involve primarily the CH₂ protons which are transformed into either α-CH₃ or iso-CH₃ groups. Because of the absence of double bonds in the IR spectra of the decomposed polymers, crosslinking reactions must involve inter- or intramolecular migration of certain protons to other active sites in the polymer chain.

In Fig. 11 are shown curves representing the dynamic thermo-gravimetric decomposition (at a heating rate of 20°K/min) of PS, PpiPrS, and PpiPrαMeS samples, all of similar molecular weight. Using the method of Coats and Redfern [16, 17], activation energy values for the decomposition of these polymers were calculated assuming zero order and first order conditions. The values are presented in Table 5. For comparison purposes, activation energy values obtained with other polymer samples, viz., PS [2], PαMeS [3], and PpiPrαMeS [5], are also listed in the table. For polymers of similar $\overline{M}_n$, the activation energies for the decompositions follow the order: $E_{PS} > E_{PpiPrS} > E_{PpiPr\alpha MeS} \geq E_{P\alpha MeS}$.

Glass Transition of PpiPrS

The glass transition temperatures (T_g) of polymers depend on the heating rates used when making the measurements [7-11, 18-23]. T_g values may [24, 25] or may not [7] depend, however, on the rate at which the polymer samples are cooled below their T_g values. Prior to making definite T_g measurements on a new polymer, it is essential therefore to study the effects that the cooling or heating rates may have on its T_g.

In Fig. 12 are shown typical DSC-2 thermograms of the undecom-posed polymer recorded in the glass transition range at various
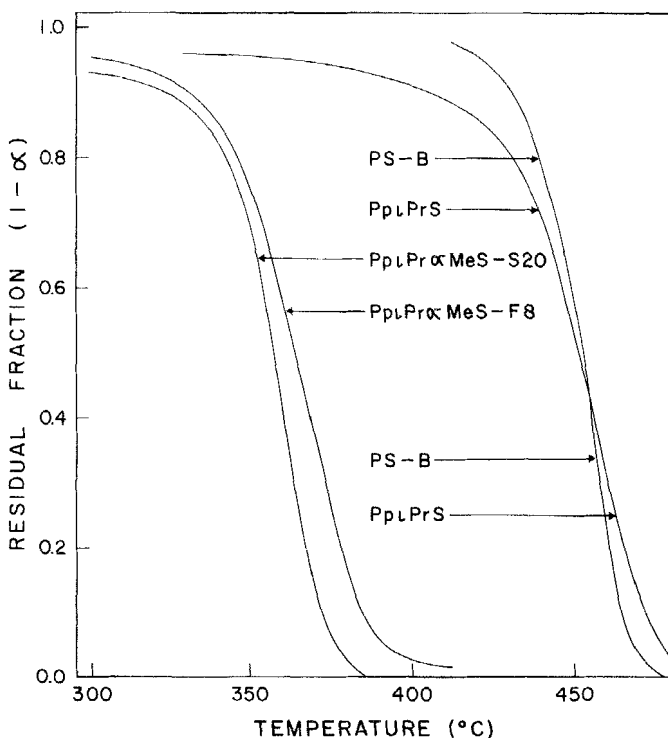
FIG. 11. Dynamic thermogravimetric decomposition of PS, PpiPrS and PpiPrαMeS samples at a heating rate of 20°K/min. See Table 5 for other data.

cooling rates. A heating rate of 40°K/min was used to bring the samples to a temperature above T_g prior to making each thermogram by cooling. The T_g values, determined as suggested in the literature [26] at the $\Delta C_p/2$ point (ΔC_p being the change in the heat capacity with glass transition), increased as the rate of cooling was decreased. T_g values of the undecomposed polymer (PpiPrS-0) subjected to seven different cooling rates are presented in Table 6 as a function of the heating rates. T_{g_e} (values extrapolated to a heating rate of 1°K/min) are likewise listed. The T_{g_e} values are found to increase from 335.5°K for a sample cooled at a rate of 320°K/min to 354.5°K when it has been cooled at a rate of 2.5°K/min. This difference of 19°K in the T_{g_e} of the undecomposed polymer is not attributed, however, to a lack of time on fast cooling for the polymer to reach its

TABLE 5. Activation Energy Values Calculated by the Method of Coats and Redfern [16, 17] for the Thermal Decomposition of Polystyrene (PS) and Three of Its Homologs

Sample	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	Activation energy (kcal/mole)[a]	
			$n = 0$	$n = 1$
PS-A	1.0	1.1	73.0	82.0
PS-B	1.8	1.1	51.4	88.5
PpiPrS	1.4	3.9	44.0	65.1
PαMeS	1.8	2.5	30.1	57.6
PpiPrαMeS-S8	1.2	1.2	30.2	-
PpiPrαMeS-F8	1.6	2.3	-	49.5
PpiPrαMeS-S20	1.8	1.3	50.5	63.7

[a]n is the order of reaction.

equilibrium state [24]. Rather, these varying T_{ge} values are attributed to structural and molecular weight changes in the polymer brought about by the thermal treatment that the polymer sample undergoes during the process of T_g measurements. It was shown earlier that 50 min isothermal decompositions of PpiPrS at 373°K increase its $\overline{M}_w$ and $\overline{M}_n$ values (See Table 1). For low cooling rates (2.5°K/min), the approximate time during which the polymer sample is thermally treated in the temperature range 300-400°K is in the vicinity of 180 min (the time required to carry out T_g measurements at four heating rates). Consequently there is a greater possibility that the polymer undergoes structural changes and increases in $\overline{M}_w$ and $\overline{M}_n$ resulting in higher T_g values. At faster cooling rates (320°K/min), the increase in $\overline{M}_w$ and $\overline{M}_n$ as well as the changes in the structure of the polymer are limited because of the relatively shorter periods (25 min) of thermal treatments. With this in mind, 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.

In Fig. 13 are shown, for a polymer sample decomposed at 100°C (PpiPrS-2), typical DSC thermograms recorded in the glass transition range at various heating rates. T_g was found to increase with increasing
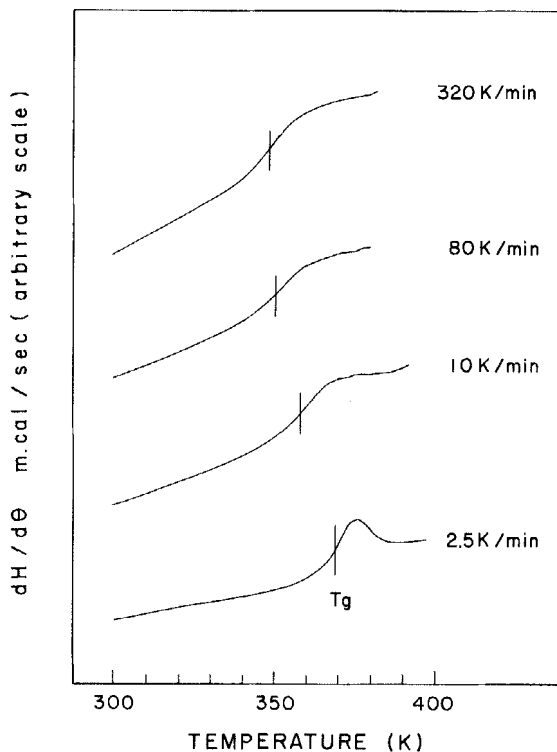
FIG. 12. Typical DSC thermograms of an undecomposed polymer
sample (PpiPrS) recorded in the glass transition region at various
cooling rates; heating rate: $40°K/min$. See Table 6 for other data.

rate of heating. For heating rates of less than $10°K/min$, T_g was
difficult to measure.

The T_g data obtained with a sample cooling rate of $320°K/min$ and
T_g heating rates of 80, 40, 20, and $10°K/min$ for the undecomposed
and a number of decomposed PpiPrS samples are summarized in
Table 7. The T_{g_e} value ($335.5°K$) of the undecomposed (PpiPrS-0)
sample is about $17°K$ less than the mean average value ($352 \pm 10°K$)
of the decomposed samples which have $\overline{M}_n$ values which are lower
than that of the undecomposed sample. Polymers PpiPrS-17,
PpiPrS-18, PpiPrS-19, PpiPrS 21, PpiPrS-22, PpiPrS-23, and PpiPrs-
15 all have $\overline{M}_n$ values of about 1.2×10^4 with $\overline{M}_w/\overline{M}_n$ ratios of 4.2,
4.8, 5.9, 8.6, 10.3, 14.8, and 22, respectively; however, their mean

TABLE 6. Effect of Thermal History on T_{g_e} Determination of an Undecomposed PpiPrS Sample

Sample cooling rate ($^\circ$K/min)	T_g at various heating rates ($^\circ$K)				T_{g_e} (1°K/min)[a]
	80°K/ min	40°K/ min	20°K/ min	10°K/ min	
320	349.5	347.0	345.0	345.0	335.5
80	351.5	348.5	347.0	347.0	337.0
40	354.5	352.0	350.0	349.0	342.5
20	357.0	353.0	352.0	-	339.5
10	360.5	357.0	357.0	356.0	351.0
5	364.5	362.0	361.0	361.0	353.0
2.5	368.5	366.5	364.0	364.0	354.5

[a]Extrapolated value at a heating rate (q) of 1°K/min by using the equation: Log q = a - (b/T_g) [8].

average T_{g_e} is 354°K. This would indicate that the T_{g_e} of the decomposed PpiPrS samples are independent of the polydispersity ($\overline{M}_w/\overline{M}_n$) ratio and that the fractions of the polymers with shorter chain lengths bring about their glass transition at about the same temperature. It could also be that the structural modification due to the increased $\overline{M}_w$ somehow compensates for the required decrease in T_g due to the higher $\overline{M}_w/\overline{M}_n$ ratios [11].

Because of the limited range of available molecular weights ($\overline{M}_n$ varying between 1.05×10^4 and 1.8×10^4) and because of the possibility that the basic structure of the different PpiPrS samples may or may not be the same, the graph of T_{g_e} as a function of $\overline{M}_n$ or $1/\overline{M}_n$ was not plotted. The overall average T_{g_e} value ($347 \pm 12^\circ$K) including values of the undecomposed and decomposed PpiPrS samples is not far removed from the value (360°K) reported in the literature [12]. An analysis of the T_{g_e} values for PS (363°K), PpMeS (364°K), PpiPrS (335.5°K), PαMeS (432°K), and PpPrαMeS (395°K) each having an $\overline{M}_n$ value of about 1.4×10^4 shows that the presence of α groups in the PS vinyl chain increases its T_{g_e} by 70°K, whereas the same groups situated on the aromatic rings have no significant effect on the T_{g_e} of PS. Furthermore, a comparison of the T_{g_e} values of PS
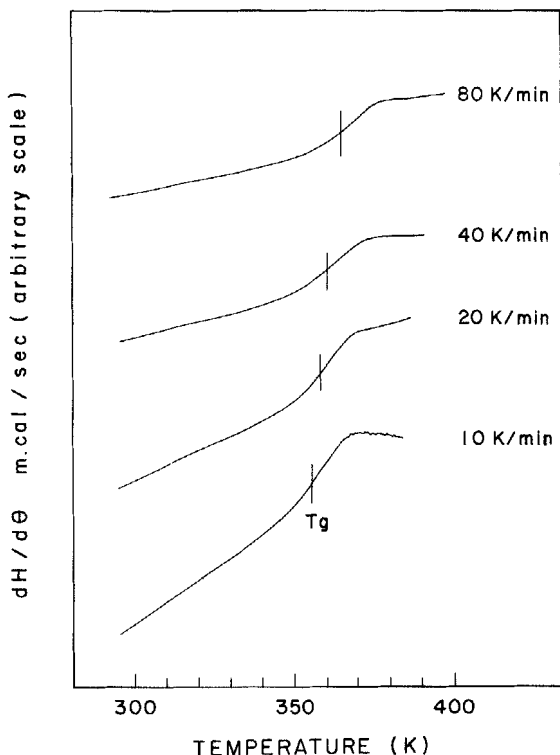
FIG. 13. Typical DSC thermograms of a decomposed polymer sample (PpiPrS-2) recorded in the glass transition region at various heating rates; cooling rate: 320°K/min. See Tables 1, 6, and 7 for other data.

with that of PpiPrS and PαMeS with that of PpiPrαMeS shows that the presence of the p-isopropyl group in the aromatic ring lowers the T_g of PS as well as that of PαMeS by about 30-35°K. This confirms earlier results [11], where it was noted that the bulkier substituent in PpiPrS increases the flexibility of the chains resulting in better chain packing and reduced steric hindrance and consequent lower T_g.

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

(1) During the isothermal decomposition of PpiPrS in the temperature range 25-150°C ($a < 3\%$), the increase in the values of $\overline{M}_w$ (GPC data) arise primarily out of inter-chain linking between the longer radical-bearing polymer molecules prior to their decomposition.

TABLE 7. Variation of T_g as a Function of Heating Rates for Undecomposed and Decomposed Samples of PpiPrS

Sample	M_n (GPC) $\times 10^{-4}$	$\overline{M}_w / \overline{M}_n$	T_g at various heating rates (°K)				T_{ge} (°K/min)
			80°K/min	40°K/min	20°K/min	10°K/min	
PpiPrS-0	1.40	3.9	349.5	347.0	345.0	345.0	335.5
PpiPrS-17	1.17	4.2	369.0	367.0	365.5	364.5	359.5
PpiPrS-18	1.18	4.8	367.0	364.0	362.0	361.0	354.0
PpiPrS-19	1.17	5.9	366.0	363.0	361.0	360.0	353.0
PpiPrS-20	1.06	8.1	363.5	361.0	359.0	358.0	351.5
PpiPrS-21	1.15	8.6	365.5	362.5	360.5	359.5	352.0
PpiPrS-22	1.18	10.3	365.5	363.0	361.0	359.5	353.0
PpiPrS-23	1.18	14.8	365.5	363.0	361.0	360.0	353.5
PpiPrS-15	1.19	22.0	365.5	363.5	361.5	360.0	354.0
PpiPrS-27	1.53	3.9	348.0	346.5	346.5	345.0	342.0
PpiPrS-28	1.47	4.2	361.5	359.0	357.0	355.5	349.0
PpiPrS-29	1.80	6.2	370.5	368.0	366.0	363.0	355.5

Similar increases in $\overline{M}_w$ for isothermal decompositions carried out at temperatures beyond $315°C$ ($\alpha > 6\%$) may, on the other hand, result from certain crosslinking reactions between the decomposed polymers themselves or in combination with the undecomposed longer polymer chains.

(2) The results of the IR and NMR analyses suggest that during the inter-chain-linking the number of iso-CH_3 groups increases. For the crosslinking reactions at $T > 315°C$, the NMR data show an increase in iso-CH_3 groups, an increase in terminal or α-CH_3 groups, and a decrease in CH_2 groups.

(3) A comparison of the activation energies of decomposition for various homologs of PS with similar $\overline{M}_n$ reveals the following:

$$E_{PS} > E_{PpiPrS} > E_{PpiPr\alpha MeS} \geq E_{P\alpha MeS}.$$

(4) A comparison of the T_{g_e} values of PS and PpiPrS and those of PαMeS and PpiPrαMeS shows that the presence of the p-isopropyl groups in the aromatic rings lowers T_g with respect to PS as well as that of PαMeS by about 30-$35°K$. This supports the earlier conclusions [11] that the bulkier substituent in PpiPrS increases the flexibility of the chains which results in better packing and lower steric hindrance and consequent lowering in the T_g values.

Further studies on the effects of other substituents, e. g., p-bromo, p-chloro, p-methoxy, and p-tert-butyl on the thermal decomposition of PS as well as on T_{g_∞} are under way and will be reported on in due course.

ACKNOWLEDGMENTS

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