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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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

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To cite this Article Malhotra, S. L. , Baillet, C. , Lam-tran, H. H. and Blanchard, L. P.(1978) 'Thermal Decomposition of Poly-p-isopropyl- α -methylstyrene', Journal of Macromolecular Science, Part A, 12: 1, 103 – 127

To link to this Article: DOI: 10.1080/00222337808081024

URL: <http://dx.doi.org/10.1080/00222337808081024>

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Thermal Decomposition of Poly-p-isopropyl- α -methylstyrene

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ABSTRACT

Kinetic studies on the decomposition of poly-p-isopropyl- α -methylstyrene samples with molecular weights ranging from 1.2×10^4 to 6.9×10^5 were carried out with the differential thermogravimetric technique. Changes in molecular weight distributions, at different temperatures, were studied by gel-permeation chromatography. The results show that the mechanism responsible for the decomposition is that of depolymerization. The order of the reaction was found to be one. The activation energy for the decomposition of polymer samples of series S (which are less branched in structure) decreases with increasing molecular weight. For the more branched samples of series F, the activation energy remains essentially constant with increasing molecular weight. For identical molecular weights, samples of series F require a

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a lower activation energy than do samples of series S. The proportions of the three steric forms, viz., isotactic, heterotactic, and syndiotactic, in the polymer, both before and after thermal treatments, did not change, suggesting that stereoregularity has no apparent effect on the decomposition of poly-*p*-isopropyl- α -methylstyrene.

INTRODUCTION

Studies related to kinetics, to gel-permeation chromatographic (GPC) molecular weight distribution changes and to the effects of stereoregularity on the thermal decomposition of polystyrene (PS) [1] and of poly- α -methylstyrene (P α MS) [2] have been reported on earlier from this laboratory. It was noticed that in order to obtain identical weight losses during the thermal decomposition of PS and P α MS of equal molecular weights, a lower temperature and a lower activation energy were required for the P α MS material. Furthermore, in the case of P α MS the mechanism of decomposition involved solely "depolymerization" while in the case of PS both random scissions and depolymerization were jointly responsible for the decomposition. The order of the reaction for the depolymerization mechanism involved in both studies was found to be one.

In the case of P α MS, the triad intensities due to the α -methyl groups, both before and after thermal treatments, remained unchanged, suggesting that there was no apparent influence of stereoregularity on the decomposition of this polymer. It should be mentioned here that in the decomposition of PS [1], various components of a sample having the same weight-average molecular weights (\bar{M}_w) decomposed at different temperatures, and consequently it was speculated that these may have different steric structures. In order to reconfirm such observations and to explore the effects of other substituents on the kinetics and on GPC molecular weight distribution changes, studies were carried out on the thermal decomposition of poly-*p*-isopropyl- α -methylstyrene (PPIP α MS). The results obtained are discussed in the present communication.

EXPERIMENTAL

Materials

Anionically prepared [3, 4] PPIP α MS samples [5] showing unimodal GPC molecular weight distributions and having \bar{M}_w ranging

from 1.2×10^4 to 6.9×10^5 were used in the present study. The PPIP α MS samples of series S were prepared in bulk at -25°C with a butyllithium-tetramethylethylenediamine complex. Those of series F were polymerized at 25°C with an Na-K alloy [3]. Calibration of the GPC instrument was performed with low polydispersity ($\overline{M}_w/\overline{M}_n$) PPIP α MS samples for which \overline{M}_w were calculated from light scattering data [4]. The tacticities of these polymers were calculated from their nuclear magnetic resonance (NMR) spectra recorded in *o*-dichlorobenzene at 100°C with tetramethylsilane as the internal standard [6].

Apparatus

A Perkin-Elmer TGS-1 thermogravimetric scanning balance and a Perkin-Elmer model DSC-2 differential scanning calorimeter were used in the present study [2].

Analyses of the PPIP α MS samples, both before and after decomposition, were carried out with a Waters Associates model 200 GPC [2]. Molecular weights were then computed by the summation method as suggested by the supplier [7].

RESULTS AND DISCUSSION

In Table 1 are summarized values of the percent weight loss α , the molecular weight \overline{M}_w , and the polydispersity \overline{P}_d ($\overline{M}_w/\overline{M}_n$), obtained both before and after the 50 min isothermal decomposition of various PPIP α MS samples. In the case of high molecular weight ($> 1.0 \times 10^5$) polymers and at high values of α , the values of \overline{M}_w decrease while those of \overline{P}_d remain unchanged during the decompositions. In the case of the remaining polymers (1.1×10^4 - 1.0×10^5), the \overline{M}_w and \overline{P}_d values do not change for all values of α .

In Fig. 1 are presented the variations of \overline{M}_w with temperature for PPIP α MS samples of series S. One notes that on heating samples for 50 min at temperatures up to 250°C , the \overline{M}_w of the polymers decrease very little. On heating beyond 250°C , some of the polymers (S-19, S-25, S-15, F-6, and S-17) show a noticeable decrease in \overline{M}_w .

In Table 2 are summarized α , \overline{M}_w , and \overline{P}_d values obtained both before and after the isothermal decomposition at 300°C of PPIP α MS samples during different periods of time. It may be noted that, except for sample F-5 whose \overline{M}_w and \overline{P}_d decreased from 2.8×10^5 to 0.93×10^5

TABLE 1. Results of 50 min Decompositions of Poly-p-isopropyl- α -methylstyrene (PPIP α MS) at Various Temperatures and the Associated Changes in GPC Molecular Weights \bar{M}_w , \bar{P}_d , Polydispersity α and Weight Loss α

Sample	Characterization index	Temperature of decomposition										
		25°C (Run 0)	150°C (Run 1)	175°C (Run 2)	200°C (Run 3)	225°C (Run 4)	250°C (Run 5)	275°C (Run 6)	290°C (Run 7)			
S-19	$\bar{M}_w \times 10^{-5}$	6.9	6.7	6.6	6.2	-	5.6	4.5	3.5			
	\bar{P}_d	4.5	4.5	4.4	4.2	-	4.1	4.0	4.0			
	α (%)	0	1.0	5.0	7.1	-	17.2	41.0	62.5			
S-25	$\bar{M}_w \times 10^{-5}$	4.3	4.2	4.1	4.1	-	4.0	3.5	2.9			
	\bar{P}_d	3.3	3.2	3.1	3.1	-	3.2	3.1	3.1			
	α (%)	0	4.1	6.5	7.9	-	13.0	25.0	46.0			
S-15	$\bar{M}_w \times 10^{-5}$	2.8	2.8	2.9	3.1	3.0	2.7	2.4	2.0			
	\bar{P}_d	4.1	4.0	4.3	4.0	3.9	4.0	4.3	4.2			
	α (%)	0	1.3	3.9	5.6	6.0	11.0	23.3	36.2			
F-5	$\bar{M}_w \times 10^{-5}$	2.8	-	-	3.8	4.0	3.4	2.9	2.3			
	\bar{P}_d	3.9	-	-	5.9	6.0	5.2	4.7	4.0			
	α (%)	0	-	-	4.3	5.0	6.3	13.3	30.3			
F-6	$\bar{M}_w \times 10^{-5}$	1.56	-	-	-	1.56	1.43	1.30	0.94			
	\bar{P}_d	3.3	-	-	-	4.4	4.0	3.7	3.3			
	α (%)	0	-	-	-	4.4	6.8	12.8	33.7			

S-17	$\bar{M}_w \times 10^{-4}$	9.3	-	-	11.0	10.0	10.6	8.7	8.0
	\bar{P}_d	2.7	-	-	2.4	2.7	2.6	2.7	2.7
	α (%)	0	-	-	2.2	4.2	7.9	17.2	37.2
S-27	$\bar{M}_w \times 10^{-4}$	7.5	-	-	7.4	7.3	8.0	6.8	5.6
	\bar{P}_d	2.4	-	-	2.5	2.4	2.5	2.4	2.5
	α (%)	0	-	-	4.9	6.6	12.3	27.0	54.1
S-9	$\bar{M}_w \times 10^{-4}$	3.8	-	-	3.7	3.8	3.7	3.7	4.0
	\bar{P}_d	1.6	-	-	1.6	1.6	1.6	1.7	1.8
	α (%)	0	-	-	1.4	2.9	7.3	16.6	39.8
S-20	$\bar{M}_w \times 10^{-4}$	2.3	-	-	2.2	2.2	2.4	2.6	2.6
	\bar{P}_d	1.3	-	-	1.5	1.5	1.5	1.6	1.6
	α (%)	0	-	-	2.7	4.9	7.8	20.5	31.4
S-10	$\bar{M}_w \times 10^{-4}$	1.2	-	-	1.3	1.3	1.4	1.4	1.3
	\bar{P}_d	1.15	-	-	1.4	1.4	1.4	1.5	1.6
	α (%)	0	-	-	1.1	3.1	5.6	10.7	22.1

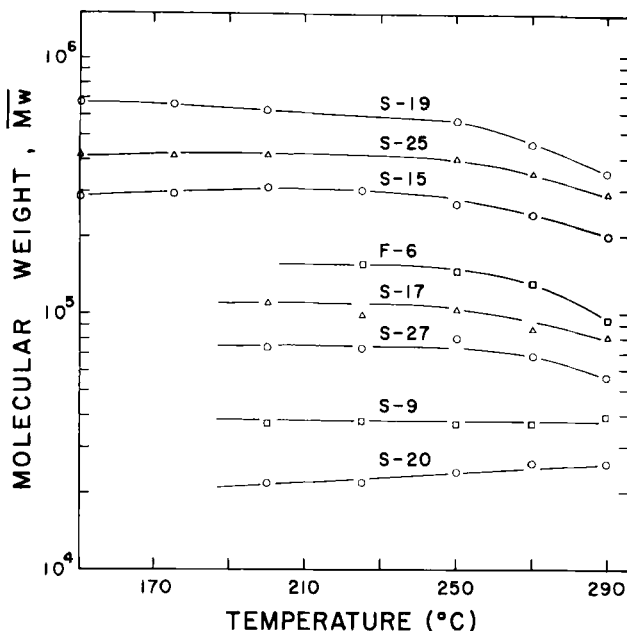


FIG. 1. Variation of molecular weight \bar{M}_w with temperature for eight poly-p-isopropyl- α -methylstyrene (PPIP α MS) samples (series S and F). See Table 1 for other data.

and from 3.9 to 2.7, respectively, at $\alpha = 70\%$, the other PPIP α MS samples ($\bar{M}_w = 1.1 \times 10^4$ to 1.56×10^5) showed no such important changes; instead, the \bar{M}_w of these polymers decreased regularly though slowly, while the \bar{P}_d values remained unchanged.

In Fig. 2 are shown the variation of \bar{M}_w in PPIP α MS samples of series S, with the volatilized fraction a , defined as the ratio of polymer mass decomposed at temperature T to its initial mass. For a values less than 0.1, \bar{M}_w does not change except in S-19, where it decreases from 6.9×10^5 to 6.2×10^5 . These results resemble those obtained in the decomposition of P α MS [2], but differ to a great extent from those found in the decomposition of PS [1] where, for comparable values of a , the \bar{M}_w decrease was 5- to 10-fold greater and sometimes even higher.

In Fig. 3 are shown the variations of \bar{M}_w with a for the PPIP α MS

TABLE 2. Isothermal Decompositions at 300° C of PPIPcMS during Different Periods and Associated Changes in \bar{M}_w , \bar{P}_d and α

Sample	Characterization index	Time of decomposition						
		0 (Run 0)	10 min (Run 8)	20 min (Run 9)	30 min (Run 10)	40 min (Run 11)	50 min (Run 12)	
F-5	$\bar{M}_w \times 10^{-5}$	2.8	-	2.3	1.5	1.0	0.93	
	\bar{P}_d	3.9	-	4.3	3.4	3.0	2.7	
	α (%)	0	-	21.0	43.9	56.9	69.7	
F-6	$\bar{M}_w \times 10^{-5}$	1.56	-	0.96	0.89	0.85	0.81	
	\bar{P}_d	3.3	-	3.5	3.6	3.3	3.7	
	α (%)	0	-	33.0	50.0	52.0	57.0	
S-17	$\bar{M}_w \times 10^{-4}$	9.3	-	10.0	9.5	7.6	6.2	
	\bar{P}_d	2.3	-	2.2	2.4	2.9	2.7	
	α (%)	0	-	23.5	34.0	58.6	70.0	
S-27	$\bar{M}_w \times 10^{-4}$	7.5	-	7.2	6.2	5.4	5.0	
	\bar{P}_d	2.4	-	2.4	2.2	2.4	2.3	
	α (%)	0	-	42.7	66.5	72.8	82.3	
F-7	$\bar{M}_w \times 10^{-4}$	6.2	5.0	5.0	4.74	4.24	3.91	
	\bar{P}_d	2.2	2.0	2.4	2.3	2.4	2.3	
	α (%)	0	14.7	26.0	34.0	44.0	53.0	

(continued)

TABLE 2 (continued).

Sample	Characterization index	Time of decomposition						
		0 (Run 0)	10 min (Run 8)	20 min (Run 9)	30 min (Run 10)	40 min (Run 11)	50 min (Run 12)	
S-9	$\bar{M}_w \times 10^{-4}$	3.8	-	4.3	4.2	4.0	3.0	
	\bar{P}_d	1.8	-	1.6	1.7	1.7	2.0	
	α (%)	0	-	22.0	30.7	48.0	68.9	
F-8	$\bar{M}_w \times 10^{-4}$	3.8	3.1	3.0	2.8	3.1	2.9	
	\bar{P}_d	2.3	2.2	2.3	2.0	2.0	2.1	
	α (%)	0	11.9	19.8	28.5	34.0	40.5	
S-20	$\bar{M}_w \times 10^{-4}$	2.3	-	2.3	2.2	2.5	2.3	
	\bar{P}_d	1.3	-	1.5	1.5	1.7	1.8	
	α (%)	0	-	16.8	23.3	35.0	59.5	
S-10	$\bar{M}_w \times 10^{-4}$	1.2	-	1.3	1.4	1.5	1.3	
	\bar{P}_d	1.15	-	1.2	1.2	1.3	1.3	
	α (%)	0	-	13.5	16.6	19.7	38.2	

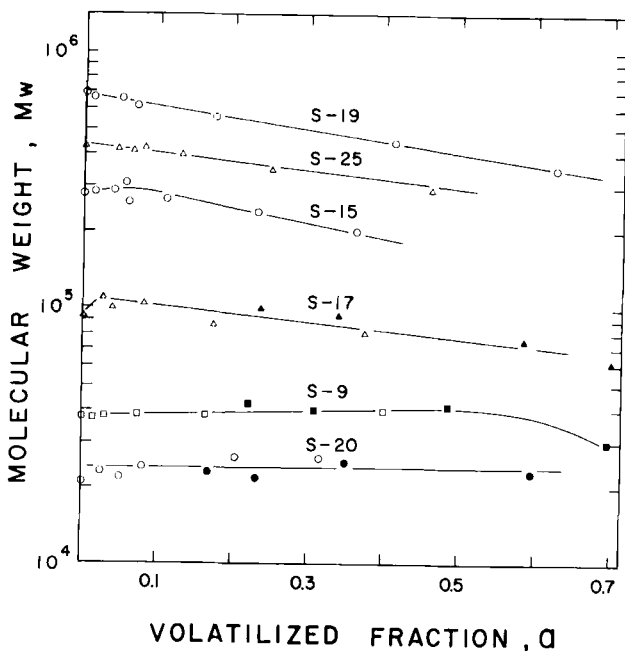


FIG. 2. Variation of \bar{M}_w with volatilized fraction α for six PPIP α MS samples (series S): (\circ , Δ , \square) data of α obtained as a function of temperature; (\bullet , \blacktriangle , \blacksquare) data of α obtained as a function of time. See Tables 1 and 2 for other data.

samples of series F. One notes that the decrease in \bar{M}_w in all of the four polymers is very gradual, even linear (except for F-8).

In order to gain some idea of the influence of substituents such as *p*-isopropyl and *p*-isopropyl plus the α -methyl group on thermal treatments, it was thought of interest to compare the results of PS, P α MS, and PPIP α MS decompositions.

Comparison of the Decompositions of PPIP α MS and P α MS

To carry out a precise comparison between these decompositions, two polymers from each study were analyzed for \bar{M}_w changes in three α value ranges: (1) less than 0.1, (2) between 0.1 and 0.2, and (3) higher than 0.2.

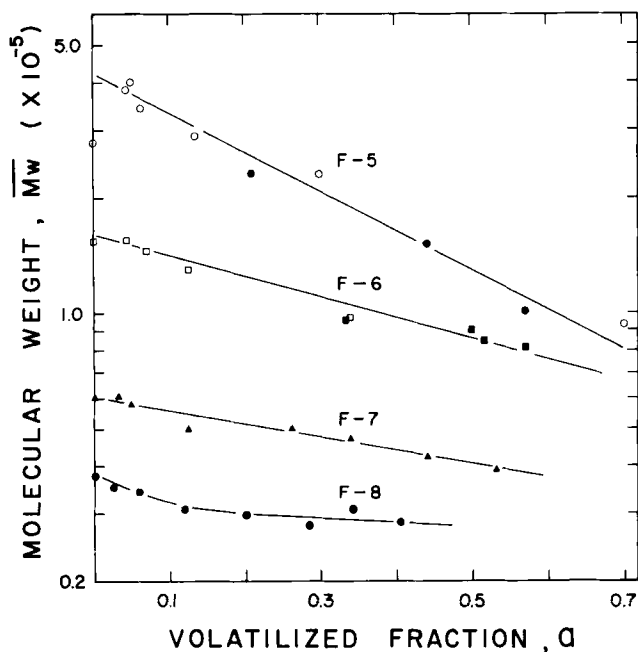


FIG. 3. Variation of \bar{M}_w with a for four PPIP α MS samples (series F): (○, □) data of a obtained as a function of temperature; and (●, ▲, ■) data of a obtained as a function of time. See Tables 1 and 2 for other data.

PPIP α MS (Sample F-6) and P α MS (Sample 5) [2]. In the case of the decomposition of sample F-6 ($\bar{M}_w = 1.56 \times 10^5$) yielding a values of 0.07, 0.13, and 0.34, isothermal heating was carried out at temperatures of 250, 275, and 290°C, respectively. The overall \bar{M}_w values of the polymer at these values of a were 1.43×10^5 , 1.30×10^5 , and 0.94×10^5 , respectively.

In the case of sample 5 ($\bar{M}_w = 1.63 \times 10^5$), for identical values of a, isothermal heating would be required at 275, 286, and 298°C with overall \bar{M}_w changing from 1.63×10^5 to 1.50×10^5 , 1.45×10^5 , and 1.35×10^5 , respectively.

PPIP α MS (Sample S-9) and P α MS (Sample M-3) [2]. In the case of the decomposition of sample S-9 ($\bar{M}_w = 3.8 \times 10^4$) yielding a values of 0.07, 0.17, and 0.40, isothermal heating was carried out at

temperatures of 250, 275, and 290°C, respectively. The overall \bar{M}_w values of the polymer at these values of a were 3.7×10^4 , 3.7×10^4 , and 4.0×10^4 , respectively.

In the case of sample M-3 ($\bar{M}_w = 4.1 \times 10^4$), for identical values of a , isothermal heating would be required at 265, 295 and 307.5°C with overall \bar{M}_w changing from 4.1×10^4 to 4.0×10^4 , 3.8×10^4 and 3.45×10^4 , respectively.

Based on these comparisons, it can be concluded that for identical values of a , in equimolecular weight polymers, the temperature of decomposition is 10 to 20°C lower for PPIP α MS than that for P α MS. The changes in \bar{M}_w with a for both polymers follow similar trends.

Comparison of the Decompositions of PPIP α MS and PS

PPIP α MS (Sample S-25) and PS (Hoechst Standard).

In the case of the decomposition of sample S-25 ($\bar{M}_w = 4.3 \times 10^5$) to a values of 0.065, 0.13, 0.25, and 0.46, isothermal heating was carried out at temperatures of 175, 250, 275, and 290°C, respectively. The overall \bar{M}_w values of the polymer at these a values were 4.1×10^5 , 4.0×10^5 , 3.5×10^5 , and 2.9×10^5 , respectively.

In the case of the decomposition of the PS [1] ($\bar{M}_w = 4.3 \times 10^5$), for identical values of a , isothermal heating would be required at 335, 360, 370, and 378°C, respectively with overall \bar{M}_w changing from 4.3×10^5 to 1.1×10^5 , 0.8×10^5 , 0.64×10^5 , and 0.44×10^5 , respectively.

PPIP α MS (Sample F-6) and PS (Pressure Chemical Standard). As mentioned above in the case of the decomposition of sample F-6 ($\bar{M}_w = 1.56 \times 10^5$) leading to a values of 0.07, 0.13, and 0.34, isothermal heating was carried out at 250, 275, and 290°C, respectively. The overall \bar{M}_w of the polymer at these values of a were 1.43×10^5 , 1.30×10^5 and 0.94×10^5 , respectively.

In the case of the decomposition of the PS [1], for identical values of a , isothermal heating would be required at 340, 358, and 368°C with overall \bar{M}_w changing from 1.6×10^5 to 0.85×10^5 , 0.68×10^5 , and 0.48×10^5 , respectively.

Based on these comparisons, it can be concluded that for identical values of a in equimolecular weight polymers, the temperature of decomposition is 70-100°C lower for PPIP α MS than that for the PS standard. Furthermore, the decreases in \bar{M}_w with a (for $a < 0.1$) are many times greater in the latter polymer.

An overall analysis of molecular weight changes associated with the decomposition of PS, P α MS, and PPIP α MS suggests that, while the mechanisms responsible for the decomposition of PS are those of random scissions and depolymerization, in the case of P α MS and PPIP α MS these decompositions are brought about by depolymerization alone.

In the earlier work [1], it was noticed on occasion that when the \bar{M}_w and \bar{P}_d changes were followed from overall results, erroneous conclusions were drawn. To avoid such conclusions in the present work and to obtain a better understanding of the decomposition process, it was decided to compare normalized GPC molecular weight distributions where the area under the GPC curves correspond to the weight of the undecomposed polymer. If one subtracts from the initial distribution curve of the undecomposed polymer the distribution curve of any subsequently decomposed polymer, one can readily visualize the changes that take place resulting from the decomposition of the higher molecular weight species.

To illustrate the above, the GPC distribution of an undecomposed PPIP α MS sample (S-19) was compared successively with those of four other samples decomposed during 50 min periods at 200, 250, 275, and 290°C, respectively. The volatilized fraction of the polymer is represented, in each case, by the area marked with vertical hash lines and the symbol (-). These same areas have, further, been converted into distributions shown in Fig. 4 in the form of dashed lines. \bar{M}_w calculations from the dashed line distributions in Fig. 4 show that on heating polymer S-19 for a period of 50 min at temperatures of 200, 250, 275, and 290°C, fractions of the polymer with a values of 0.07, 0.17, 0.41, and 0.62, respectively, and having \bar{M}_w of 1.62×10^6 , 1.31×10^6 , 8.6×10^5 , and 6.9×10^5 , respectively have disappeared.

In Fig. 5 is presented a successive comparison of the GPC molecular weight distribution of another undecomposed PPIP α MS sample (S-25) with those of three other samples decomposed during 50 min periods at 200, 250, and 290°C, respectively. It would appear that under these conditions fractions of the polymer with a values of 0.08, 0.13, and 0.46 and with \bar{M}_w of 6.6×10^5 , 6.3×10^5 , and 5.9×10^5 , respectively, have disappeared.

Based on the analyses of Figs. 4 and 5, it can be concluded that in the decomposition of the high molecular weight PPIP α MS samples (S-25 and S-19), fractions of polymer having \bar{M}_w as high as 6.6×10^5 (S-25) or even higher (1.62×10^6 , S-19) depolymerize. It may be worthwhile adding here that in the case of PS standard ($\bar{M}_w = 1.8 \times 10^6$), the mechanism of the decomposition reaction for values of a less than 0.1 was that of random scissions [1] which drastically reduced the chain lengths of the polymer. For values of a greater than

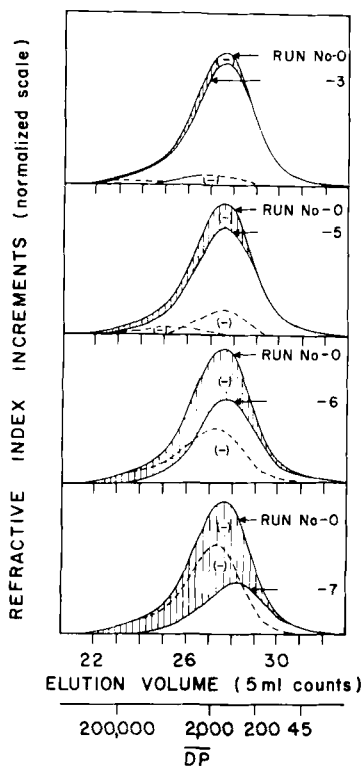


FIG. 4. Graphical method of analysis where the GPC molecular weight distribution curves are broken down into various components for the case of PPIPaMS sample S-19 subjected to 50 min isothermal treatments at different temperatures. See Table 1 for other data.

0.1, depolymerization reactions began to operate and, at a \overline{DP} (degree of polymerization) of about 300 ($\overline{M}_w = 3.5 \times 10^4$), these became the principal mode of operation. During the course of such depolymerization reactions (case of PS ($\overline{M}_w = 1.0 \times 10^4$) [1]), it was noted that the maxima in the GPC molecular weight distributions of both undecomposed and decomposed (a values as high as 0.73) PS did not change, and their \overline{M}_w values remained constant. These results are somewhat different from the depolymerization phenomenon observed in the present study, where the GPC maxima do vary (Fig. 4 and 5) and the fractions of polymer possessing higher \overline{M}_w depolymerize earlier

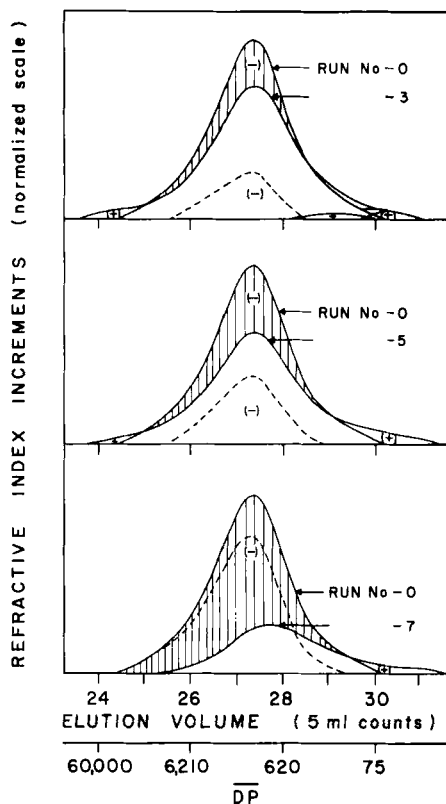


FIG. 5. Graphical method of analysis where the GPC molecular weight distribution curves are broken down into various components for the case of PPIP α MS sample S-25 subjected to 50 min isothermal treatments at different temperatures. See Table 1 for other data.

than do those of lower \bar{M}_w . To find the critical \bar{M}_w where the depolymerization reaction in the decomposition of PPIP α MS resembles that of PS, PPIP α MS samples with lower \bar{M}_w were subjected to various isothermal treatments. In Figs. 6 and 7 are shown the normalized GPC molecular weight distributions of undecomposed and decomposed polymer samples S-15 ($\bar{M}_w = 2.8 \times 10^5$) and F-6 ($\bar{M}_w = 1.56 \times 10^5$), respectively. It may be noted that the GPC maxima in these depolymerizations do change slightly. In the case of S-15, for a values of 0.11, 0.23, and 0.36, polymer fractions having overall \bar{M}_w of 3.6×10^5 ,

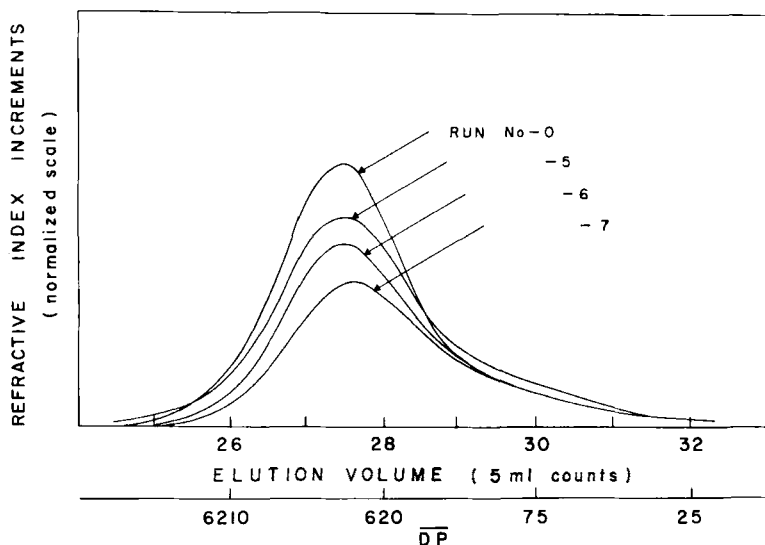


FIG. 6. GPC molecular weight distributions of PPIP α MS sample S-15 subjected to 50 min isothermal treatments at different temperatures. See Table 1 for other data.

4.1×10^5 , and 4.2×10^5 depolymerize completely. In the case of F-6, for a values of 0.04, 0.13, and 0.34, the polymer fractions having overall \bar{M}_w of 3.3×10^5 , 3.3×10^5 , and 2.8×10^5 depolymerize completely.

From these analyses (Table 1) it would appear that the critical \bar{M}_w for the PS type depolymerization in PPIP α MS samples is lower than 1.56×10^5 . Isothermal treatments at various temperatures on PPIP α MS samples of \bar{M}_w lower than 1.56×10^5 , viz., S-17 (0.93×10^5), S-27 (0.75×10^5), S-9 (0.38×10^5), S-20 (0.23×10^5), and S-10 (0.11×10^5) revealed (see Table 1) that the absolute value (for values of α ranging from 0 to 0.4) of the critical \bar{M}_w for PS type depolymerization in the case of PPIP α MS is 0.4×10^5 , although for values of α of about 0.2 the results of S-17, S-27, and S-9 decompositions can also be fitted to a PS-type depolymerization. It should be added that in the case of P α MS the critical \bar{M}_w was also 0.4×10^5 (samples M-3, M-9 [2]) although for values of $\alpha < 0.1$, this value could be stretched to 1.0×10^5 .

In order to explore further this critical \bar{M}_w , isothermal decompositions were carried out at 300°C on various PPIP α MS samples for

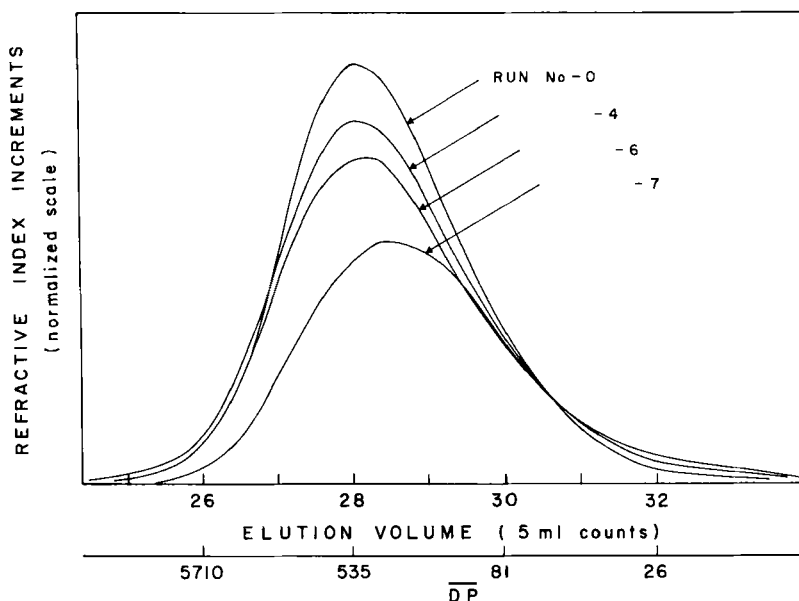


FIG. 7. GPC molecular weight distributions of PPIP α MS sample F-6 subjected to 50 min isothermal treatments at different temperatures. See Table 1 for other data.

different periods of time and the results of these studies are presented in Table 2. One notes that the absolute critical \bar{M}_w value in this table is that of PPIP α MS sample S-20 ($\bar{M}_w = 2.3 \times 10^4$). This clearly demonstrates that the critical \bar{M}_w value is arbitrarily dependent upon the conditions of decomposition. This is supported further by the normalized GPC molecular weight distributions of undecomposed and decomposed PPIP α MS (samples F-6 and F-7) shown in Figs. 8 and 9.

An analysis of the curves reveals that in the case of sample F-6, isothermal treatments at 300°C for 20, 30, 40, and 50 min periods give a values of 0.33, 0.50, 0.52, and 0.57, respectively, whereas the respective fractions of sample F-6 which depolymerize between 0-20, 20-30, 30-40, and 40-50 min periods have \bar{M}_w values of 2.8×10^5 , 1.2×10^5 , 1.0×10^5 , and 1.0×10^5 , thus yielding a critical \bar{M}_w value of about 1.0×10^5 . In the case of sample F-7, isothermal treatments at 300°C for 20, 30, 40, and 50 min give a values of 0.26, 0.34, 0.44, and 0.53, respectively, whereas the respective fractions of sample

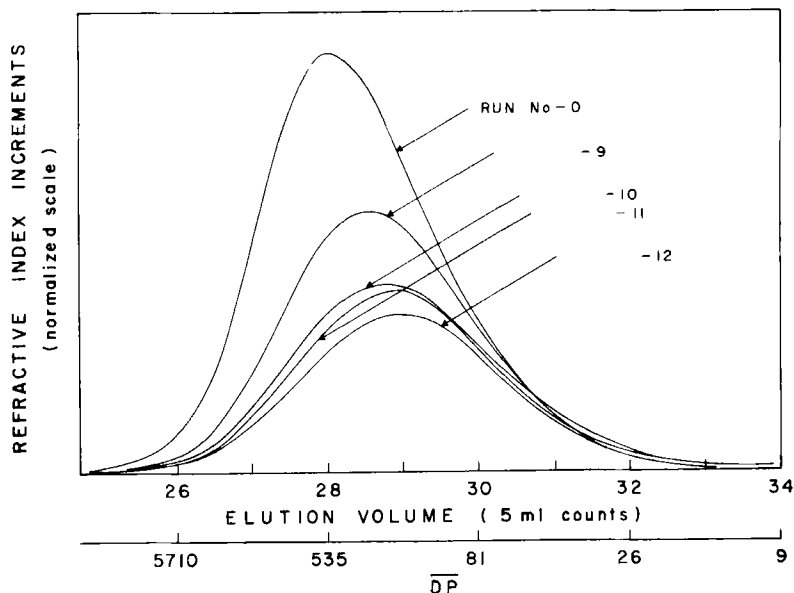


FIG. 8. GPC molecular weight distributions of PPIP α MS sample F-6 subjected at 300°C to isothermal treatments for different periods of time. See Table 2 for other data.

F-7 which depolymerize in 0-20, 20-30, 30-40, and 40-50 min have \bar{M}_w values of 1.0×10^5 , 0.76×10^5 , 0.71×10^5 and 0.6×10^5 , thus yielding a critical \bar{M}_w value of $0.6-0.7 \times 10^5$.

Different critical \bar{M}_w values for various PPIP α MS samples could also originate from the structural and configurational differences in these polymers. In an earlier study on the glass transition temperatures of PPIP α MS [5] it was shown that the structure of most of the polymers used does not correspond to that of the regular PPIP α MS whose different protons, viz., benzene, methine, β -methylene, iso-methyl and α -methyl bear a ratio of 4:1:2:6:3. The discrepancies in structure of polymers belonging to the same series were, however, of a similar nature and thus their influence on thermal decompositions is hard to correlate. PPIP α MS samples S-15 ($\bar{M}_w = 2.8 \times 10^5$) and F-5 ($\bar{M}_w = 2.8 \times 10^5$) originating from different series do show different patterns of α and \bar{M}_w changes during the course of their thermal decompositions because of their structural differences. In an earlier

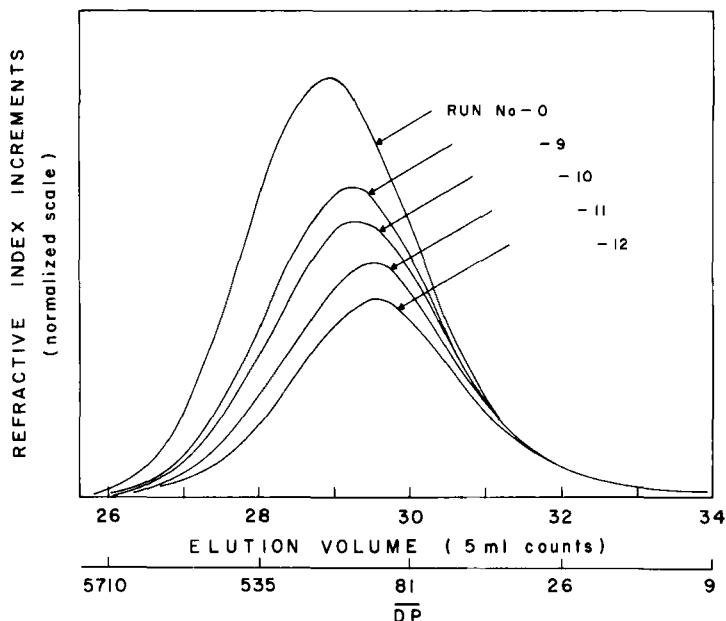


FIG. 9. GPC molecular weight distributions of PPIP α MS sample F-7 subjected at 300°C to isothermal treatments for different periods of time. See Table 2 for other data.

study [4], PPIP α MS sample F-5 was shown to be more branched than sample S-15.

Effect of Polymer Stereoregularity on Decomposition

To verify the effect of polymer stereoregularity on the decomposition of PPIP α MS, two polymers, S-15 and F-6 (same stereoregularity as that of F-5 [5]), were selected. The NMR analyses of these polymers presented in Table 3 showed that they carry different proportions of the three steric configurations, viz., isotactic, heterotactic, and syndiotactic, and are not 100% of one or the other. In Fig. 10 are shown the NMR spectra of undecomposed (S-15-0) and decomposed PPIP α MS (S-15-4 to -7) and in Fig. 11 are presented the NMR spectra of undecomposed (F-6-0) and decomposed PPIP α MS (F-6-4 to -7) samples. Based on these spectra, in Table 3 are presented structural and configurational analyses both before and after thermal decomposition.

TABLE 3. Structural and Configurational Analyses before and after Thermal Decomposition of PPIPcMS Samples S-15 and F-6

Sample	Decomposition temperature (°C)	True weight loss α (%)	Molecular weight (GPC) $M_w \times 10^{-3}$	Structure of polymer before and after decomposition ^a				Intensity of triads due to α -methyl groups ^b				Propagation statistics		
				-CH	-CH ₂	H ₃ C	CH	-CH ₃	(α)	mm	mr		rr	P
S-15-0	25	0.0	283	1.1	2.2	5.3	3.3	0.18	0.41	0.41	0.53	0.33		
S-15-3	200	5.6	311	1.1	2.2	5.3	3.3	0.17	0.41	0.42	0.55	0.30		
S-15-4	225	6.0	257	1.05	2.2	5.4	3.25	0.18	0.40	0.42	0.51	0.32		
S-15-5	250	11.0	267	1.0	2.1	5.4	3.3	0.17	0.41	0.42	0.55	0.30		
S-15-6	275	23.3	241	0.95	2.2	5.7	3.15	0.17	0.41	0.42	0.55	0.30		
S-15-7	290	36.2	200	1.0	2.1	5.5	3.4	0.17	0.41	0.42	0.55	0.30		
F-6-0	25	0.0	156	1.0	2.3	5.7	3.1	0.15	0.40	0.45	0.57	0.31		
F-6-4	225	4.4	156	1.0	2.3	5.3	3.3	0.15	0.40	0.45	0.57	0.31		
F-6-5	250	6.8	143	1.0	2.3	5.4	3.2	0.16	0.39	0.45	0.54	0.30		
F-6-6	275	12.8	158	1.1	2.3	5.4	3.2	0.15	0.40	0.45	0.57	0.31		
F-6-7	290	33.7	94	1.0	2.4	5.5	3.1	0.16	0.39	0.45	0.54	0.30		

^a Benzene protons have not been considered.
^b Data of Leonard and Malhotra [6].

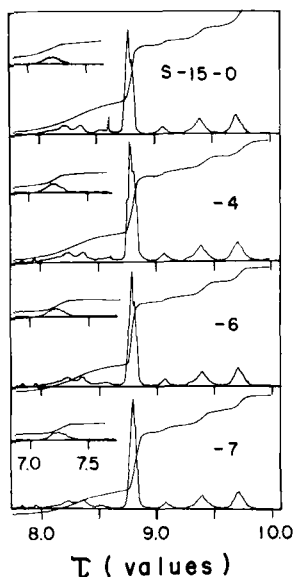


FIG. 10. NMR spectra of undecomposed and decomposed samples of PPIP α MS (S-15). See Tables 1 and 3 for other data.

One notes that PPIP α MS samples S-15 ($m = 0.18$, $m_r = 0.41$, and $r_r = 0.41$) and F-6 ($m = 0.15$, $m_r = 0.40$, and $r_r = 0.45$) show more or less the same triad intensities, both before and after the thermal decompositions. Furthermore, the structure of these polymers, both before and after the decompositions, remain more or less the same. This suggests that in the case of the PPIP α MS samples ($P_{m/r} = 0.53$ or 0.57 and $P_{r/m} = 0.33$ or 0.31 , respectively, the influence of stereoregularity on decomposition is negligible.

Decomposition Kinetics

In dynamic thermogravimetry, the rate law for the decomposition of polymer may be expressed as:

$$da/dT = (k/q)f(a) \quad (1)$$

where a is that fraction of the polymer which is volatilized and is defined as the ratio of polymer mass decomposed at a temperature T to

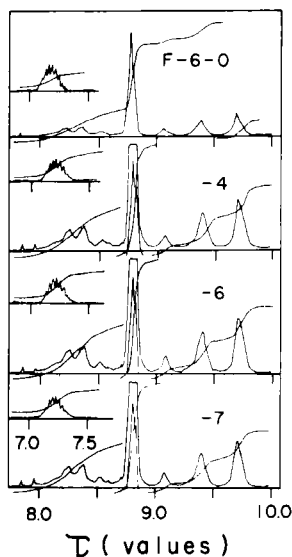


FIG. 11. NMR spectra of undecomposed and decomposed samples of PPIP α MS (F-6). See Tables 1 and 3 for other data.

its initial mass; $f(a)$ is a function of a ; q is the heating rate (in $^{\circ}\text{C}/\text{min}$), and k is the rate constant.

For decompositions where weight loss is due primarily to a depolymerization reaction, as in the present case, $f(a)$ has the following form:

$$f(a) = (1 - a)^n \quad (2)$$

where n is the order of the reaction. Substituting this in Eq. (1), one obtains:

$$da/(1 - a)^n = (k/q)dT \quad (3)$$

Coats and Redfern [8, 9] have suggested that if $\int_0^a [da/(1 - a)^n]/T^2$ is plotted as a function of $1/T$ for different values of n , that value of n which yields a straight line may be used to compute the value of the activation energy.

In Figs. 12 and 13 are shown dynamic thermogravimetric curves for PPIP α MS series S and series F, respectively. The polymers had

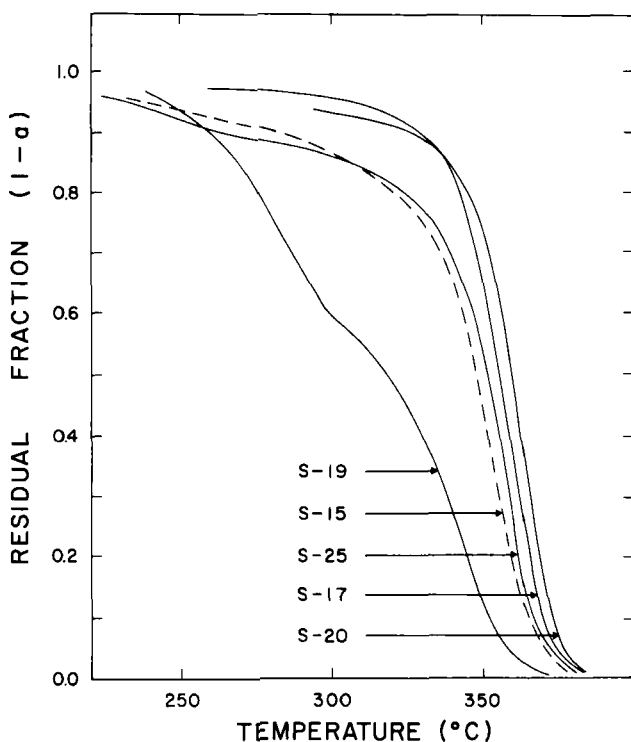


FIG. 12. Influence of molecular weight on the dynamic thermogravimetric decomposition of PPIP α MS samples (series S) heated at a rate of 20°C/min. See Tables 1 and 4 for other data.

molecular weights \bar{M}_w ranging from 1.0×10^4 to 1.53×10^5 and were subjected to a heating rate of 20°C/min, the initial mass of polymer being 2 mg in all cases. The curves indicate that the higher the molecular weight of the polymer, the lower is the temperature required to achieve 100% decomposition. For identical molecular weights, PPIP α MS samples of series S achieve 100% decomposition at a lower temperature than that required for the samples of series F. By using the method of Coats and Redfern [8, 9], activation energies were calculated and are presented in Table 4. For most of the polymers studied, an order of reaction of one was found to yield straight lines. This is in agreement with what had been observed earlier in the case of the decomposition of PS [1] and P α MS [2], where the depolymerization mechanism also followed first-order kinetics. As it was sometimes difficult to choose between zero and one for the

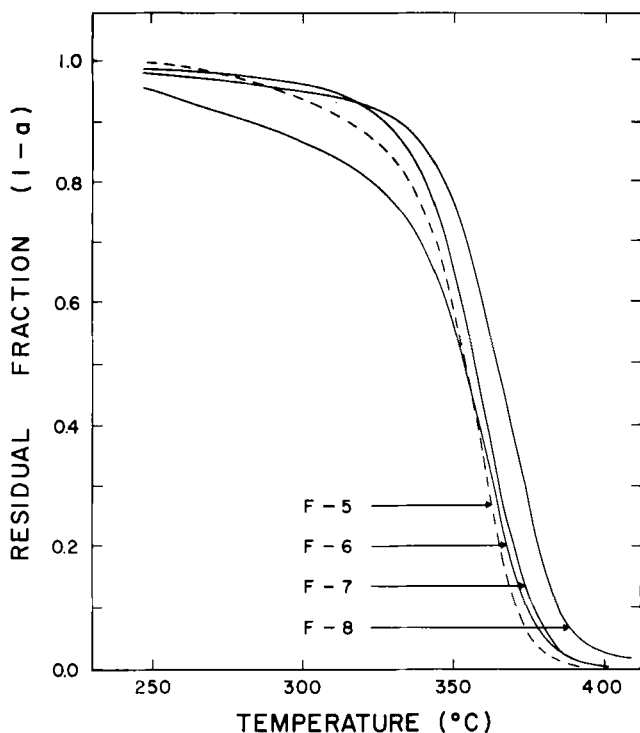


FIG. 13. Influence of molecular weight on the dynamic thermogravimetric decomposition of PPIPaMS samples (series F) heated at a rate of $20^{\circ}\text{C}/\text{min}$. See Tables 1 and 4 for other data.

order of reaction, activation energies were calculated for both values of n . The results in Table 4 indicate that for PPIPaMS samples of series S the activation energies decrease with increasing molecular weight, whereas for those of series F activation energies remain constant, except in the case of F-6 where the value is somewhat lower. For identical molecular weights, PPIPaMS samples of series F have lower activation energies than those associated with the samples of series S. A comparison of the results obtained in the present work with those obtained in the case of PS and PaMS reveals that the activation energies associated with PaMS and PPIPaMS are of the same order of magnitude while those for PS are considerably higher. It would appear that α -methyl and p -isopropyl groups facilitate the formation of radicals which bring about the depolymerization reaction and consequently the lowering of the activation energy involved.

TABLE 4. Activation Energy as a Function of Molecular Weight^a

Sample	Molecular weight $\bar{M}_n \times 10^{-3}$	Activation energy (kcal/mole)	
		For $n = 0^b$	For $n = 1^b$
S-8	12	30.2	-
F-8	16	-	49.5
S-20	18	50.5	63.7
S-9	24	-	61.4
F-7	30	-	52.4
S-27	32	-	64.1
S-17	40	-	60.0
F-6	47	21.0	41.0
S-15	68	30.5	56.4
F-5	70	-	50.9
S-25	130	30.2	43.5
S-19 ($a < 0.4$)		24.2	24.1
S-19 ($a > 0.4$)	153	11.9	30.9

^aMethod of Coats and Redfern [8, 9].

^b n is the order of reaction.

The principal conclusions to be drawn from this study, keeping in mind the results obtained in the PS and P α MS decompositions, may be outlined as follows. To obtain identical weight losses during the isothermal decomposition of equimolecular weight samples of PS, P α MS, and PPIP α MS, the temperature required follows the order: PS > P α MS > PPIP α MS. As in P α MS, the mechanism responsible for the decomposition of PPIP α MS is that of depolymerization, whereas random scissions and depolymerization jointly play a role in the case of PS. The depolymerization reaction in the decomposition of PPIP α MS is that of depolymerization, whereas random scissions and depolymerization jointly play a role in the case of PS. The depolymerization reaction in the decomposition of PS, P α MS, and PPIP α MS follows first-order kinetics. The critical molecular weight at which the weight loss is primarily due to the PS type depolymerization

reaction in P α MS and PPIP α MS is about 4.0×10^4 . The activation energy for the decomposition of PPIP α MS is of the same order of magnitude as that for P α MS, but much lower to that of PS. The stereoregularity of the polymer has no apparent effect on the decomposition of PS, P α MS and PPIP α MS.

Further studies are in progress on the decomposition of poly(p-isopropyl- α -methylstyrene-isoprene) and will be reported on in due course.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial assistance received from the National Research Council of Canada, the Department of Education of the Government of Quebec and Laval University.

The work described in this paper forms part of the general research program undertaken by the Groupe de Recherches en Sciences Macromoléculaires at Laval University.

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Accepted by editor December, 1, 1977

Received for publication December 7, 1977