

Application of Thermogravimetric Analysis to the Thermal Decomposition of Polybutadiene

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Synopsis

Thermogravimetric analysis (TGA) has been used extensively to determine the thermal stability of polymers. The present study indicates that the isothermal decomposition of polybutadienes (PBDs) is significantly different from that in the heat mode. The isothermal decomposition of PBDs is an exothermic reaction occurring at 350°–375°C. This decomposition is shown to be rapid and temperature specific. It appears to be related to the cyclization reaction reported previously by several investigators. Decomposition of PBDs in the heat mode (10°C/min) occurs at 447°–461°C. This is about 100°C higher than that observed in the isothermal mode. Further TGA experiments indicate that a period of slow heating stabilizes PBD and can eliminate the exothermic decomposition at about 360°C. This stabilization appears to be related to the ease with which both 1,2- and 1,4-PBDs thermally crosslink. Heating 1,4-PBD for 6 min at 270°C gives rise to 92% gel. 1,2-PBD is shown to crosslink more extensively. It is shown that polymers which do not thermally crosslink or cyclize, such as polystyrene, decompose similarly in the two modes of heating.

INTRODUCTION

Thermogravimetric analysis (TGA) has been used extensively to determine the thermal stability of polymers. The present study indicates that the isothermal decomposition of butadiene polymers is significantly different from that in the heat mode. Experiments have been carried out which indicate the speed with which polybutadiene (PBD) crosslinks as well as the nature of its decomposition.

EXPERIMENTAL

Polymers investigated in this study include polystyrene (Styron 680, Dow); 1,4-PBDs (Diene 35 and 55, Firestone; Taktene 1202, Polysar); and 1,2-PBD (Philprene 1217, Phillips).

Experiments were carried out on du Pont 951 thermogravimetric analyzer. Analysis included four types of TGA experiments: heat mode; isothermal mode; isothermal mode with accompanying temperature changes recorded; and the isothermal decomposition of preheated samples.

TGA in the heat mode measures the loss of weight as a function of temperature. The samples were heated in nitrogen (50 cc/min) from room temperature to 600°C at 10°C/min. The decomposition temperature was determined from the intersection of the tangents drawn to the lines before and after the major initial weight loss.

TGA in the isothermal mode measures the loss of weight as a function of time at a constant temperature. The furnace was preheated to 315°–400°C and the

sample introduced from ambient conditions. The actual sample temperature varied 20°–50°C above the programmed temperature. Experiments were run in nitrogen and in air. The percent residue after 2 min of isothermal heating was recorded.

Use of a two-pen recorder permitted the determination of the change in sample temperature accompanying a weight loss in the isothermal mode. This gave an indication whether a decomposition was exothermic or endothermic. The change in temperature per milligram of sample was recorded.

The preheat experiment consisted of heating the samples at 10°C/min to temperatures ranging from 245° to 350°C. The sample was then cooled and inserted into a furnace at 360°C. The preheat treatment was carried out in nitrogen; the isothermal heating was run in nitrogen and in air (50 cc/min). The percent residue remaining after 2 min of isothermal heating was plotted against the temperature to which the sample was preheated.

Thermal crosslinking of PBD rubber was carried out in a Perkin-Elmer differential scanning calorimeter. PBDs (55% *trans*-1,4 and 77% 1,2) were heated in nitrogen at 250°–270°C from 0.1 to 20 hr. Gel content and equilibrium weight swelling index were determined in toluene.

RESULTS

Data in Table I indicate that PBDs, when heated at 10°C/min, decompose between 447° and 461°C, with the 1,4-PBDs decomposing earlier than 1,2-PBD. A typical heat curve for predominantly 1,2-PBD (Fig. 1) indicates that its thermal decomposition occurs in a single step at a high temperature, similar to that of polystyrene (Fig. 2).

When PBD (77%, 1,2) is heated isothermally at 320°C (actual sample temperature is 340°C), no decomposition occurs in the first 10 min. After 2 min of heating at 325°C (sample temperature is 350°C), 35% of the sample volatilizes. Isothermal decomposition of 1,2-PBD occurs 100°C below the decomposition temperature in the heat mode (461°C).

The isothermal decomposition of 1,4-PBDs is also rapid and temperature specific (Fig. 3). They decompose isothermally at temperatures 25°C above that for the 1,2-PBD.

Isothermal heating of polystyrene at 370°C (sample temperature is 400°C, 5°C above the decomposition temperature in the heat mode) causes only 2% to volatilize in the first 2 min. Although polystyrene and PBD display similar decomposition curves in the heat mode, their isothermal modes of decomposition are significantly different.

When PBD (55% *trans*-1,4) is heated isothermally at 370°C, weight loss occurs

TABLE I
Thermogravimetric Analysis of Polybutadiene in the Heat Mode^a

Sample	Structure	Decomposition temperature, °C
Diene 55	55% <i>trans</i> -1,4	447
Taktene 1202	98% <i>cis</i> -1,4	455
Philprene 1217	77% 1,2	461

^a Nitrogen; 10°C/min.

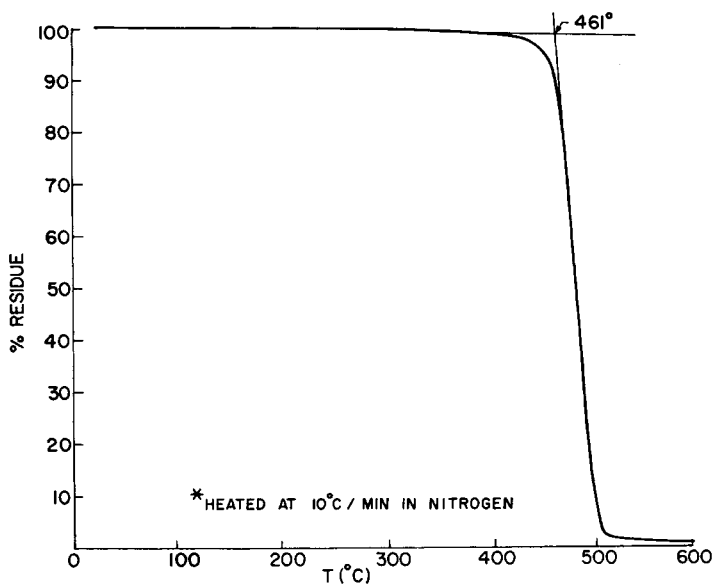


Fig. 1. Thermal degradation of polybutadiene (77% 1,2) heated at 10°C/min in nitrogen.

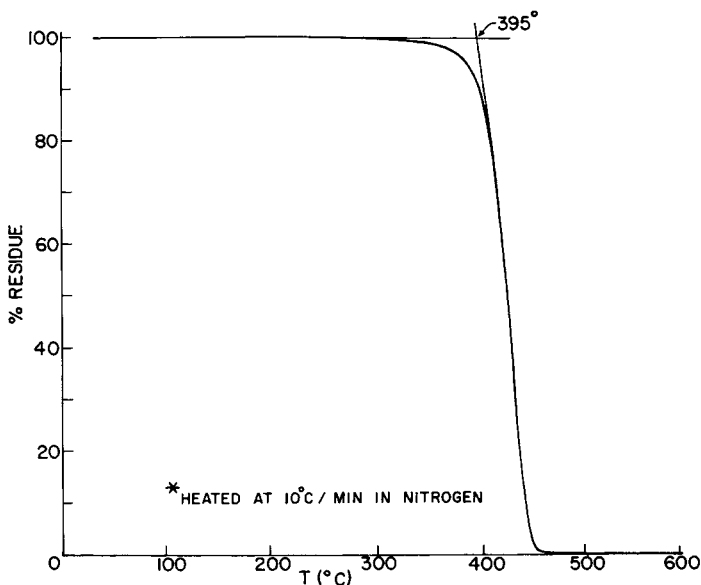


Fig. 2. Thermal degradation of polystyrene heated at 10°C/min in nitrogen.

when the sample temperature reaches 397°C, at which time the temperature increases 15°C (Fig. 4). Data in Table II indicate that PBDs with different microstructures undergo an exothermic decomposition as well. The decomposition of *cis*-1,4-PBD causes the greatest amount of volatilization but is the least exothermic.

When PBD (55% *trans*-1,4) is heated at 10°C/min to just below its decomposition temperature in the heat mode (447°C) and then inserted into a furnace held isothermally at that temperature, no exotherm is observed with weight loss. It appears that the decomposition in the heat mode occurring at ~450°C is an

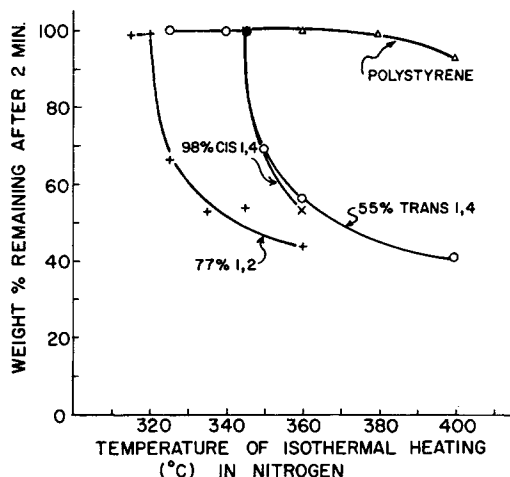


Fig. 3. Effect of temperature on the isothermal degradation of butadiene rubbers and polystyrene: (O) 55% *trans*-1,4 PBD; (X) 98% *cis*-1,4-PBD; (+) 77% 1,2-PBD; (Δ) polystyrene.

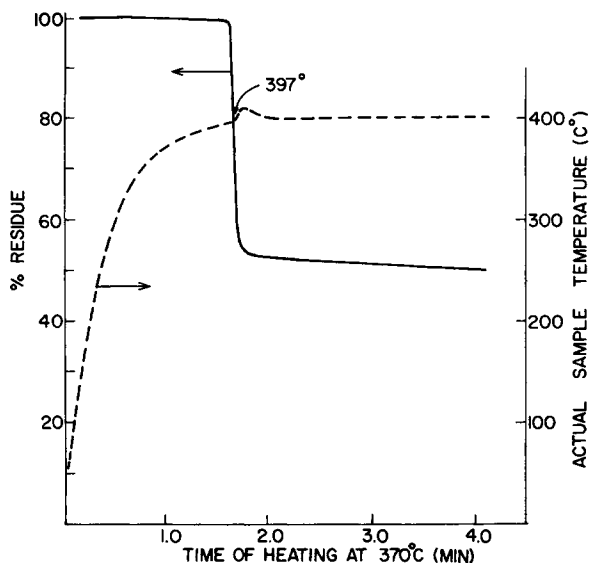


Fig. 4. Isothermal degradation of polybutadiene (55% *trans*-1,4) in nitrogen.

endothermic depolymerization, in contrast to the exothermic decomposition observed in the isothermal mode at $\sim 355^\circ\text{C}$.

These data indicated that a slow period of heating ($10^\circ\text{C}/\text{min}$) stabilizes PBD (55% *trans*-1,4) to the exothermic decomposition at $\sim 355^\circ\text{C}$. To examine this observation further, the effect of preheating PBD (77% 1,2) on its isothermal decomposition was studied.

Isothermal heating of PBD (77% 1,2-PBD) at 360°C causes 58% to volatilize in nitrogen and 65% in air (after 2 min). This is an exothermic decomposition, as previously described. If the sample is heated at $10^\circ\text{C}/\text{min}$ to above 250°C , cooled, and then heated isothermally at 360°C , the amount of weight loss in nitrogen is decreased (Fig. 5). If the sample is preheated at $10^\circ\text{C}/\text{min}$ to 350°C ,

TABLE II
Thermogravimetric Analysis of Polybutadiene in the Isothermal Mode

Sample	Sample temperature at decomposition, °C	$\Delta T/\text{mg}$ sample, ^a °C	% residue after initial weight loss
55% <i>trans</i> -1,4-PBD	397	+0.352	45.0
98% <i>cis</i> -1,4-PBD	397	+0.238	37.5
77% 1,2-PBD	357	+0.414	43.2

^a Sample weights ~65 mg.

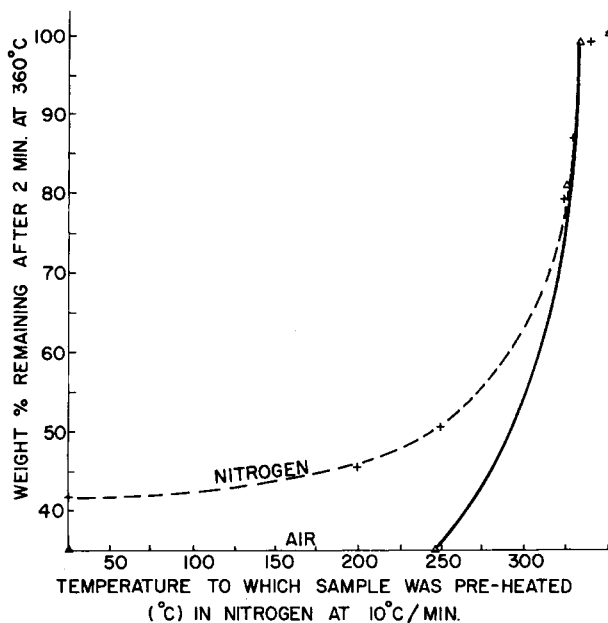


Fig. 5. Effect of preheating on the thermal degradation of polybutadiene (77% 1,2) at 360°C. (— + —) isothermal degradation in nitrogen; (— Δ —) isothermal degradation in air.

no decomposition occurs when heated isothermally at 360°C, in either nitrogen or air. It appears that the slow preheat treatment stabilizes PBD (77% 1,2) to the exothermic decomposition at ~360°C.

DISCUSSION

The thermal decomposition of PBD has been variously reported to occur in the range of 325°–470°C.¹⁻⁵ The thermal cyclization of PBD has also been reported.^{2-4,6} To describe the thermal behavior of PBD, an explanation of the decomposition in both the heat and isothermal modes, as described above, must be sought.

Cyclization has been shown through the use of infrared and NMR spectroscopy to occur upon heating PBD.^{2-4,6} Weight loss and the appearance of spectral lines relating to cyclic structures are shown to occur at ~350°C.

The exotherm accompanying weight loss in the isothermal decomposition of PBDs appears to be related to this cyclization reaction.⁵ The cyclic nature of the residue is indicated by its solubility in toluene. The decomposition of predominantly *cis*-1,4-PBD appears less exothermic because a *cis*-*trans* isomerization (an endothermic reaction) accompanies the cyclization reaction.² The lower decomposition temperature for PBD (77% 1,2) suggests that 1,2-PBD more readily undergoes cyclization.⁶ A cyclization mechanism also accounts for the stable residue formed in isothermal decomposition.

TGA in the heat mode and the preheating experiment indicate that a period of heating stabilizes both 1,2- and 1,4-PBD to the exothermic decomposition at $\sim 350^\circ\text{C}$. The decomposition of 1,4-PBD in the heat mode appears to be an endothermic depolymerization occurring at $\sim 450^\circ\text{C}$.

Data in Table III indicate that PBD (55% *trans*-1,4) begins to crosslink after only 6 min of heating at 270°C , as indicated by the formation of 92% insoluble PBD and the decreasing value of swelling index. Thus, it is reasonable to assert that the PBD has crosslinked by the time 350°C is reached in the heat mode.

Infrared data indicate that 1,2-PBD loses unsaturation upon heating more readily than the 1,4-PBDs (Table IV), in line with observations elsewhere.^{4,6} It has also been determined that 1,2-PBD more extensively crosslinks than 1,4-PBD. Heating 1,2-PBD for 1 hr at 250°C causes 99.7% gel formation (swelling index of 4.0). Similar heat treatment of 1,4-PBD gives rise to 98.3% gel and a swelling index of 6.0.

Data have been presented which indicate the nature of the exothermic decomposition of PBDs in the isothermal mode of heating. This decomposition appears to be related to the cyclization reaction. A period of slow heating has been shown to stabilize both 1,2- and 1,4-PBDs to this isothermal decomposition. This stabilization may be related to the ease of thermal crosslinking of both 1,2- and 1,4-PBDs.

TABLE III
Thermal Crosslinking of Polybutadiene (55% *trans*-1,4) at 270°C ^a

Heating time, hr	Weight swelling index
0	—
0.1	10.6
0.2	7.2
0.5	5.4
1.0	4.7
5.0	3.3
20.0	2.0

^a Heating in DSC-1; 92% gel formation at 0.1 hr.

TABLE IV
Changes in polybutadiene (55% *trans*-1,4) Microstructure Due to Thermal Crosslinking

Temperature, ^a $^\circ\text{C}$	Microstructure		
	<i>cis</i> -1,4	<i>trans</i> -1,4	vinyl-1,2
Control	34	58	8
290	15	41	1.2
310	20	30	1.1

^a Sample heated for 2 hr; control without heat treatment.

Polymers that do not thermally crosslink or cyclize, such as polystyrene, decompose similarly in the two modes of heating.

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