Effect of thermal crosslinking on decomposition of polybutadiene

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(Received 12 January 1979; revised 19 April 1979)

The high rate of thermal crosslinking below pyrolysis temperatures for polybutadienes (PBDs) of varying microstructure is shown. Thermal crosslinking of PBD affects both its dynamic mechanical properties as well as its decomposition, as measured by thermogravimetric analysis (t.g.a.). Increasing the amount of crosslinking causes less of the sample to decompose in the first step. A mechanism is proposed which qualitatively explains the relationship between crosslinking, cyclization, and depolymerization in PBD decomposition. This mechanism also explains the unusual t.g.a. behaviour previously reported for PBD.

INTRODUCTION

Thermogravimetric analysis (t.g.a.) has been used extensively to determine the thermal stability of polymers. We recently reported that polybutadiene (PBD) decomposition is significantly affected by the experimental conditions[1]. When PBD (77% 1,2) is heated isothermally at 360°C, ~50% of the sample decomposes in the first 2 min. When PBD (77% 1,2) is heated at 10°C/min, decomposition occurs at 461°C. It was shown that a slow heat treatment stabilizes the PBD to the isothermal decomposition at 360°C. It was proposed that the stabilization is related to the ease of thermal crosslinking of PBD.

The unusual decomposition behaviour of PBD has been similarly noted by Brazier and Schwartz[2]. They reported that the PBD decomposition occurs in two steps. Increasing the heating rate causes more weight loss in the first step. They further proposed that the first step is a depolymerization reaction, yielding butadiene and vinyl cyclohexane, as previously suggested by Golub[3,4]. Polymer which does not undergo depolymerization in the first step crosslinks and cyclizes, giving a residue which decomposes in the second step[1,2]. They have shown that in the temperature range of the first stage of degradation, the reactions yield an exotherm, while the second step is endothermic. Other researchers have considered microstructural changes prior to and during degradation[3–6]. Thermal crosslinking of PBD has also been reported[7–9].

The purpose of this work is to provide additional evidence for the high rate of PBD thermal crosslinking and to show the effect of this crosslinking on decomposition.

EXPERIMENTAL

Polymers used in this study include polystyrene (Styron 680, Dow); high (98%) *cis*-1,4-PBD (Taktene 1202, Polysar); (55%) *trans*-1,4-PBD (Diene 35 and 55), Firestone); and high (77%) 1,2-PBD (Philprene 1217, Phillips).

PBD samples were heat-treated in a Perkin–Elmer differential scanning calorimeter with a nitrogen purge. PBD samples were irradiated in a Van de Graaff generator at a rate of 0.25 mrad/pass in a nitrogen atmosphere. Prior to heat treatment and irradiation these samples were extracted in acetone. The gel content and dynamic mechanical properties were obtained for the treated samples. Gel and swelling index data were obtained in toluene. Swelling index is defined as wet weight/dry weight. Dynamic mechanical measurements were obtained from a Nonius torsion pendulum over the temperature range −150° to 300°C.

T.g.a. experiments were carried out on a DuPont 951 thermogravimetric analyser. The samples were heated in nitrogen (50cm^3/min) at rates of 10–100°C/min. The decomposition temperatures reported were measured using a thermocouple adjacent to the sample bucket. The samples used in the t.g.a. study were not extracted in acetone.

RESULTS AND DISCUSSION

The effect of heating PBD (55% *trans*-1,4) isothermally at 220°–330°C on the weight swelling index in toluene is given in *Figure 1*. Heating for 6 min at 330°C produces 92% gel with a swelling index of 4.6. At temperatures as low as 200°C 89% gel forms after 1 h of heating.

The effect of heat treatment on the dynamic mechanical properties of PBD is shown in *Figure 2* and *Table 1*. Thermal treatment of PBD increases the glass transition temperature (T_g) and shear modulus. Heat treatment for 2 h at 330°C shifts the T_g from −90° to 220°C. This shift occurs more rapidly than previously reported and without prevulcanization[9]. Data in *Table 1* indicate that irradiation of PBD causes considerably less crosslinking than thermal treatment as indicated by smaller shifts in the T_g and shear modulus values.

The formation of gel during programmed heat experiments was determined (*Table 2*). Heating PBD (77%, 1,2) at 10°C/min to 350°C causes 100% gel formation with less than 1% weight loss. Similar heat treatment of predominantly 1,4 PBDs gives more than 90% gel with less than 1% weight loss. Accordingly, decomposition temperatures reported from programmed heat experiments are those of crosslinked PBD.

Dow Chemical Release No B-600-007-79

0032–3861/79/091155–05$02.00

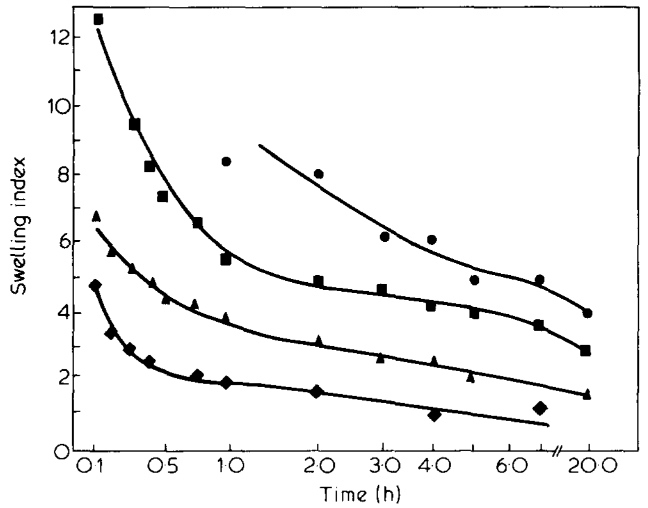

Figure 1 Thermally crosslinked polybutadiene. Diene 35 was extracted in acetone to remove antioxidant, stored under nitrogen, heat treated in DSC-1 for 0.1–20 h at 220–330°C nitrogen purge: ●, 220°C; ■, 250°C; ▲, 290°C; ◆, 330°C

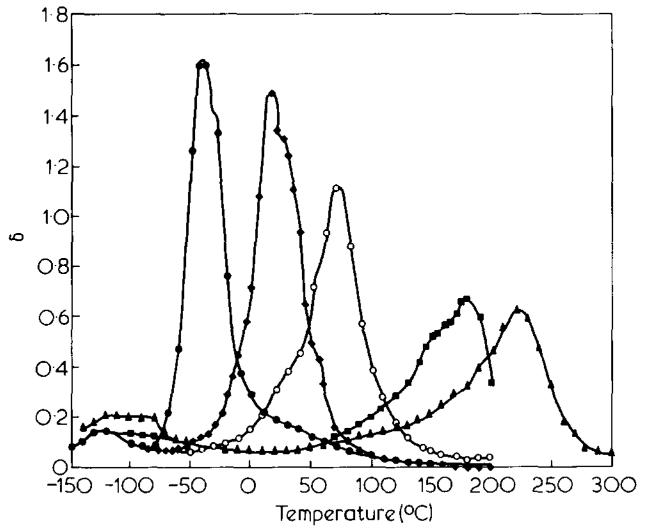

Figure 2 Logarithmic decrement of damping of heat treated polybutadiene. Heat treatment: 2 h at ●, 290°C; ◆, 300°C; ○, 310°C; ■, 320°C; ▲, 330°C

The effect of heating rate on PBD decomposition is shown in *Figure 3*. The data obtained for PBD ($\sim$98% *cis*-1,4-) are similar to those previously reported[2]. Varying the heating rate for PBD(*trans*(55%)-1,4) gives similar curves. In each case, increasing the heating rate from 10° to 100°C/min increases the decomposition temperature $\sim$50°C and the weight loss in the first step to 50%. The effect of heating rate on PBD (77% 1,2) is greater than with 1,4-PBDs. When heated at 100°C/min, a two-step decomposition occurs, with 57% weight loss in the first step. Heating at 10°C/min causes a single decomposition step at 461°C.

The effect of heating rate on the decomposition of a polymer which does not crosslink thermally (polystyrene) is shown in *Figure 4*. Increasing the heating rate causes the measured decomposition temperature to increase, but the shape of the curve is not changed. At the fast heating rate, large temperature gradients can occur, causing the sample to exhibit temperature lag.

When the heating rate is increased, both the measured decomposition temperature and the amount of heat treatment prior to decomposition have been changed. To determine the effect of heat treatment alone, PBDs were subjected to various prior heat treatments and then degraded at 100°C/min. These data are given in *Figure 5*.

Pre-heating PBD increases the temperature at which decomposition begins and decreases the amount of weight loss in the first step. It appears that thermal crosslinking of PBD inhibits the decomposition in the first step. PBD (77% 1,2), which has been shown to crosslink more readily than 1,4-PBDs, shows the greatest differences in decomposition behaviour when heat treated. Preheating PBD (77% 1,2) at 10°C/min to 350°C decreases the weight loss in the first step from 57% to less than 10%.

Data indicating that PBDs of varying microstructures readily exhibit thermal crosslinking have been shown. It has also bern shown that thermal crosslinking of PBD affects its decomposition. Based on these observations, a mechanism for PBD decomposition is proposed (*Figure 6*). It differs from previous mechanisms[2–6,10] in that the effect of thermal crosslinking prior to chain scission on PBD decomposition is considered.

The tendency of PBD readily to crosslink is related to the fact that the polybutadienyl radical is capable of attacking double bonds and propagating through the polymer. One radical produces up to 40–50 crosslinks[1,11,12]. Although the initiation of this chain reaction is not clear at this time, either abstraction of an allylic hydrogen or a bimolecular hydrogen transfer reaction are possible initiation steps.

The degree of crosslinking affects the main chain scission reaction. The activation energy for main chain scission of saturated polymers is higher than that of unsaturated polymers[13]. Thus, the activation energy for main chain scission of a highly crosslinked PBD will be greater than that of a less crosslinked polymer. This is indicated in *Figure 5* for PBD (77% 1,2). The temperature at which weight loss begins for the heat-treated sample is 40°C higher than that of the sample with no previous heat treatment.

When chain scission occurs, three competitive reactions take place, namely, crosslinking, cyclization and depolymerization. As long as there is unsaturation in the PBD,

Table 1 Dynamic mechanical properties of heat-treated polybutadiene (55%) *trans*-1,4

Temperature (°C) (2 h, heating)	Glass transition temperature (°C)	Plateau shear modulus G' (dyne/cm^2)
No heat treatment	−90	$\sim 1 \times 10^7$
290	−42	2.5×10^7
300	15	4.5×10^7
310	71	6.2×10^7
320	180	$\sim 1.5 \times 10^8$
330	220	3.2×10^8
10 Mrad	−88	1.15×10^7
30 Mrad	−84	1.64×10^7

Table 2 Thermal crosslinking of PBD during programmed heat treatment (10°C/min to 350°C)

PBD microstructure before heat treatment	Gel (%)
(98%) *cis*-1,4	93.7
(55%) *trans*-1,4	96.3
(77%)-1,2	100.0

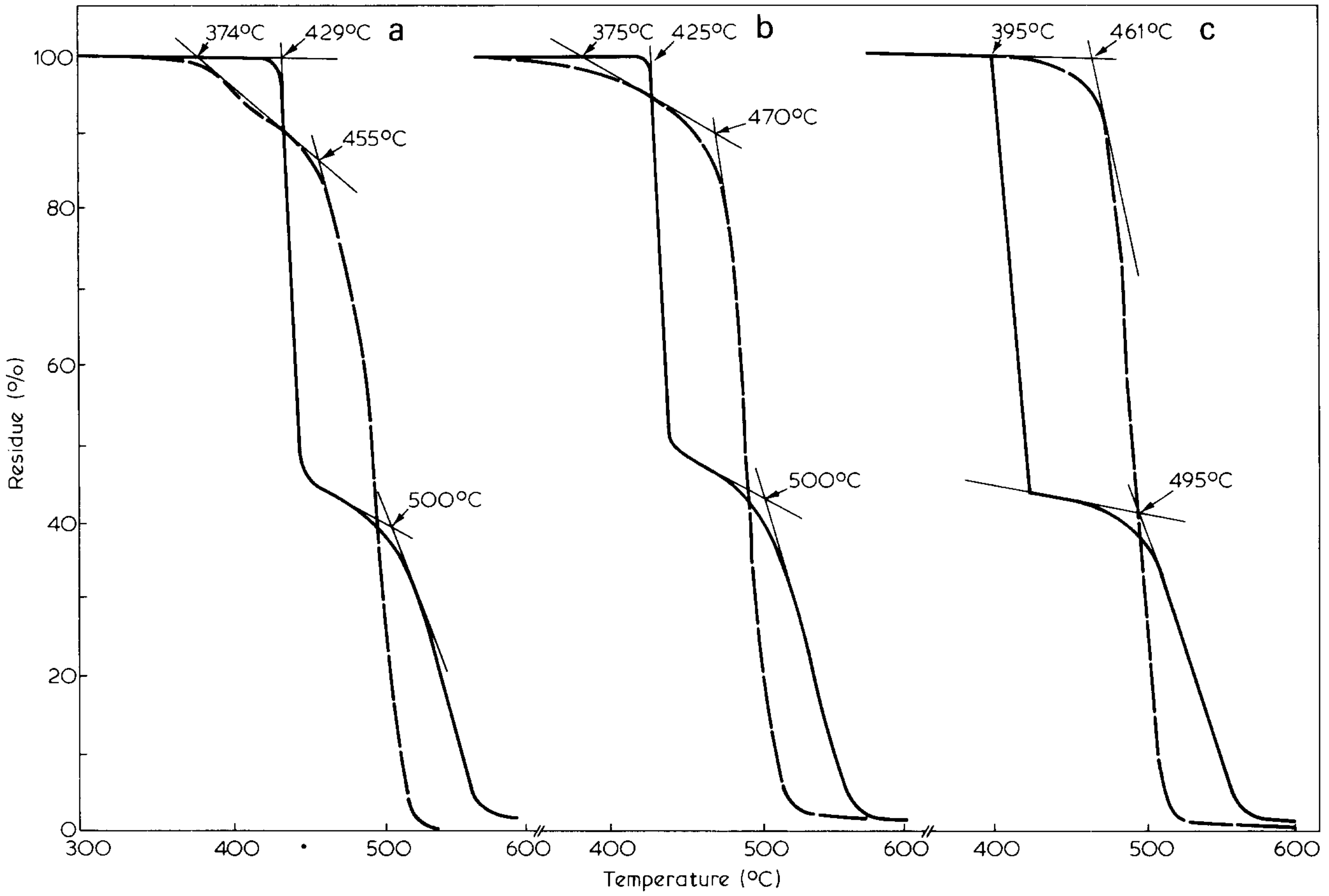

Figure 3 Effect of heating rate on thermal decomposition of PBD. (— — —, 10°C/min; ———, 100°C/min. (a) (98%) *cis*-1,4; (b) (55%) *trans*-1,4 (c) (77%) 1,2

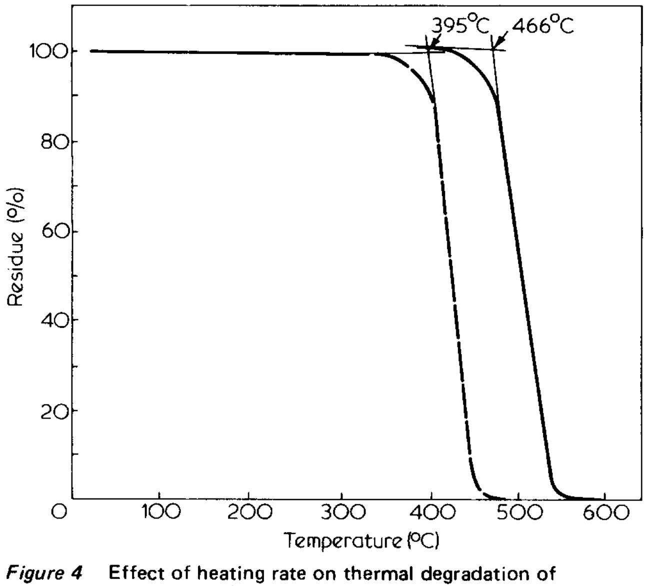

Figure 4 Effect of heating rate on thermal degradation of polystyrene. — — —, 10°C/min; ———, 100°C/min

both crosslinking and cyclization can occur. More work is needed to discern the competitive nature of these two reactions at pyrolysis conditions.

The degree of crosslinking prior to chain scission will affect the depolymerization reaction. Chain scission of a highly crosslinked PBD (obtained from a slow heating rate) will result in less butadiene formation. At a faster heating rate, there is less crosslinking and chain scission causes rapid formation of butadiene. In the second decomposition step, highly crosslinked and cyclized PBD is degraded.

This mechanism is consistent with data presented by Brazier and Schwartz[2]. When PBD (>95% *cis*-1,4) is heated at 10°C/min, 7% volatilizes in the first step, of which 24% is butadiene. When heated at 100°C/min, 51% volatilizes in the first step of which 52% is butadiene. Tamuro and Gillham also reported an increase in butadiene volatilization with increasing heating rate[10]. Also consistent with this mechanism are flash pyrolysis experiments in which butadiene is the most abundant volatile formed[14].

Brazier and Schwartz have explained these data in terms of the excess energy in the chain end radical formed with chain scission. At faster heating rates, the excess energy is increased, and depolymerization is favoured over cyclization[2]. This interpretation would not explain the effect of heat treatment on decomposition behaviour as indicated in *Figure 5*. A crosslinking mechanism, as described in *Figure 6*, would explain the effects of both varying heating rates and prior heat treatment.

CONCLUSION

The high rate of thermal crosslinking and the effect of this crosslinking on PBD decomposition have been shown. Increasing the degree of crosslinking increases the decomposition temperature. A mechanism has been proposed which qualitatively describes the relationship between crosslinking, cyclization and depolymerization in PBD degradation. This

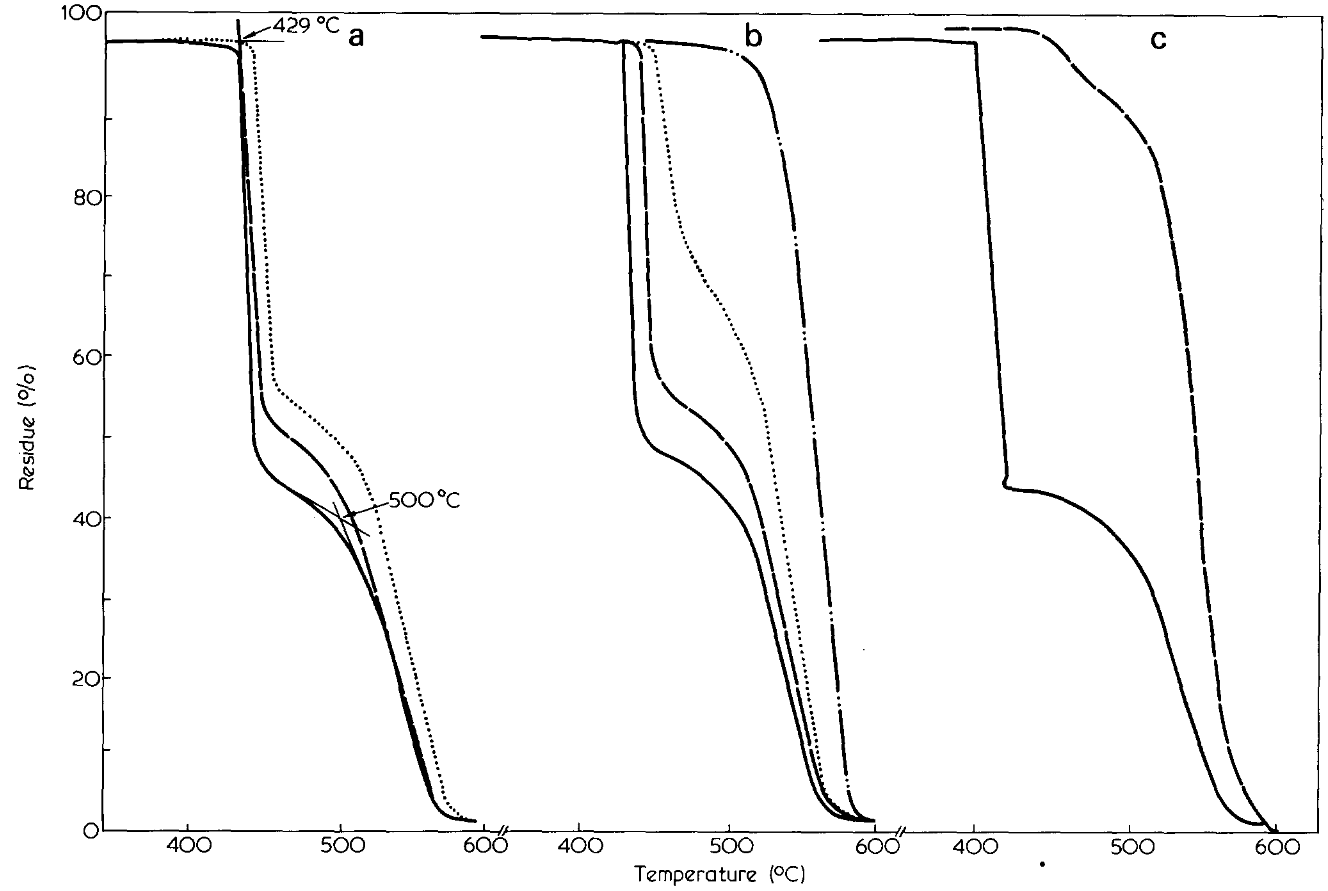

Figure 5 Effect of heat treatment on thermal decomposition of PBD (100°C/min). (a) (98%) *Cis*-1,4; ——, no heat treatment; — — — —, heat at 10°C/min to 350°C; . . . , heat at 5°C/min to 350°C. (b) (55%) *trans*-1,4; ——, no heat treatment; — — — —, heat at 10°C/min to 350°C; . . . , heat at 10°C/min to 375°C; — · · —, heat at 10°C/min to 330°C, isothermal for 2h. (c) (77%) 1,2; ——, no heat treatment; ——, heat at 10°C/min to 350°C

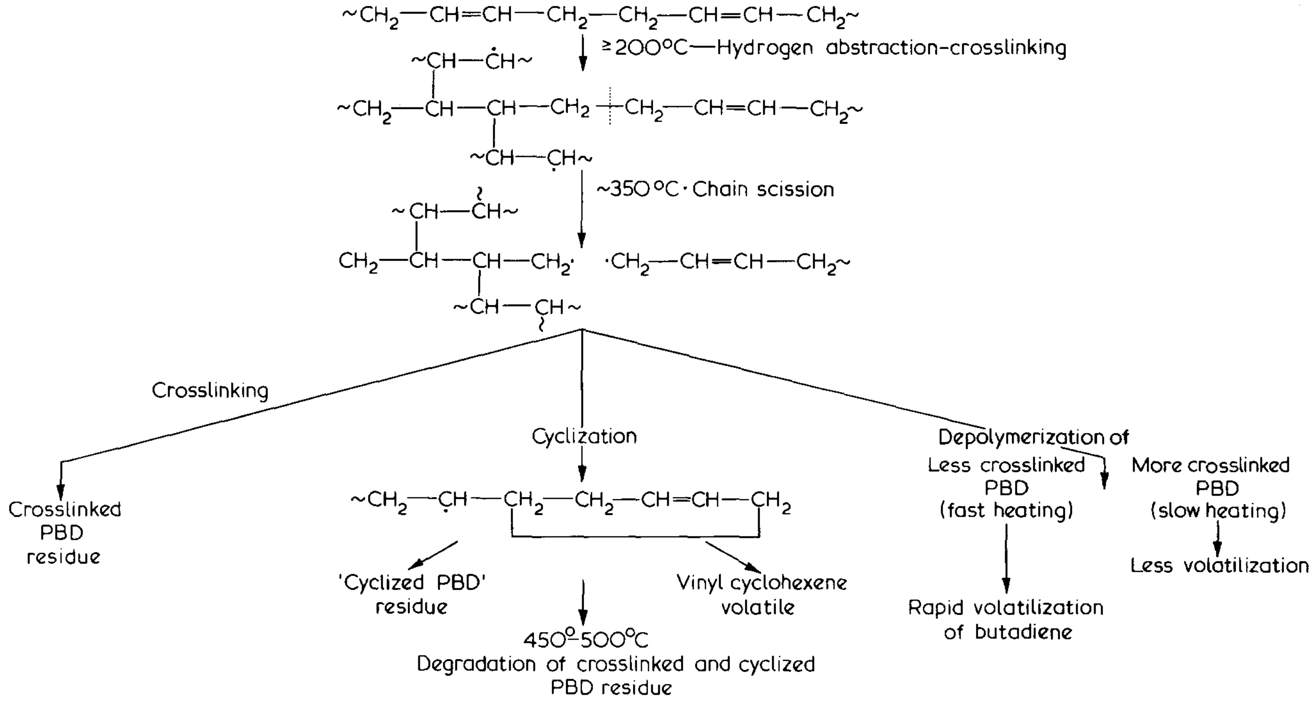

Figure 6 Thermal decomposition of PBD

mechanism also explains the unusual t.g.a. behaviour previously reported for PBD.

ACKNOWLEDGEMENTS

The authors wish to thank S. G. Turley for the dynamic mechanical data and E. S. Huyser for his consultations. They also wish to thank The Dow Chemical Company for permission to publish this work.

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