The Effect of Heating Rate on the Thermal Degradation of Polybutadiene

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Synopsis

Using derivative thermogravimetric analysis (DTG), polybutadiene is shown to degrade by two distinct weight loss events when heated dynamically. The volatile products of the first stage are almost exclusively depolymerization products (butadiene and vinylcyclohexene). The residue—cyclized and crosslinked polybutadiene—degrades in the second stage. Increasing the heating rate or sample size results in increased depolymerization; and at a 100°C/min heating rate, up to 50% of the initial sample weight is converted to depolymerization products. Differential scanning calorimetry (DSC) indicates that degradation is exothermic in the temperature range of the first weight loss stage. The determined exothermicity (0.95 kJ/g polybutadiene) is independent of heating rate. Infrared observations show *cis–trans* isomerization in the same temperature range. Kinetic analysis of the DTG data yields an apparent activation energy of 251 kJ/mole for depolymerization, while for the overall reactions in the first stage, DSC data yield 170 kJ/mole. Why the exothermicity of the degradation is independent of the depolymerization/cyclization ratio is not clear.

INTRODUCTION

Considerable information on the thermal degradation of polybutadiene has been published and reviewed.[1,2] Early studies concentrated on the analysis of pyrolysis products and residues,[3,4] while more recent work has been concerned with microstructure changes accompanying degradation[5-7] and correlation of specific pyrolysis product with structural units in the polybutadiene chain.[8] In all published work, the sample was pyrolyzed in nitrogen or vacuum, either under isothermal conditions or by heating at a single known rate. Derivative thermogravimetric analysis (DTG) of polybutadiene was reported by Brazier and Nickel,[9] and it was shown that the heating rate and sample size have a profound effect upon the weight loss–temperature profile. Using DTG–gas chromatography, volatile pyrolysis products from the stages of degradation have now been determined and are reported in detail in this paper.

Pyrolysis–chromatography and pyrolysis–infrared spectroscopy combinations are extensively used for the analysis of polymeric compositions. In these methods, a pyrolysis product is determined and correlated with a quantitative amount of the component in the composition from which the product is formed. The large effect of heating rate on the degradation of polybutadiene can cause serious lack of reproducibility in the analysis of polybutadiene and polybutadiene blends if careful attention is not given to exactly reproducing the same heating rate from sample to sample. An alternative procedure for the determination of polybutadiene was reported by Sircar and Lamond[10] who used the exother-
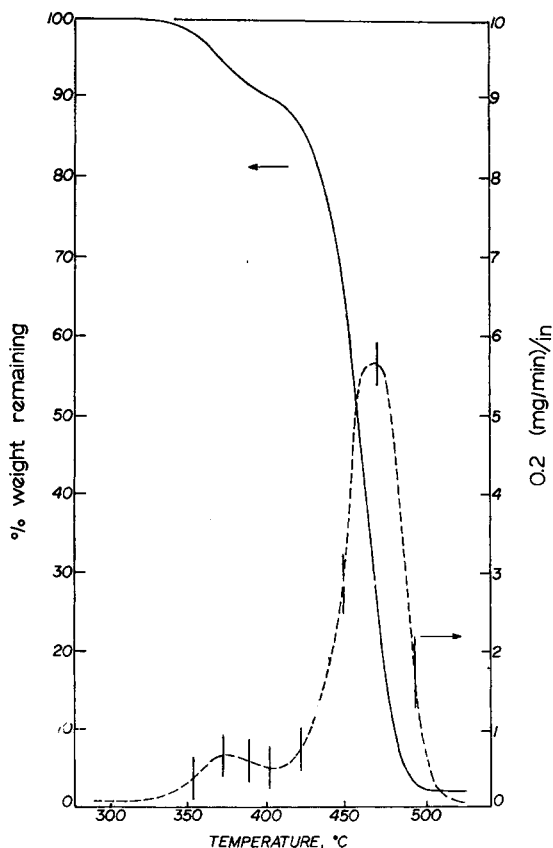
Fig. 1. TG and DTG thermograms of polybutadiene. Heating rate 10°C/min in nitrogen atmosphere; flow rate 100 ml/min; sample size 5.5 mg.

micity of degradation as determined by differential scanning calorimetry (DSC) to estimate polybutadiene both in polybutadiene and styrene–butadiene rubber vulcanizates. In the present work, DSC was used to determine the heat of degradation as a function of heating rate.

EXPERIMENTAL

All results reported here were obtained using Taktene 1220 (Polysar Ltd.), a high-cis (>95%) 1,4-polybutadiene. DTG analysis of a range of commercial polybutadienes including high-trans 1,4, vinyl 1,2, and liquid polybutadienes have been previously reported.[9] All materials give similar DTG thermograms. Taktene 1220 was used as supplied after it was shown that repeated purification had no effect upon the DTG/DSC observations.

A du Pont 951 TG/DTG was interfaced with a Perkin–Elmer 3920 gas chromatograph. The interface, constructed from eight-position microvolume valves (Carle Instruments #2026), was similar in design to that published by Chiu[11] but allowed up to eight samples of the volatile products to be collected from each DTG experiment. The interface was maintained at temperatures up to 200°C to prevent condensation in the collection loops of samples waiting for GC analysis.
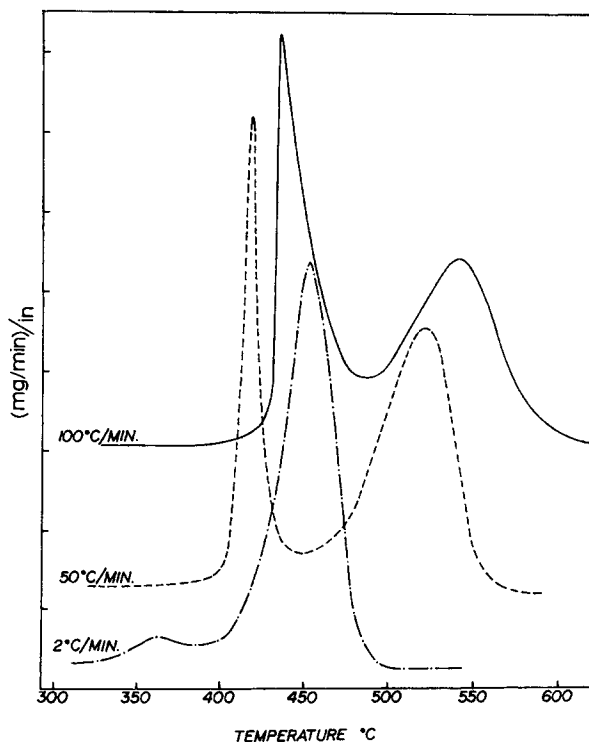
Fig. 2. Effect of heating rate on polybutadiene degradation. DTG thermograms at 2°, 50°, and 100°C/min. All samples 5.5 mg.

The collection loops were made of 0.020-in.-internal diameter stainless steel, and sample volumes ranged from 100 to 200 μl.

All analyses were performed in an 18-ft $\times$ 0.125-in. stainless steel column packed with 18% bis(2-ethylhexyl)tetrachlorophthalate on 80–100 mesh nonacid washed Chromosorb W. A back flush column was incorporated into the system to prevent any very high boiling products from entering the main column.

Heats of degradation (ΔH) were determined using a du Pont DSC cell base II and standard cell. Films of polybutadiene were cast directly into the sample pan from cyclohexane solution. This procedure ensured good contact between sample and sample pan and resulted in good reproducibility in ΔH determinations. The DSC was calibrated using indium, tin, and zinc. All infrared spectra were obtained using a Beckman IR 4240 spectrophotometer.

RESULTS

Figure 1 illustrates tpyical TG/DTG thermograms of polybutadiene obtained at a 10°C/min heating rate with a nitrogen atmosphere (flow rate 100 ml/min). Polybutadiene leaves ~2% carbonaceous residue at 550°C. The vertical markers on the DTG thermogram indicate points at which samples of the volatile pyrolysis products were collected for analysis. It is immediately apparent from the DTG thermogram that two stages of weight loss occur with maximum rates of weight loss achieved at 373° and 470°C. Figure 2 illustrates DTG thermograms ob-

TABLE I
Degradation of Polybutadiene—Effect of Heating Rate and Sample Size

| | Maximum degradation rate, min^{-1} | First-stage | |
		Temperature of maximum degradation rate, °C	Weight loss, %
Scan rate, °C/min[a]			
2	0.00312	362	6
5	0.0091	375	7
10	0.0230	387	7
20	0.052	402	10
50	1.08	418	33
100	1.85	434	51
Sample size, mg[b]			
5.50	0.023	387	7
9.45	0.022	387	8
19.50	0.031	387	8
50.20	0.896	nonreproducible	37–47

[a] All 5.50-mg sample.
[b] Heating rate 10°C/min.

tained at heating rates of 2°, 50°, and 100°C/min. As the heating rate increases, the extent of the first weight loss stage increases such that by a 100°C/min heating rate, approximately 50% of the sample weight is lost in the first stage.

The only published[10] DTG thermogram of polybutadiene (Ameripol CB 441, oil-extended polybutadiene) does not show the first distinct weight loss stage at a heating rate of 10°C/min. All commercial polybutadienes studied here (Taktene, Budene 101, Cisdene 1203 and Arco, Nisso, and Hystl liquid polybutadiene) exhibited the two weight loss stages.[9]

Table I summarizes the observed weight loss, the maximum degradation rate, and the temperature at which it occurs for the first-stage weight loss as a function of heating rate for a constant sample size of 5.5 mg. Increasing the sample size can also result in a large increase in the first-stage weight loss even at low heating rates, as shown in Table I. The 50-mg sample at 10°C/min behaves similarly to the 5.5-mg sample at 100°C/min. The sample size at which the large increase in the first stage is observed is not reproducible but appears to be generally above 20 to 30 mg.

Figures 3 and 4 illustrate typical chromatograms of volatile fractions collected at the maximum degradation rate of the first stage and at a point where the second stage has just commenced. The sample was heated at 50°C/min. The major products from the first stage are butadiene and the dimer 4-vinylcyclohexene, together with minor amounts of other hydrocarbons which were not identified. At the start of the second stage, significant butadiene is still observed, but 4-vinylcyclohexene content is very low. Fractions collected at the maximum rate of the second stage had little butadiene or vinylcyclohexene and were a complex mixture of many hydrocarbons.

Table II summarizes the calculated butadiene and vinylcyclohexene content of fractions collected at the maximum rate of the first stage. At a 10°C/min heating rate, about 66% of the fraction can be accounted for by these two prod-
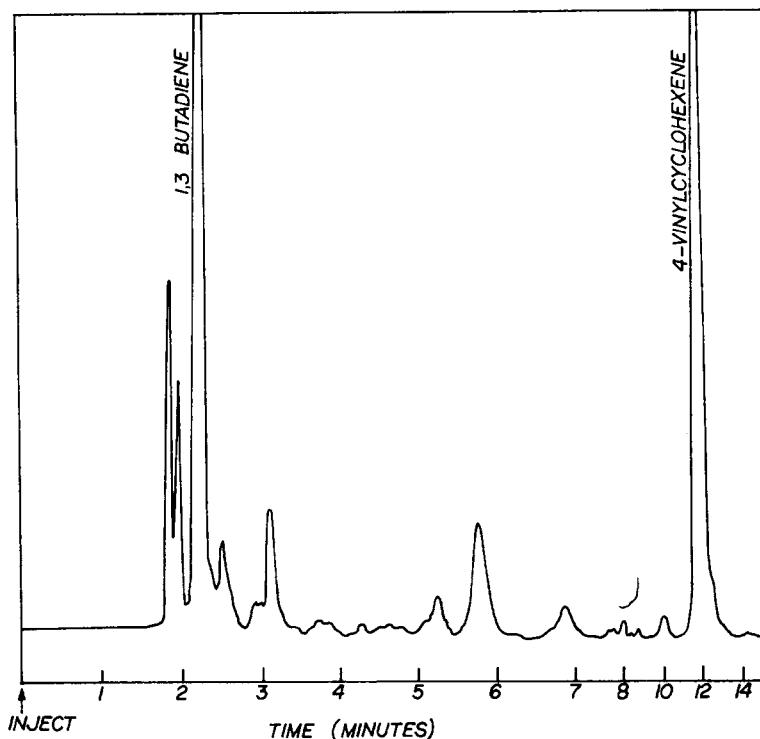
Fig. 3. Chromatogram of volatile products collected at maximum degradation rate temperature (418°C) of first degradation stage. Heating rate 50°C/min; sensitivity 128 × 1.

ucts, whereas at 100°C/min, the same two products amount to more than 95% of the fraction. Further, it is observed that the butadiene content increases with increasing heating rate, while the vinylcyclohexene content remains constant. No higher molecular weight products were detected when a cool glass wool plug was inserted into the effluent volatile stream, and the calculated butadiene and vinylcyclohexene contents are believed to correspond to percentages of the total weight lost in the first stage.

Figure 5 illustrates typical DSC degradation thermograms for polybutadiene obtained at heating rates of 2° and 100°C/min. Actual thermograms were obtained on a time base rather than temperature base to allow direct comparison of areas and ΔH calculation. The thermograms are shown on temperature base for ease of reproduction. The exotherms are identical to those published[10] for Ameripol CB 220. The baselines for area calculation were drawn as shown by simply extending the baseline before degradation commenced through the exotherm. Table III records the calculated ΔH values at several heating rates. Within the experimental error (±10%), ΔH is independent of heating rate. Our value of 0.88 ± 0.04 kJ/g is in good agreement with the literature value of 0.95 kJ/g quoted[10] for Ameripol CB 220. Comparison of the DTG and DSC thermograms on the same temperature scale and the same heating rate show that the DSC exotherm commences before weight loss is observed. For example, at 2°C/min, heat evolution commences at 275°C, whereas weight loss is not observed until 320°C. The temperature of maximum heat evolution and weight loss are closer, viz., 350° and 360°C, respectively.
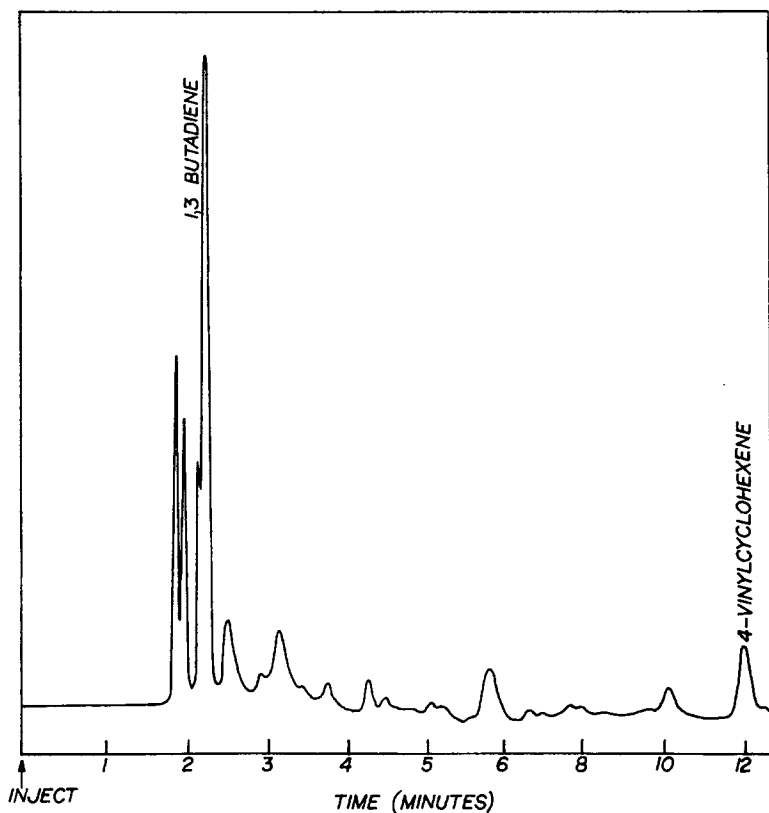
Fig. 4. Chromatogram of volatile products collected in second stage of degradation at 500°C from 50°C/min heating rate experiment. Same sensitivity (128 × 1) as Fig. 3.

The exothermicity was also observed for *trans*-polybutadiene, styrene–butadiene copolymer (Polysar Krylene 1500, 23.5% bound styrene), and hydroterminated liquid polybutadiene (Hystl B-3000, greater than 90% vinyl content). ΔH values calculated are included in Table III. The ΔH value for the SBR with 23.5% styrene, 0.66 kJ/g, is in fair agreement with the calculated value of 0.70 kJ/g, assuming the ΔH arises only from the butadiene content. The Hystl resin value of 1.07 kJ/g suggests that the vinyl content has little effect on the observed exothermicity.

TABLE II

Butadiene and Vinylcyclohexene Content of Volatile Fraction from First Weight Loss Stage

Heating rate, °C/min	Total weight loss of initial sample, %	Butadiene, wt %[a]	Vinylcyclohexene, wt %[a]
10	7	24	42
20	10	24	44
50	33	41	38
100	51	52	43

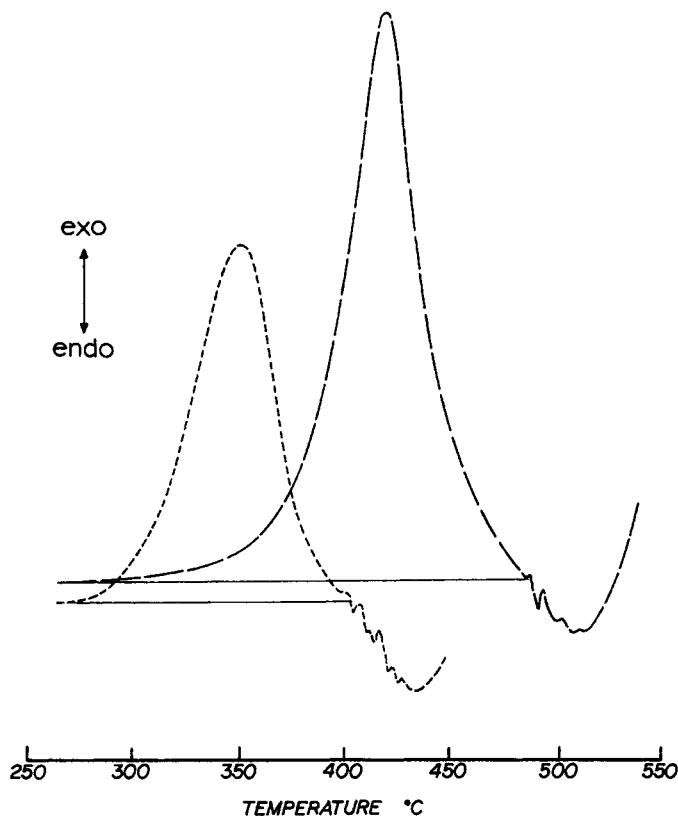[a] Calculated from area response in GC.

Fig. 5. DSC thermograms of polybutadiene at 2° and 100°C/min heating rates: (- - -) 2°C/min, 8.83 mg, 0.2 (mcal sec^{-1}) in.$^{-1}$; (– – –) 100°C/min, 7.37 mg, 5.0 (mcal sec^{-1}) in.$^{-1}$; (——) baseline constructed for area measurement.

Infrared observations on polybutadiene films heated in the DTG at 10°C/min are recorded in Table IV for samples heated to 340° and 370°C. Above 370°C, degradation was sufficient to rupture the films. Film thickness altered with heating; and in order to compare spectra, all absorbances were normalized to the 1450 cm^{-1} absorption, assuming this absorption was constant. The 1450 cm^{-1} absorption is the —CH deformation frequency in —CH$_2$— groups.

TABLE III
Exothermicity of Polybutadiene Degradation—Effect of Heating Rate

Polybutadiene	Heating rate, °C/min	Sample size, mg	T_{max}, °C	ΔH, kJ/g (±10%)
Taktene 1220	2	8.89	350	0.88
	5	8.59	365	0.88
	10	8.60	377	0.92
	20	8.30	388	0.92
	50	6.82	407	0.85
	100	6.57	425	0.89
trans-Polybutadiene	20	5.50	388	0.85
Krylene 1500	20	3.35	390	0.66
Hystl C-3000	20	6.76	358	1.07

TABLE IV
Infrared Absorbance Changes with Temperature of Polybutadiene Films

Wavelength, cm^{-1}	Assignment	Relative absorbance[a]		
		Control	340°C[b]	370°C[b]
3075	—CH stretching	0.19	0.19	—
2970 to 2850	CH$_3$ and —CH$_2$—	2.89	2.06	1.18
(three bands)	stretching	2.25	2.50	3.12
		1.60	1.77	2.04
1660	C=C stretching (nonconj.)	0.38	0.17	0.06
1450	—CH deformation in CH$_2$	1.00	1.00	1.00
1408	—CH$_2$ in plane deformation	0.85	0.91	—
990	CH deformation (vinyl)	0.24	—	—
965	CH deformation (trans)	0.11	1.14	1.48
910	CH$_2$ deformation (vinyl)	0.16	0.15	0.12
765		0.350	0.23	0.09
730	CH deformation cis	1.66	1.04	0.49

[a] Absorbance relative to 1450 cm^{-1} at 1.00.

[b] Film heated to these temperatures under DTG conditions (see text).

DISCUSSION

From the above results, the following observations on the degradation can be made: Polybutadiene degrades in two discrete weight loss stages, the maximum rates of which are separated by ~100°C. The relative extent of each degradation stage is dependent upon both heating rate and sample size. Analysis of the volatile products from the first weight loss stage indicates that this stage is predominantly depolymerization. Depolymerization increases with increasing heating rate and sample size. An exothermic event is observed in the same temperature range as the first weight loss stage; however, the exothermicity is independent of the heating rate and, therefore, the extent of each weight loss event. The exothermicity is also virtually independent of the microstructure of the polybutadiene. Any mechanism written for the degradation of polybutadiene should, therefore, account for the above observations.

The mechanism of polybutadiene degradation as suggested by Golub and Gargiulo[5] is illustrated in Figure 6. Main-chain scission results in chains with radical ends which can either undergo depolymerization (butadiene and vinylcyclohexene) or cyclization to "cyclized" polybutadiene. The mechanism as written in Figure 6 for polybutadiene degradation is analogous to that proposed for polyisoprene degradation; however, in both DTG and DSC, differences are apparent between polybutadiene and polyisoprene. The DTG thermogram of polyisoprene[9] has a single peak at 373°C, and weight loss is complete by 430°C. A shoulder is apparent on the high-temperature side of the peak. In DSC analysis, a small endotherm is observed in the temperature range of weight loss. Cyclization of polyisoprene is well documented;[12] and, although catalyzed by Lewis acids, NMR and infrared spectroscopy also confirm thermal cyclization of that polymer.[5] The DTG results, therefore, indicate that cyclized polyisoprene degrades just above the depolymerization temperature of polyisoprene. Endothermicity of the cyclized polyisoprene degradation could then mask any exothermic processes. In comparison, cyclized polybutadiene appears more thermally stable and degrades at higher temperatures, thus separating the two peaks observed in the DTG.
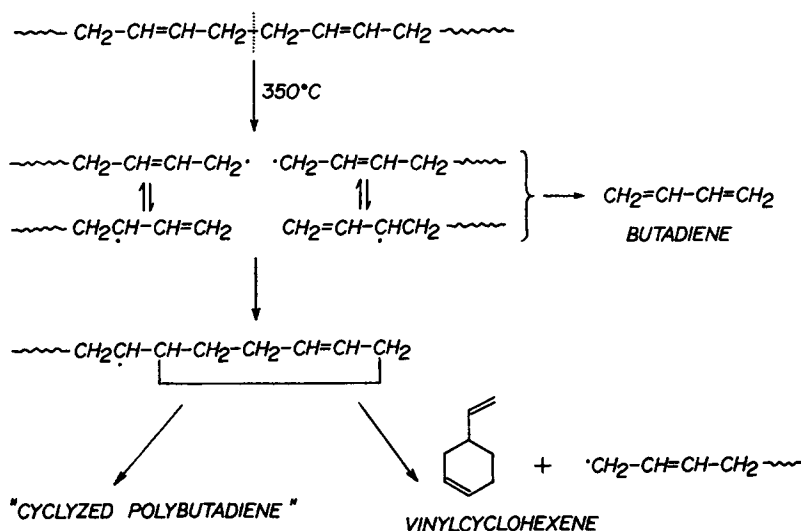
Fig. 6. Polybutadiene degradation mechanism after Golub and Gargiulo.[5]

The degree of cyclization in the residue after the first weight loss stage is probably small and increases in competition with degradation in the second stage. After 50% weight loss, polybutadiene is extensively cyclized and unsaturation is virtually eliminated.[5] At 370°C, however, under the present thermal conditions, the predominant changes in the infrared spectra arise from cis–trans isomerization. The 965 cm^{-1} trans absorption increases and the broad 735 cm^{-1} cis absorption decreases. The decrease in the 990 and 910 cm^{-1} absorptions indicates removal of vinylic groups, in good agreement with Grassie and Heaney.[7] The latter authors showed that vinyl groups are removed at temperatures as low as 230°C and proposed a mechanism in which removal of the pendent vinyl group results in crosslinking. An activation energy of 62.7 kJ/mole was calculated for this process. Coffman[13] also reported that crosslinking and cyclization occur in polybutadiene heated in air or nitrogen at 250°C and calculated an activation energy of 163 kJ/mole from hardening data. Thus, the residue remaining after the depolymerization stage is crosslinked and probably partially cyclized. Sulfur vulcanization of polybutadiene has no effect on the DTG thermogram[9] or the DSC exotherm.[10] The addition of carbon black has no effect on polybutadiene degradation; however, it does result in a two-stage degradation when added to synthetic polyisoprene[14] (not natural rubber), suggesting that thermal cyclization and crosslinking are catalyzed by carbon black.

Apparent activation energies were calculated from both the DTG and DSC data. Although complex kinetic derivations are available to correct for changes in reactant mass with extent of reaction, because our interest is only in the first stage of weight loss and this is generally less than 10% of the initial sample weight, we assume with first-order kinetics that the rate is simply the rate of weight loss. A simplified method[15] for estimating activation energies from DSC thermograms was also used. Figure 7 illustrates the Arrhenius plots obtained. The activation energy calculated from the DTG data is 251 ± 15 kJ/mole at heating rates from 2° to 20°C/min. From the DSC data, we obtain 170 ± 12 kJ/mole.

Since butadiene and vinylcyclohexene are the major volatile products formed in the first weight loss, the DTG activation energy corresponds to the depoly-
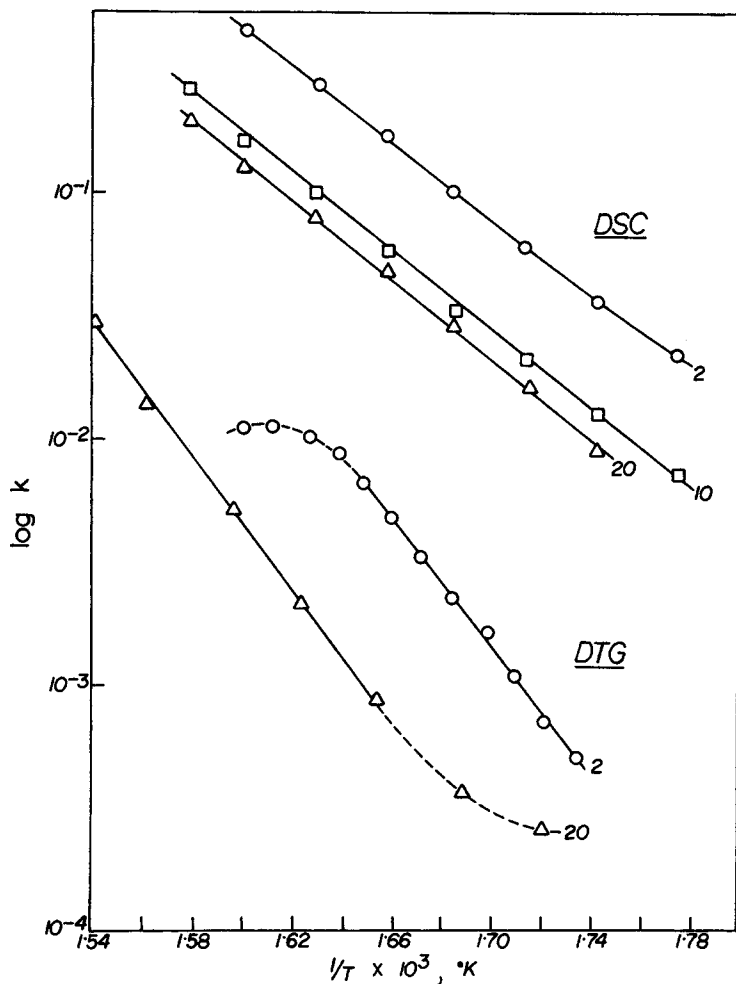
Fig. 7. Arrhenius plots from DTG and DSC data on polybutadiene degradation. For assumptions made, see text. Heating rate in °C/min.

merization process. The 251 kJ/mole value is in good agreement with that of 259 kJ/mole reported from isothermal studies.[4] The activation energy is closer to that found experimentally for main-chain scission of saturated polymers (e.g., polyethylene[2]) than that of 179 kJ/mole calculated[16] for unsaturated polymers such as polybutadiene and polyisoprene. Activation energies for the formation of butadiene and vinylcyclohexene are not known; however, assuming they are similar to those for the formation of isoprene and dipentene from polyisoprene would give 217 kJ/mole for butadiene and 176 kJ/mole for vinylcyclohexene. The increasing yield of butadiene compared to vinylcyclohexene (Table II) would then be expected as the heating rate (and temperature) increases.

The apparent activation energy calculated from the DSC data refers to the overall value for all processes in the temperature range of the exotherm, provided the process is not thermally neutral. Heats of depolymerization are not known; but again comparing polybutadiene to polyisoprene degradation, values of −40 kJ/mole for butadiene and zero kJ/mole for vinylcyclohexene[16] would be ex-

pected. The activation energy for *cis–trans* isomerization[5] is 130 kJ/mole at 260°C, and the heat of *cis–trans* isomerization is expected to be endothermic. Sircar and Lamond[10] assumed *cis–trans* isomerization to be endothermic to explain the decrease in the observed exothermicity as *cis* content increased. The present results give similar exothermicities for *trans-* and *cis*-polybutadiene within the experimental error of ±10%. The removal of vinyl groups by cross-linking or cyclization does not appear to make a major contribution to the DSC exotherm since the observed exothermicity for polybutadiene with high vinyl content (Table III) is only ~10% greater than that of *cis*-polybutadiene with low vinyl content.

From the above discussion, it appears that the exothermicity cannot be related with confidence to any single process in polybutadiene degradation that we have determined. As ΔH is independent of the relative extent of depolymerization and cyclization, either the major contribution to ΔH arises from a precursor reaction to both processes or the heats of depolymerization and cyclization are similar in magnitude. In the first case, main-chain scission would be the precursor reaction to both depolymerization and cyclization, and indeed the estimated DSC activation energy of 170 kJ/mole is close to the expected value for chain scission of unsaturated nonconjugated chains of 179 kJ/mole. The observed effect of heating rate on the relative extent of depolymerization and cyclization could be explained on the basis of the excess energy in the chain-end radical on formation. As the excess energy increases, depolymerization would be favored over cyclization.

CONCLUSIONS

Degradation of polybutadiene under a dynamic heating program proceeds through two stages of weight loss. Analysis of the volatile products from the first stage of weight loss shows that it is primarily depolymerization. Material not undergoing depolymerization cyclizes and crosslinks, yielding a residue which degrades in the second stage. Increasing the heating rate and/or sample size results in increased depolymerization at the expense of cyclization. Increasing sample size above 20–30 mg also results in increased depolymerization even at lower heating rates.

The two major products of depolymerization are butadiene and vinylcyclohexene. Butadiene content of the depolymerization fractions increases with increasing rate as anticipated from the relative activation energies of butadiene and vinylcyclohexene formation.

Differential scanning calorimetry indicates that in the temperature range of the first stage of degradation, the overall process is exothermic. In this temperature range, several processes are occurring including vinyl group removal and cis–trans isomerization in addition to main-chain scission and subsequent depolymerization and cyclization. The observed heat of degradation is independent of the extent of cyclization and depolymerization, suggesting that either both processes show similar energetics or both have the same exothermic precursor reaction.

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