Study of thermal degradation of polybutadiene in inert atmosphere: 1. Evidence of temperature and time of heating in i.r. and n.m.r. spectra

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The degradation of polybutadiene by heating in inert atmosphere at various temperatures for different time intervals was characterized by i.r. and ^{1}H n.m.r. methods. It was established that by i.r. analysis it is possible to assess both the temperature and the duration of the heating to which the sample had been subjected.

(Keywords: i.r.; n.m.r.; polybutadiene; thermal degradation)

Introduction

In previous communications from this laboratory[1,2], it has been established that the thermal history of some polymeric materials (polyethylene and the polyamides) can be revealed from i.r. spectra, and that in this way it is possible to determine both the temperature and the duration of heating to which the sample has previously been subjected. This finding may be of practical importance in various technical applications, or for determining the type of thermal stress to which the polymers have been exposed. We have now attempted to find out whether a similar procedure could be applied for polymeric materials containing polybutadiene (PB).

In numerous earlier studies[3–9], the pyrolysis of various PB polymers and their copolymers or blends (mostly with polystyrene) was studied by different methods, mostly applying continuous progressive heating to 500°C, or isothermal treatment at ~350°C. At ~200°C PB itself becomes insoluble, presumably in consequence of some degree of crosslinking. According to thermogravimetric analysis[8], weight loss sets in at ~350°C, to become appreciable at >380°C. Up to 380°C, the amount of volatile degradation products that do not condense at ambient temperature is negligible[8]. By d.s.c. analysis the degradation process is exothermic up to ~380°C and endothermic at higher temperatures[8]. By i.r. analysis of the non-volatile residue and of the condensed volatile products, and by n.m.r. analysis of the latter and of the soluble portions of the residue it was established[3,4] that the polymer first undergoes a saturation–cyclization process, in which the vinyl groups are the first to disappear. Aromatic structures appear at higher temperatures. The insoluble part of the residue has not been studied by n.m.r. so far.

In this work we have attempted to characterize by i.r. and n.m.r. spectra the samples of PB heated in inert atmosphere at a series of temperatures for defined periods of exposure.

Experimental

Changes occurring in the course of thermal degradation were studied with a sample of PB rubber, ASADENE 55AS (density 885 kg m^{-3}). By i.r. analysis[10] it contains 34% of *cis*-1,4-PB, 54% of *trans*-1,4-PB and 11% of 1,2-PB units.

Samples of the polymer were thermally degraded in the apparatus described previously[1]. The volatile products that are liquid at ambient temperature were trapped and returned into the reaction space by means of an air condenser. I.r. spectra of the initial polymer and of the solid thermally degraded samples were measured by the KBr technique using a Perkin-Elmer spectrometer (model 983G), in the range 4000–300 cm^{-1}, with a resolution of 3 cm^{-1}. The liquid degradation products were measured in a cell of thickness 0.025 mm, with NaCl windows, in the range 4000–600 cm^{-1}.

^{1}H n.m.r. spectra of the soluble degradation products dissolved (10% w/v) in $CDCl_3$ with hexamethyldisiloxane (HMDS) as internal standard ($\delta = 0.05$ ppm) were measured with a Bruker spectrometer (model AC 300) at 300 MHz and ambient temperature.

Results and discussion

The PB rubber was subjected to thermal degradation for 1 h at 150 and 600°C, and for 0.5, 1, 2 and 4 h at 200, 250, 300, 400 and 500°C. With increasing heating time at 200°C, the rubber gradually loses its elasticity and its toughness increases; after 4 h at 250°C, the sample is almost rigid. After treatment at 300°C, the products are hard and brittle, and their colour has changed from light yellow to opaque dark brown. Prolonged treatment at 400°C produces a stiff black product and a colourless or yellowish liquid. At 500°C, a black highly viscous substance is produced, in addition to a colourless or yellowish liquid. The final product of thermal degradation after 1 h at 600°C is a dark liquid. The gaseous products formed by heating to 400°C and above were disregarded in this study. The products heated to 200 and 250°C are insoluble, those heated to 300°C and higher are soluble in chloroform.

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Table 1 I.r. analysis of the condensed solid (S) and liquid (L) products of thermal degradation of polybutadiene (PB); intensities in band maxima[a] and their ratios

Polymer (°C/h)	I_{743} × 10^3	I_{909} × 10^3	I_{965} × 10^3	I_{1373} × 10^3	I_{743}/I_{965}	I_{909}/I_{965}	I_{1373}/I_{965}	I_{1446}/I_{1435}	I_{1237}/I_{1349}
PB	–	0.246	0.910	–	–	0.270	–	0.975	0.654
150/1S	–	0.245	0.905	–	–	0.271	–	0.980	0.653
200/0.5S	–	0.242	0.897	–	–	0.270	–	0.992	0.783
200/1S	–	0.235	0.877	–	–	0.268	–	1.000	0.731
200/2S	–	0.205	0.771	–	–	0.266	–	1.007	0.583
200/4S	–	0.167	0.634	–	–	0.263	–	1.012	0.571
250/0.5S	–	0.191	0.698	0.011	–	0.274	0.016	1.018	0.567
250/1S	–	0.141	0.657	0.039	–	0.222	0.059	1.059	0.378
250/2S	–	0.065	0.584	0.047	–	0.111	0.080	1.102	0.282
250/4S	–	0.035	0.524	0.057	–	0.067	0.109	1.133	0.252
300/0.5S	0.030	0.026	0.080	0.084	0.375	0.325	1.050	–	–
300/1S	0.032	0.019	0.066	0.095	0.485	0.288	1.439	–	–
300/2S	0.035	0.008	0.036	0.106	0.972	0.222	2.944	–	–
300/4S	0.040	0.004	0.030	0.117	1.333	0.130	3.900	–	–
400/0.5S	0.034	0.22	0.067	0.101	0.507	0.299	1.507	–	–
400/1S	0.049	0.015	0.027	0.108	1.815	0.556	4.000	–	–
400/2S	0.055	0.007	0.012	0.112	4.583	0.583	9.333	–	–
400/4S	0.062	–	0.005	0.118	12.400	–	23.600	–	–
500/0.5S	0.049	0.020	0.031	0.199	1.581	0.710	6.419	–	–
500/1S	0.071	–	0.014	0.175	5.071	–	12.500	–	–
500/2S	0.091	–	0.005	0.160	18.600	–	32.000	–	–
500/4S	0.153	–	–	0.143	–	–	–	–	–
400/1L	0.108	0.436	0.233	0.228	0.464	1.871	0.979	–	–
400/2L	0.155	0.227	0.116	0.270	1.336	1.957	2.328	–	–
400/4L	0.257	0.118	0.054	0.281	4.759	2.185	5.204	–	–
500/0.5L	0.200	0.222	0.081	0.242	4.469	2.741	2.988	–	–
500/1L	0.312	0.126	0.046	0.238	6.783	2.739	5.174	–	–
500/2L	0.408	0.098	0.037	0.225	11.027	2.679	6.081	–	–
500/4L	0.445	0.075	0.028	0.221	15.893	2.649	7.893	–	–
600/1L	0.522	0.085	–	0.156	–	–	–	–	–

[a] Band assignments[11–14]: 743 cm^{-1}, 1 or 1,2-substituted benzene ring; 909 cm^{-1}, γ_ω(CH) of –CH=CH$_2$ group; 965 cm^{-1}, γ_ω(CH) of *trans*-HC=CH– group; 1237 cm^{-1}, δ(CH) of *trans*-HC=CH– in crystalline PB; 1349 cm^{-1}, δ(CH) of *trans*-HC=CH– in amorphous PB; 1373 cm^{-1}, bending vibration of CH$_3$ group; 1435 cm^{-1}, CH$_2$ bending vibration in s-*trans*-conformation of 1,4-*trans*-PB; 1446 cm^{-1}, CH$_2$ bending vibration in *gauche* conformation of 1,4-*trans*-PB.

Table 2 ^{1}H n.m.r. analysis of the condensed solid (S) and liquid (L) products of thermal degradation of polybutadiene (10% w/v in CDCl$_3$)

Sample (°C/h)	% of total ^{1}H Olefinic ^{1}H	Aromatic ^{1}H
Original PB	35	0
200/4S	32	–
300/0.5S	2.6	2.5[a]
300/4S	1.3	3.6[a]
400/0.5S	2.7	2.8[a]
500/0.5S	0.9	5.6[a]
500/4S	0	13.1[b]
400/2L	2.3	5.2[a]
500/0.5L	1.5	8.3[b]
500/2	0.4	15.0

[a] Centre of aromatic band above 7.2 ppm

[b] Centre of aromatic band below 7.2 ppm

The solid and the condensed liquid degradation products were separately analysed by i.r. and n.m.r. methods. The changes in i.r. spectra after thermal treatment of PB, interpreted on the basis of refs 11–14, are summarized in *Table 1*, and the results of n.m.r. analysis in *Table 2*. I.r. spectra in the ranges of 3200–2700 and 1800–600 cm^{-1} of the original rubber and of the products of its thermal degradation after 1 h of heating at various temperatures are shown in *Figure 1*.

After 1 h of heating PB at 150°C, the i.r. spectra do not show any appreciable change. At 200°C, with increasing time of heating, the band intensities are mainly decreasing for the vinyl group bands (909, 991, 1637 and 3069 cm^{-1}), and for the bands of the *trans*-vinylene (965 cm^{-1}) and *cis*-vinylene groups (725 and 1402 cm^{-1}). The intensity of the band of the bending vibration of methylene groups in chains with s-*trans* conformation (1435 cm^{-1}) is decreasing, while that assigned to chains with *gauche* conformation (1446 cm^{-1})[12] is increasing. The band intensity ratio I_{1237}/I_{1349}, generally considered to indicate the degree of crystallinity in PB, reaches its maximum value after 0.5 h of heating at 200°C, and decreases later on.

In i.r. spectra of samples heated to 250°C (*Figure 1b*), a new band assigned to a methyl group bending vibration[13] appears at 1373 cm^{-1}. The intensity of this new band gradually increases with increasing heating time. The intensities of the bands of the vinyl group, of the *trans*-vinylene group and of the *cis*-vinylene group are decreasing. In spite of this, the i.r. spectrum is still essentially that of PB. The falling value of the peak intensity ratio I_{909}/I_{965} means that the intensity of the vinyl group band decreases more rapidly than that of the *trans*-vinylene band.

On heating PB to 300°C (*Figure 1c*), the i.r. spectra show that the intensities of the bands of the vinylene groups are rapidly decreasing, so that the PB spectral pattern is practically lost. After prolonged heating at 300°C, the bands of the *cis*-vinylene group are no longer apparent, and after heating to 400°C, only the vinyl bands

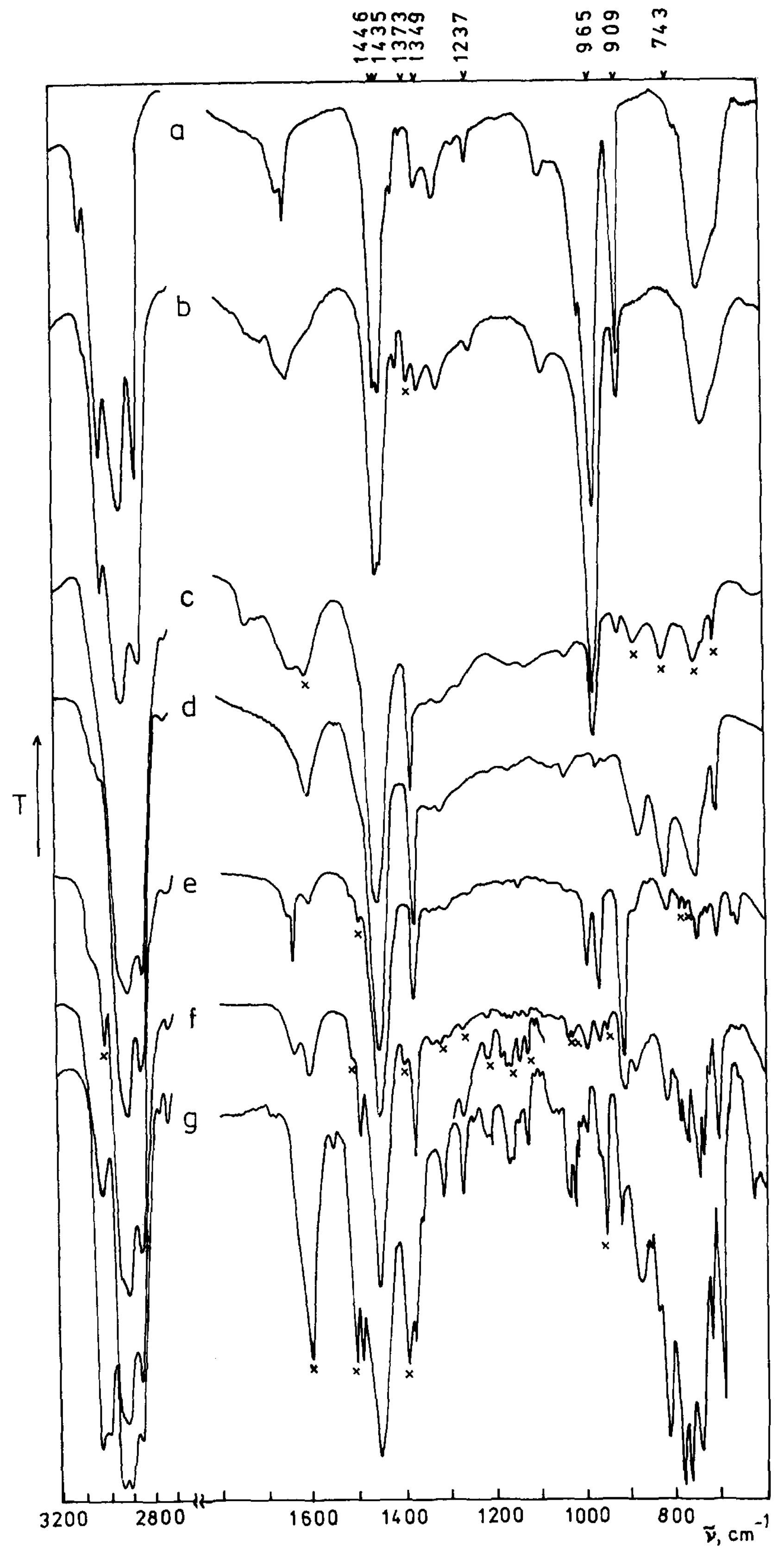

Figure 1 I.r. spectra of condensed solid (S) and liquid (L) products of thermal degradation of polybutadiene. Heating temperature (°C)/time (h): (a) original PB; (b) 250/1S; (c) 300/1S; (d) 500/1S; (e) 400/1L; (f) 500/1L; (g) 600/1L. Frequencies of the peaks used for quantitative characterization are indicated on the top scale. ×, Newly appearing peaks in the spectra

at 909 and 991 cm^{-1}, and the band of the *trans*-vinylene groups at 965 cm^{-1} remain barely detectable. At these temperatures, the bands of saturated hydrocarbon structures become prominent: the band of the CH_3 bending vibration at 1373 cm^{-1}, and the shoulder at 2950 cm^{-1} (on the CH_2 stretching band at 2925 cm^{-1}) corresponding to methyl groups on tertiary or quaternary carbon. In addition, after heating to 300°C, weak new bands appear at 697, 743, 813, 875 and 1599 cm^{-1} (*Figure 1c*), corresponding to vibrations of aromatic structures. The intensities of these bands, as well as those of the saturated structures, increase with the heating time and with the elevation of the heating temperature to 400 and 500°C.

The i.r. spectra of the liquid condensates produced by heating PB to 400°C (*Figure 1e*) contain, besides the bands of aliphatic structures, new bands at 767, 784, 1492 and 3015 cm^{-1}, corresponding to the vibrations of aromatic rings. With prolonged heating time, the intensities of all bands of the aromatic and aliphatic structures are increasing, and those of the unsaturated structures are rapidly decreasing. Bands of the vinyl and *trans*-vinylene groups, which no longer appear in the spectra of the solid product of degradation at 400°C, can still be observed in the spectra of the liquid phase, indicating that the compounds carrying vinyl groups mostly pass into the liquid fraction.

The i.r. spectra of the liquid products of PB degradation at 500°C (*Figure 1f*) show new bands at 945, 1020, 1033, 1118, 1156, 1204, 1265, 1309, 1391 and 1511 cm^{-1}. A comparison with the i.r. spectra of aromatic hydrocarbons[14] indicates that the liquid degradation products contain considerable amounts of *o*-, *m*- and *p*-xylene. Prolonged heating leads to an increase of the intensities of all bands of aromatic structures, while the intensities of all bands of unsaturated structures are rapidly decreasing; an intensity decrease is also observed for the bands of the methyl and methylene bending and stretching vibrations.

A similar result is reached by i.r. analysis of the liquid product obtained by heating PB to 600°C for 1 h (*Figure 1g*), which represents a complex mixture of aliphatic and aromatic hydrocarbons. A considerable qualitative difference is observed between the spectra of samples 500/1L and 600/1L (*Figures 1f* and *g*). The prominent peak at 1600 cm^{-1} together with the bands at 1510, 1395 and 945 cm^{-1} indicate the presence of compounds with condensed aromatic rings.

The ^1H n.m.r. spectrum of the original PB in $CDCl_3$ solution is shown in *Figure 2a* exhibiting bands of aliphatic protons at 1–2 ppm, and of olefinic protons at 4.8–5.6 ppm. In this spectrum, the ratio of the intensities of olefinic to aliphatic protons corresponds approximately to 1:2, and the intensities of the weak peaks of 1,2-structures at ~4.9 ppm correspond to the composition as determined by the i.r. method.

The sample heated to 200°C for 4 h, swollen to equilibrium in $CDCl_3$, has the appearance of a gel which is sufficiently homogeneous for conventional high resolution ^1H n.m.r. measurement; its spectrum, shown in *Figure 2b*, exhibits bands with relatively sharp peaks but extremely broad wings of so called super-Lorentzian shape, which is typical of swollen crosslinked polymer networks[15]. Except for this band-shape, the spectrum in *Figure 2b* does not differ much from that in *Figure 2a*, with many free vinyl groups still remaining intact.

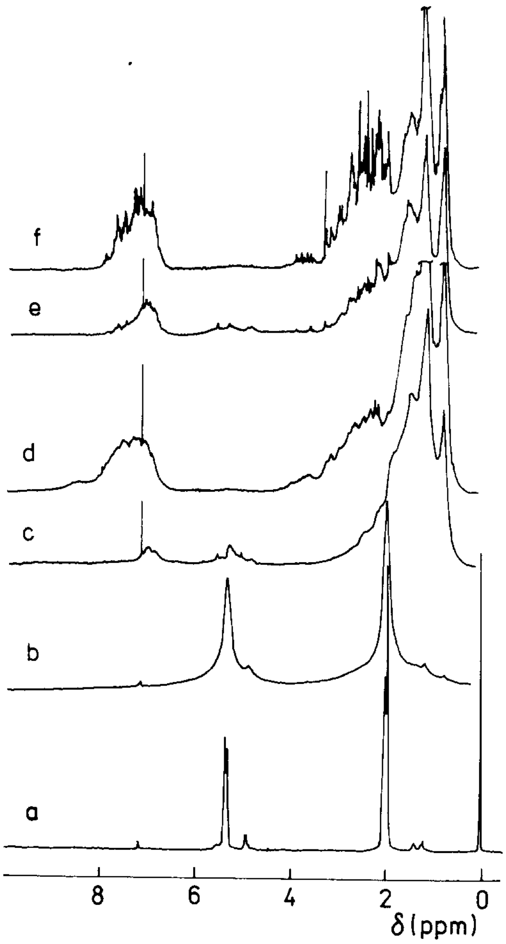

Figure 2 300 MHz high resolution ^1H n.m.r. spectra of condensed solid (S) and liquid (L) products of thermal degradation of polybutadiene (10% w/v in $CDCl_3$ with HMDS, spectral width 6 kHz, 30° pulse, pulse repetition time 2.7 s). Heating temperature (°C)/time (h): (a) original PB; (b) 200/4S; (c) 300/0.5S; (d) 500/4S; (e) 500/0.5L; (f) 500/2L

Characteristic is the appearance of a new weak band at 0.85 ppm, assigned to methyl groups in saturated structures[3,4]. The sample heated to 250°C for 2 h does not swell sufficiently for conventional ^1H n.m.r. measurement. Analysis of the solid state and magic angle spinning n.m.r. spectra of these samples is the subject of part 2 of this work[16].

The samples heated to 300°C and above are soluble and therefore can be analysed by conventional n.m.r. methods. After only 0.5 h of heating at 300°C, the character of the ^1H n.m.r. spectrum changes profoundly (*Figure 2c*); the integrated intensity of olefinic peaks drops to only 2.6% of the total proton spectrum intensity, and adsorption corresponding to 2.5% of total intensity appears in the aromatic range at ~7 ppm. The spectrum is dominated by a broad band in the aliphatic range, with little fine structure and only two pronounced sharp peaks, at 0.85 and 1.25 ppm. With prolonged heating time the content of olefinic protons further decreases, and that of aromatic protons increases. The centre of the aromatic peak lies above the sharp peak of residual $CHCl_3$ at 7.2 ppm, and thus predominantly corresponds to isolated aromatic rings.

According to ^1H n.m.r. analysis, by heating to 500°C (*Figure 2d*), the content of olefinic protons in the solid products gradually drops to zero, and the content of aromatic protons increases to 13% of total H. The centre of the aromatic peak shifts to lower field, indicating an increasing proportion of structures with condensed aromatic rings. At the same time, the broad aliphatic band begins to split into a multitude of sharp peaks, indicating the presence of a great number of various low-molecular compounds.

^{1}H n.m.r. analysis of the liquid products of heating PB at 500°C (*Figure 2e, f*) likewise indicates an increased fraction of aromatic structures. In contrast to the solid products of heating at the same temperature, the absorption in the olefinic proton range has not completely disappeared. In both the aliphatic and the aromatic range the spectrum shows an enormous number of sharp peaks, indicating decomposition into a very large number of low-molecular compounds.

Conclusions

According to our i.r. and n.m.r. analysis, the process of thermal degradation of PB in inert atmosphere proceeds in several distinct stages. (1) Up to 250°C, the dominating process is crosslinking, with preferential consumption of vinyl groups; even after prolonged heating, the PB molecule still dominates the spectral characteristics. (2) At 300°C, the activation energy needed for a breakdown of the polymer molecule is reached. The effect is quite dramatic, because after only 0.5 h at 300°C, the product becomes soluble, the content of olefinic hydrogens drops to a mere 2.6%, and aromatic structures begin to appear. According to ^{1}H n.m.r., most of the material consists of a great number of saturated structures, still of oligomeric character at this stage. The picture is qualitatively the same at 400°C. (3) At 500°C, a further limit is reached: the broad n.m.r. bands are split into a multitude of sharp peaks indicating degradation to low-molecular level. Many new peaks assignable to substituted aromatic rings appear in the i.r. spectrum, and ^{1}H n.m.r. indicates the presence of compounds with condensed aromatic rings. Nevertheless, the spectral pattern of a mixture of saturated compounds still dominates both the i.r. and ^{1}H n.m.r. spectra of the products of degradation at 500°C.

To summarize, it may be stated that the composition of the solid and condensed liquid products of thermal degradation of PB depends on temperature and time. By prolonged heating at a lower temperature, products comparable to those obtained at higher temperature cannot be generated. Making use of the specific sensitivity of i.r. spectra to the presence of some of the degradation products, it is possible to assess both the temperature and duration of the heat treatment to which the sample has previously been subjected, from a comparison of the peak intensities and their ratios for selected peaks (provided that the spectrum of the original polymer is known), even when only the degradation products that are solid or liquid at ambient temperature are available.

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