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THERMAL DEGRADATION OF COPOLYMERS OF BUTADIENE AND ACRYLONITRILE

N. GRASSIE and A. HEANEY
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

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Abstract—Ten copolymers of butadiene and acrylonitrile have been prepared covering the composition range 100–25 mole % butadiene; reactivity ratios are $r_{\mathrm{butadiene}} = 0{\cdot}50$, $r_{\mathrm{acrylonitrile}} = 0{\cdot}07$. The thermal analysis techniques (TVA, TGA and DSC) have been applied to determine the general features of the thermal degradation of these copolymers. The fractions of products comprising permanent gases, products volatile at 20°, chain fragment material and residue have been separated and analysed. The constituent parts of the overall reaction have been discussed and the whole represented in the form of an integrated reaction mechanism.

Copolymers and polymer and copolymer blends incorporating two or all three of the monomers: acrylonitrile, butadiene, and styrene, have become important commercial materials. It is therefore important to have information about their stability towards the various degradative agencies. A description of the thermal degradation of copolymers of styrene and acrylonitrile has been given [1]; this paper extends this work to the butadiene–acrylonitrile copolymer system.

EXPERIMENTAL

Purification of materials

1,3-Butadiene (Air Products Ltd.) was purified by distillation (three times) under vacuum, the first and last 10 per cent being discarded at each distillation. Acrylonitrile (Hopkin & Williams Ltd.) was purified by washing with 10% NaOH to remove inhibitor, repeatedly with water to remove NaOH, drying over CaH_2 and twice distilling under vacuum. The initiator 2,2′-azoisobutyronitrile was purified by recrystallization from alcohol.

Preparation of copolymers

Chosen volumes of purified monomers were distilled under vacuum into dilatometers containing 1 per cent w/v of initiator. Polymerizations were carried out in bulk at 60° to approx. 5 per cent conversion. The polymer was precipitated by pouring the polymerization mixture into a large volume of methanol, purified by repeated soaking and pressing in methanol followed by drying at 60° under vacuum for 5 days. Thereafter, copolymers were stored in the dark under nitrogen at −18°.

Analysis of copolymers

Ten copolymers were prepared covering the entire composition range and copolymer compositions were calculated from elemental analyses determined using a Perkin–Elmer 240 Elemental Analyser. Molecular weights of copolymers soluble in toluene were measured using a Mechrolab 501 High Speed Membrane osmometer. Composition and molecular weight data are presented in Table 1.

Thermal analysis

The Thermal Volatilization Analysis (TVA) technique has been devised and described in detail by McNeill [2]. A polymer sample is heated in vacuum under temperature programmed conditions at 10°/min from room temperature

Table 1. Copolymer composition and molecular weight data

Butadiene (mole %)		Elemental analysis				
Polymer	Feed	C (%)	H (%)	N (%)	Total	$\overline{M}_n$
100	100	88·68	11·02	—	99·70	18.000
89	92·8	86·76	10·51	2·76	100·03	17.500
80	85·9	84·77	10·14	5·17	100·08	20.000
75	80·0	83·69	9·88	6·49	100·06	21.700
66	68·3	81·76	9·19	8·81	98·76	27.000
52	34·1	78·81	8·61	12·84	99·90	—
41	11·5	76·39	7·96	15·50	99·95	—
33	6·4	74·37	7·61	17·70	99·68	—
30	4·5	73·88	7·39	18·35	99·62	—
25	2·0	73·18	7·14	19·86	100·13	—

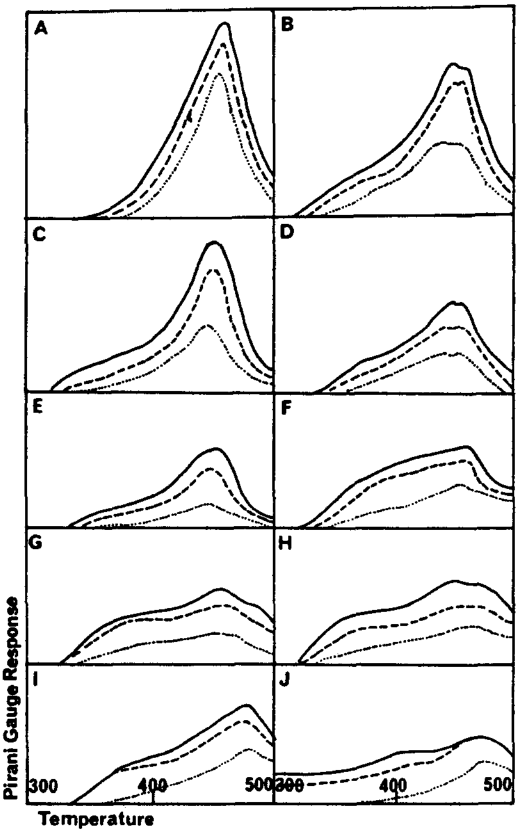


Fig. 1. TVA thermograms of homopolymers and copolymers. ——, 0° trace: ----, −75° trace; ······ −196° trace. (A, Polybutadiene; B, 89% butadiene; C, 80%; D, 75%; E, 66%; F, 52%; G, 41%; H, 33%; I, 25%; J, polyacrylonitrile).

to 500°. The gaseous products are divided into four streams which pass through traps at 0°, −45°, −75° and −100°, and are finally recombined into a single stream which passes through a trap at −196°. The pressures of gas passing through each trap are monitored by Pirani gauges, the outputs from which are continuously recorded as a single thermogram. Direct comparison of the five curves thus gives an immediate picture of the distribution of products volatile at room temperature in terms of their volatilities at the trap temperatures. The −45° and −100° traces are omitted from the thermograms in Fig. 1 for the sake of clarity, and because they contribute nothing additional to the discussion. The results are only qualitative since the Pirani gauge response is not linear with pressure. Products volatile at degradation temperatures but involatile at room temperature condense just outside the furnace and are not recorded.

The Du Pont 900 and 950 instruments were used for Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Enthalpies of degradation were calculated from DSC thermograms by the standard methods set out in the Du Pont handbook supplied with the DSC module.

Degradation techniques and separation of products

Degradations were performed using the "sealed tube" technique previously described in detail [1]. Essentially this is a technique in which polymer is degraded in a closed tube in vacuum with the facility to separate the products into a number of fractions which are thus available for more detailed analysis. In the present instance, the fractions were as follows: (1) gases non-condensible at −196°; (2) products gaseous at 20°; (3) products liquid at 20°; (4) chain fragments volatile at degradation temperatures but involatile at 20°; (5) involatile residue.

From all polymers and copolymers at all extents of reaction, the predominating product was always the chain fragment fraction. This fraction was very susceptible to oxidative attack as demonstrated by the rapid appearance of i.r. bands due to oxygen-containing structures. Analyses were therefore carried out immediately after separation. The products gaseous at 20° increased with the acrylonitrile content of the copolymer, but were never more than 3–4 per cent of degradation products; permanent gases were present only in trace amounts while no significant amount of products liquid at 20° was ever detected. Details are given in Table 2.

Spectral measurements

Infra-red spectra were obtained using a Perkin–Elmer 275 double beam grating spectrometer, the gaseous products in a 10-cm cell, the chain fragments by smearing a thin film between NaCl plates and the residue by means of the KCl disc technique.

A Unicam SP 800 was used for measurement of u.v. spectra and mass spectra were obtained by means of an A.E.I. MS 12 instrument.

Gas–liquid chromatography

Permanent gases were separated at room temperature using a Gallenkamp chromatograph with thermal conductivity detector. Otherwise a Microtek GC 2000R instrument fitted with a temperature programmer and flame ionization detector was used. In each case, silica gel columns were found appropriate.

RESULTS

Reactivity ratios

Published values of reactivity ratios for this system are conflicting. Values were therefore deduced from the monomer feed and copolymer composition data in Table 1 using the method of Fineman and Ross [3]. The copolymer composition equation may be written in the two forms,

$$(N_1 - 1)/X_1 = r_1 - r_2(N_1/X_1^2) \qquad (1)$$

and

$$(N_2 - 1)/X_2 = r_2 - r_1(N_2/X_2^2), \qquad (2)$$

in which N_1 and X_1 are the monomer feed and copolymer composition ratios, normally written M_1/M_2 and $d(M_1)/d(M_2)$, and r_1 and r_2 are the reactivity ratios. N_2 and X_2 are equal to $1/N_1$ and $1/X_1$, respectively. Thus values of the reactivity ratios may be obtained from the slopes of the plots in Figs. 2 and 3 which are more accurate than the values obtained from the intercepts. These values are compared in Table 3 with others which have been obtained previously and are seen to agree favourably with values obtained recently for the copolymerization in solution in dimethyl formamide.

Table 2. Degradation of copolymers of butadiene and acrylonitrile at 390°

Copolymer (% butadiene)	Time	Residue	Products (% by wt)			Mole ratio
			Chain fragments	NH_3	HCN	NH_3/HCN
100	0·5	87·5	16·1	—	—	—
	1	76·0	17·0	—	—	—
	2	68·4	25·7	—	—	—
	3	52·2	31·1	—	—	—
	4	52·0	49·2	—	—	—
	5	42·5	51·8	—	—	—
	6	37·4	51·8	—	—	—
	7	30·3	68·5	—	—	—
80	0·5	76·4	21·3	0·75	0·27	4·4
	1	63·8	27·5	0·66	0·23	4·5
	2	47·5	47·0	0·99	0·44	3·5
	3	41·6	52·4	1·03	0·57	2·9
	4	33·4	62·1	0·85	0·40	3·4
	5	21·5	74·0	1·06	0·865	2·0
	6	29·6	72·0	0·98	0·761	2·0
	7	21·4	71·9	1·19	0·48	3·9
66	0·5	65·0	28·5	1·18	0·57	3·3
	1	48·5	47·5	1·19	0·90	2·1
	2	34·7	72·3	1·78	1·75	1·6
	3	35·8	67·8	1·97	1·60	1·9
	4	16·7	76·4	2·07	1·96	1·7
	5	20·2	74·1	2·19	2·11	1·7
	6	16·4	69·9	2·54	2·22	1·8
	7	19·0	72·5	2·20	1·92	1·8
41	0·5	52·4	49·0	3·75	2·69	2·2
	1	37·2	56·0	4·52	3·61	2·0
	2	25·3	68·6	4·38	3·42	2·0
	3	23·5	76·5	4·84	4·03	1·9
	4	23·3	70·4	5·16	4·12	2·0
	5	21·5	70·9	5·11	3·89	2·1
	6	19·1	69·4	4·65	3·86	1·9
	7	19·7	74·4	5·28	4·48	1·9
25	0·5	34·2	61·0	3·69	3·86	1·5
	1	29·0	63·0	3·28	3·03	1·7
	2	27·2	65·4	3·52	3·56	1·6
	3	31·0	65·1	3·29	2·38	2·2
	4	32·3	60·9	3·91	2·75	2·3
	5	22·2	78·3	3·64	2·87	2·0
	6	21·3	72·6	3·82	3·39	1·8
	7	23·8	68·6	4·21	3·62	1·9

Table 3. Reactivity ratios for the butadiene/acrylonitrile system

$r_{\text{butadiene}}$	$r_{\text{acrylonitrile}}$	Temp.	Conditions	Ref.
0·18	0·03	5	Emulsion oil phase	[4]
0·28	0·02	5	Emulsion water phase	[4]
0·35	0·0	50	Bulk	[5]
0·35	0·05	50	Emulsion	[6]
0·46	0·0	50	Emulsion	[7]
0·33	0·25	60	Emulsion	[8]
0·1	0·06	40	Radiation grafting	[9]
0·3	0·02	40	Radiation grafting	[9]
0·58	0·067	60	Solution (DMF)	[10]
0·50	0·07	60	Bulk	Present work

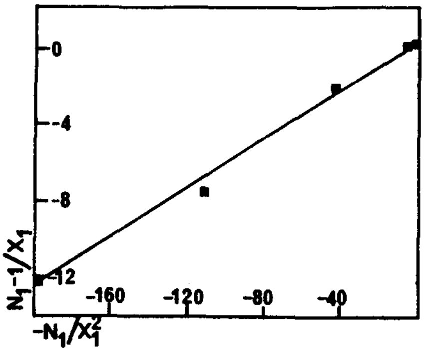


Fig. 2. Fineman–Ross plot for $r_{\text{acrylonitrile}}$.

Thermal analysis

TVA thermograms for the whole range of copolymer compositions are illustrated in Fig. 1. It should be emphasized that TVA records only the more volatile products and gives no evidence of the large fraction of short chain fragments ("cold ring") which are involatile at 0° which is the highest TVA trap temperature. In the thermogram of polybutadiene (A), the lack of coincidence of the traces indicates a mixture of products with a range of volatilities. Concurrent production of these products is indicated by the occurrence at the same temperature of the rate maximum of each trace. This breakdown pattern is like that of polyethylene and similar polymers [2]. The peak is really a doublet which persists even in 75% butadiene copolymer. The − 196° trace indicates a high proportion of permanent gases like methane and hydrogen.

In the 89% butadiene copolymer (Fig. 1B), the rate of production of volatile products is somewhat less. A broad shoulder has appeared at lower temperature which, by reference to Fig. 1J, is to be associated with the acrylonitrile component. The proportion of permanent gas is still high, although less than for polybutadiene. These trends continue with increasing acrylonitrile content until, with 52% butadiene, the broad thermogram has no well-defined maxima. With further increase in acrylonitrile content, the thermogram becomes progressively more like that of pure polyacrylonitrile.

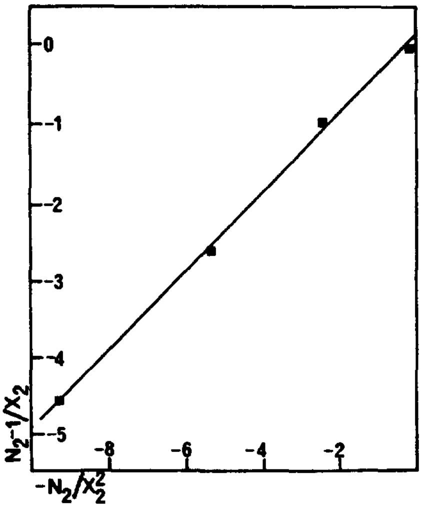


Fig. 3. Fineman–Ross plot for $r_{\text{butadiene}}$.

In pure polyacrylonitrile, the high rate of volatilization even at 300° is due to the violent reaction associated with the nitrile group polymerization which occurs at 250° and which is eliminated by the incorporation of only a few per cent of comonomer [11]. Nevertheless, the presence of acrylonitrile units does have a destabilizing effect since there is a lowering of almost 30° in the temperature at which volatile products appear on passing progressively from polybutadiene to butadiene copolymer.

The polybutadiene and 89% butadiene copolymer leave no significant residue after the TVA runs are complete. The remaining copolymers leave increasing amounts of residue which changes from dark brown solids for the 80% and 75% butadiene copolymers to black chars from copolymers richer in acrylonitrile. The involatile chain fragments, which condense on the cooler parts of the reaction tube, vary from pale yellow from butadiene to dark red from the 25% butadiene copolymer. The colour is associated with conjugated structures, especially in the acrylonitrile units, in the residue and chain fragments.

TGA thermograms have been obtained for all the copolymers and those presented in Fig. 4 illustrate the general trends. They confirm the destabilizing effect of acrylonitrile revealed by TVA, and the concurrent stabilization of the residues at 500°.

DSC thermograms confirm these trends and enthalpies of the degradation process were calculated. These are related to copolymer composition in Fig. 5. The increase with butadiene content is consistent with the increase in fragmentation and volatilization evidenced by the decrease in the amount of residue.

These thermal analyses suggest that temperatures in the range 350–400° are suitable for studying the degradation reaction under isothermal conditions.

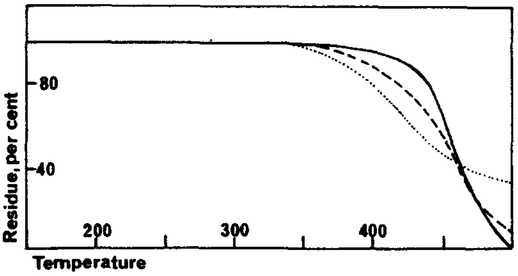


Fig. 4. TGA thermograms for, ——, polybutadiene; ----, 52% butadiene copolymer; ······, 25% butadiene copolymer.

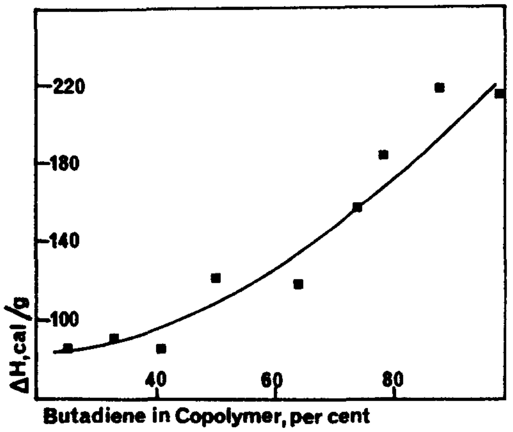


Fig. 5. Enthalpies of degradation calculated from DSC thermograms.

Identification and analysis of products

Permanent gases. Infra-red spectra of the permanent gas fraction from a number of the copolymers degraded for 7–24 hr within the temperature range 350–400° showed peaks only at 3018 and 1304 cm^{-1} with accompanying rotational bands, characteristic of methane. Two components were revealed by GLC and identified as hydrogen and methane by comparison of the peak retention times with those of pure samples of these gases.

Products volatile at 20°. Infra-red, GLC and mass spectrometry were used to identify products volatile at 20° from the whole range of copolymers degraded at 350–400°. A typical i.r. spectrum is illustrated in Fig. 6. By comparison with the spectra of pure compounds, it is clear that the major peaks at 3337, 1629, 960 and 930 cm^{-1} and the accompanying rotational bands are due to ammonia and complex peak formations in the regions 3400–3200, 1500–1300 and 800–650 cm^{-1} to hydrogen cyanide. The existence of some aliphatic material is indicated by absorption in the 3100–2800 cm^{-1} region.

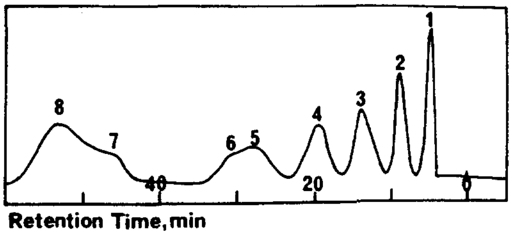


Fig. 7. GLC trace of products volatile at 20° obtained by degradation of a 52% butadiene copolymer at 400° for 7 hr. 1, Methane; 2, ethane; 3, ethylene; 4, propane; 5, propylene; 6, butane; 7, butene; 8, butadiene.

A typical GLC trace of this product fraction is illustrated in Fig. 7. The flame ionization detector was not sensitive to ammonia; hydrogen cyanide was retained on the column. Thus the trace records the hydrocarbon gases which were identified by comparing the retention times with those of known pure compounds. The use of mass spectrometry for the analysis of complex hydrocarbon mixtures is not particularly profitable but mass spectra of this fraction from the whole range of copolymer compositions indicates that most of the constituents are within the range C_1–C_4, although small peaks up to $m/e = 100$ indicate traces of hydrocarbons up to C_7.

These hydrocarbon gases comprise about one-tenth of this fraction but no detailed quantitative analysis has been attempted.

Ammonia and hydrogen cyanide were estimated quantitatively by standard i.r. spectroscopic methods. The peak at 1175 cm^{-1} was used for the estimation of ammonia. For the products from copolymers containing 80 and 66% butadiene, the peak at 726 cm^{-1} was used for the measurement of hydrogen cyanide.

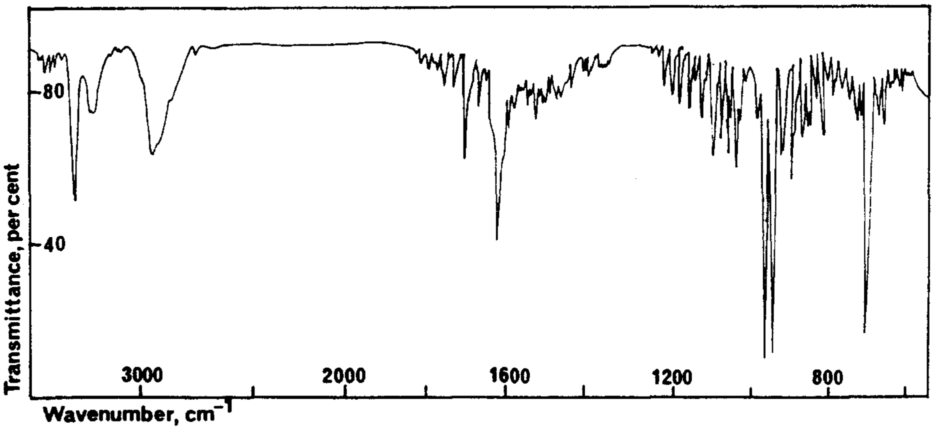


Fig. 6. Infra-red spectrum of products volatile at 20° obtained by degradation of a 52% butadiene copolymer at 352° for 7 hr.

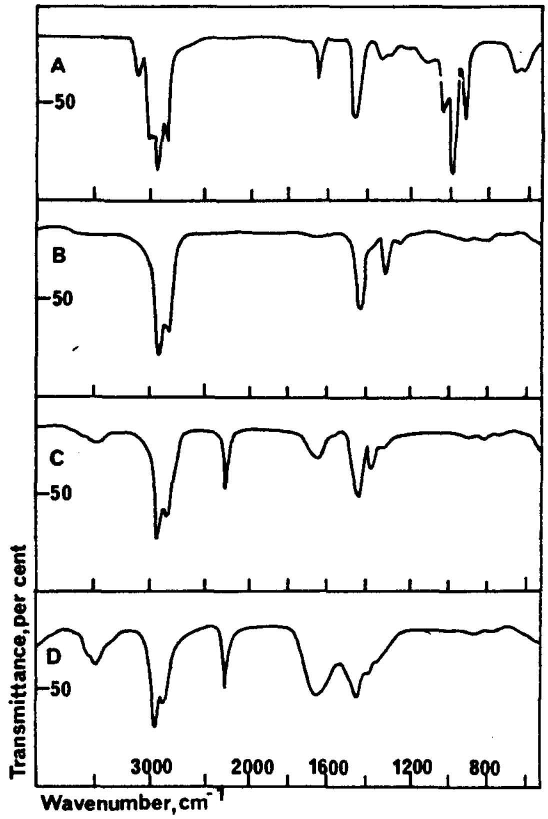


Fig. 8. Infra-red spectra of chain fragments resulting from degradation at 390°. A, Polybutadiene, 7 hr; B, 52% butadiene copolymer, 7 hr; C, 41% butadiene copolymer, 1 hr; D, 25% butadiene copolymer, 1 hr.

However, the optical density at this frequency was too high in the case of the 41 and 25% butadiene copolymers for which the 713 cm^{-1} peak was used. Calibration curves relating pressure to optical density were prepared for pure samples of each gas and ammonia and hydrogen cyanide pressures estimated by applying them to the spectra of the product gases. The absolute amounts of ammonia and hydrogen cyanide were finally calculated knowing the volume of the system and are recorded in Table 2.

Products liquid at 20°. No significant amounts of products liquid at room temperature were obtained from polybutadiene or any of the copolymers. It must be assumed that amounts of hydrocarbons larger than C_4 were so small that they were completely volatile under the conditions of reduced pressure in which the separation into fractions was made. Even in the 75% acrylonitrile copolymer, acrylonitrile and acetonitrile and vinyl acetonitrile [12] (products characteristic of the degradation of polyacrylonitrile) could not be identified.

Chain fragment material. The major proportion of degradation products consists of "cold ring" or chain fragment material. From polybutadiene, this fraction is light yellow and has a molecular weight of 353. With increasing acrylonitrile in the copolymer, the molecular weight remains fairly constant, although the colour deepens. Ultraviolet spectral measurements indicate, however, that there is no change in the nature of the chromophore.

Infra-red spectra of chain fragments are shown in Fig. 8. Comparing these with the spectrum of undegraded polybutadiene in Fig. 9A, it is clear that the chain fragments have lost most of the *cis*-1,4 unsaturation (750–650 cm^{-1}) and that there is a marked reduction in the intensity of peaks at 962 and 908 cm^{-1} due to *trans*-1,4 and 1,2(vinyl) structures, respectively.

These changes in the pattern of unsaturation have already been discussed separately in greater detail [13], since it is felt that they do not play a significant part in the decomposition reactions under discussion. Increased relative absorption at 1372 cm^{-1} indicates an increase in the concentration of methyl groups, providing evidence for hydrogen transfer reactions during degradation.

In the chain fragment fractions from the copolymers, nitrile absorption remains at 2240 cm^{-1}, but new absorptions occur at 3600, 3470, 3380, 3210, 2185, 1700–1550 and 820 cm^{-1}. The 2185 cm^{-1} band also

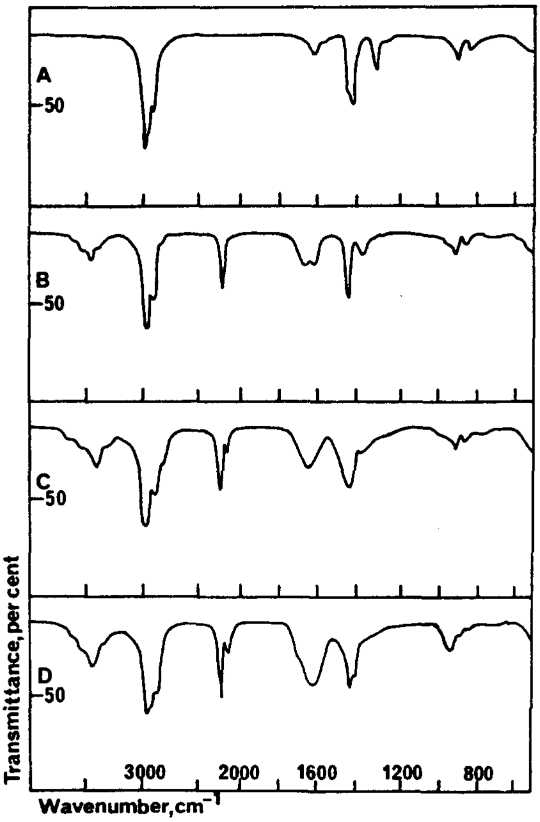


Fig. 9. Infra-red spectra of residues after degradation at 390°. A, Undegraded polybutadiene; B, polybutadiene, 6 hr; C, 80% butadiene copolymer, 4 hr; D, 41% butadiene copolymer, 6 hr.

appears in the cold ring fraction from the degradation of polyacrylonitrile and has been assigned to unsaturated nitriles [11], although the frequency is lower than that normally associated with these structures (2240–2210 cm^{-1}). Iminonitriles or aminosubstituted unsaturated nitriles have been proposed [11], since these structures exhibit reduced nitrile frequencies in the i.r. [14]. The N—H bands above 3000 cm^{-1} and the absorption in the 1700–1550 cm^{-1} region can also be explained in terms of these structures. The broad and weak absorption at 820 cm^{-1} indicates the presence of some trisubstituted olefinic structures, although this absorption is not well defined and does not appear in the spectrum of the chain fragments from butadiene. Unsuccessful attempts were made to separate the constituents of these chain fragment fractions using gel permeation chromatography.

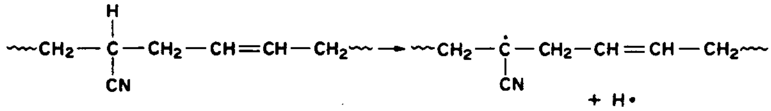
Residue. Large amounts of residue always remained after degradation at 350–400°. It was insoluble and brittle even at low extents of degradation and pale yellow to black depending upon extent of degradation and acrylonitrile content. Some typical i.r. spectra are presented in Fig. 9. In each case, unsaturation has almost disappeared in the residues although the weak absorptions at 870 and 820 cm^{-1} indicate exomethylene and trisubstituted olefinic structures, respectively. Increase in methyl absorption at 1372 cm^{-1} occurs as in the chain fragments (Fig. 8).

The peaks at 2185 and 3210 cm^{-1} which appear in the spectra of chain fragments from high acrylonitrile copolymers are not present in the spectra of the corresponding residues. It is possible that the structure responsible results directly from a scission reaction, or that these structures, once formed in the polymer, provide weak points for scission with retention of structural identity. On the other hand, these structures may represent the first stage of a two-stage process which has gone to completion in the residue but not in the chain fragments due to their volatilization away from the hot zone.

DISCUSSION

The general features of the degradation reaction over the whole copolymer composition range are reminiscent of the behaviours of the pure homopolymers. Thus the major volatile product is always the chain fragment fraction (as in both homopolymers) together with very much smaller amounts of low molecular weight hydrocarbons (as from polybutadiene) and ammonia and hydrogen cyanide (as from polyacrylonitrile). It is interesting, however, to consider some of the characteristic changes which occur as the composition of the copolymer is changed.

The thermal analysis data in Figs. 1 and 4 show that the threshold degradation temperature is lowered by the introduction of acrylonitrile units into polybutadiene. This is most probably to be associated with the introduction into the polymer molecule of tertiary hydrogen atoms, the tertiary carbon—hydrogen bond being further weakened by the pressure of nitrile unsaturation in the α position.

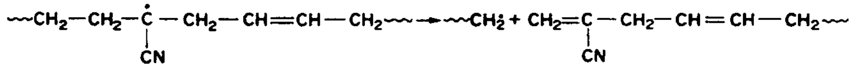


$${\sim}CH_2-\underset{CN}{\overset{H}{C}}-CH_2-CH=CH-CH_2{\sim} \rightarrow {\sim}CH_2-\underset{CN}{\dot{C}}-CH_2-CH=CH-CH_2{\sim} + H\cdot$$

(I)

Thus initiation of the overall radical degradation sequence is facilitated. Table 2 tends to confirm this common initiation process since the principal products are obviously formed simultaneously rather than concurrently.

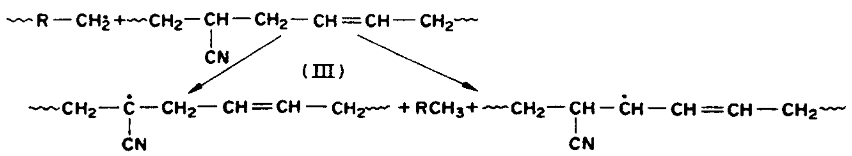
The tertiary radical thus formed should then be expected to undergo chain scission of the type



$${\sim}CH_2-CH_2-\underset{CN}{\dot{C}}-CH_2-CH=CH-CH_2{\sim} \rightarrow {\sim}CH_2^{\cdot} + CH_2=\underset{CN}{C}-CH_2-CH=CH-CH_2{\sim}$$

(II)

which will ultimately lead to chain fragments. The radical thus formed should be expected to undergo transfer reactions with reactive hydrogen atoms, thereby accounting for the appearance of methyl absorption in the i.r. spectra of residue and chain fragments. The most reactive centres are the tertiary hydrogen atoms on the acrylonitrile groups and the methylene groups in the α position with respect to the butadiene unsaturation,

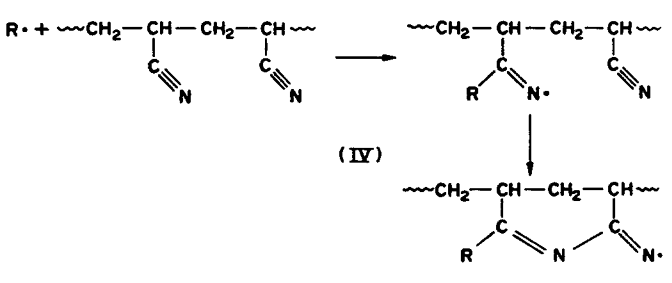


$${\sim}R-CH_2^{\cdot} + {\sim}CH_2-\underset{CN}{CH}-CH_2-CH=CH-CH_2{\sim}$$

$${\sim}CH_2-\underset{CN}{\dot{C}}-CH_2-CH=CH-CH_2{\sim} + RCH_3 + {\sim}CH_2-\underset{CN}{CH}-\dot{C}H-CH=CH-CH_2{\sim}$$

(III)

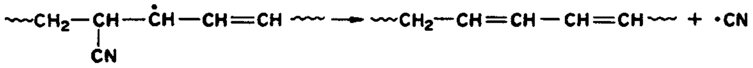
Alternatively, chain terminal radicals or hydrogen atoms or other small radicals in the system may react with nitrile groups, as proposed by Grassie and McGuchan [11], to initiate the polymerization of nitrile groups which is the characteristic reaction leading to thermal coloration in polyacrylonitrile



(IV)

and accounts, at least in part, for the colour which develops in chain fragments and residue and which deepens with increasing acrylonitrile content of the copolymer.

The two radicals produced in reaction (III) should be expected to undergo further scission, as in reaction (II), but the most probable source of hydrogen cyanide may be further decomposition of the second of these radicals in a reaction analogous to that which is believed to occur in the thermal decomposition of poly(vinyl chloride) and which results ultimately in the evolution of hydrogen chloride.

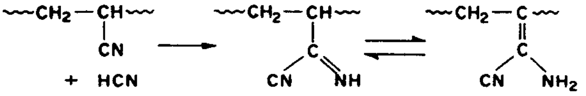


$$\sim CH_2-\underset{CN}{CH}-\dot{C}H-CH=CH\sim \longrightarrow \sim CH_2-CH=CH-CH=CH\sim + \cdot CN$$

(V)

the nitrile radical abstracting a hydrogen atom elsewhere in the system [reaction (VI)].

Although HCN and NH_3 are the principal volatile products of the thermal degradation of polyacrylonitrile, it has never been possible to formulate a satisfactory mechanism for the production of the latter. However, as in the present system, they are always produced simultaneously and it has been suggested that the HCN reacts with nitrile groups to form an α-iminonitrile structure or the corresponding tautomeric form



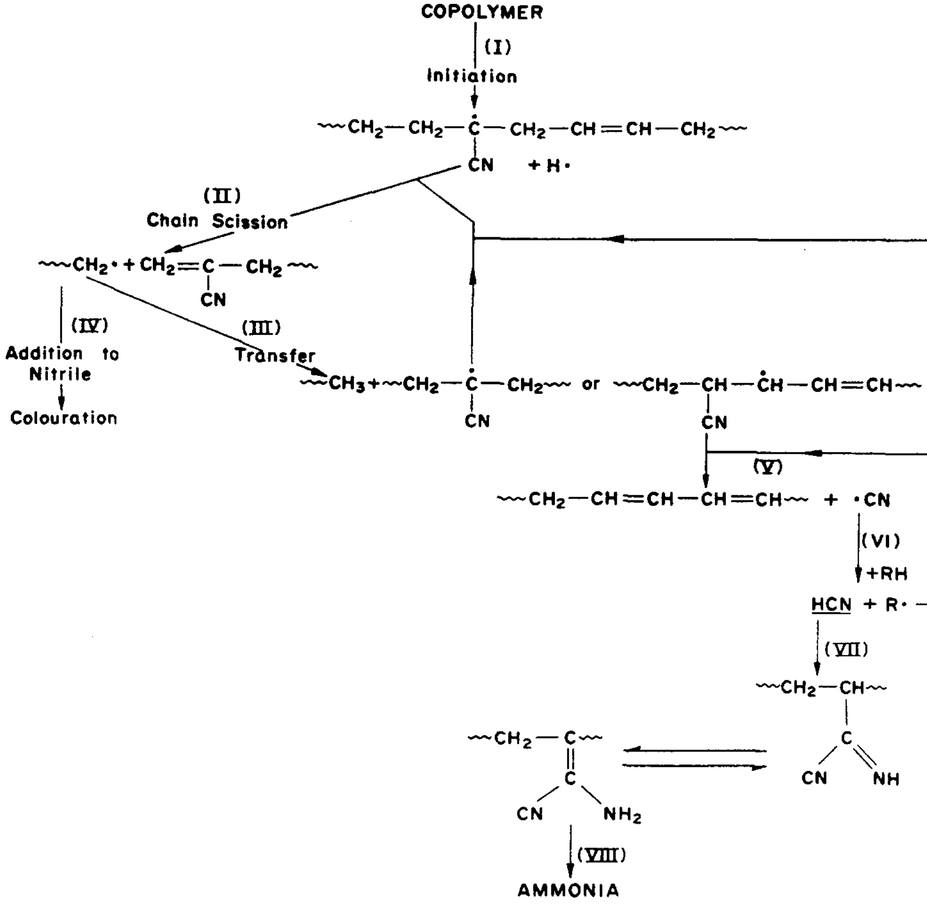
(VII)

decomposition of the latter producing NH_2 radicals and ultimately ammonia by transfer of a hydrogen atom [reaction (VIII)].

Reaction (VII) would also account for the i.r. absorption at 2185 cm^{-1} which is found in the chain fragments and which has been attributed to amino substituted unsaturated nitriles [11]. This mechanism for the production of unsaturated nitriles and ammonia is further supported by the fact that absorption at 2185 cm^{-1} is not observed in the residue. Thus the relatively labile amino substituted unsaturated nitrile structure would be rapidly decomposed at the relatively high temperature of the residual polymer in the reaction zone, but would be at least partially preserved when fragments evaporate to cooler portions of the reaction vessel.

Table 2 demonstrates that over the copolymer composition range, with the possible exception of the 80% butadiene copolymer, the molar ratio NH_3/HCN is 2 within experimental error. It has not been possible to account for this in precise mechanistic terms but it does suggest a close link between NH_3 and HCN production of the type suggested. The higher value of the ratio, particularly in the early stages of the decomposition of the 80% butadiene copolymer, may be due to greater experimental error as a result of the smaller quantities available for analysis.

These various suggested constituent processes may be represented in the form of an integrated reaction mechanism as follows:—



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Résumé—On a préparé dix copolymères de butadiène et d'acrylonitrile couvrant le domaine de compositions 100–25% molaires de butadiène; les taux de réactivité sont: $r_{\text{butadiène}} = 0{,}50$, $r_{\text{acrylonitrile}} = 0{,}07$. On a appliqué diverses techniques d'analyse thermique (TVA, TGA, et DSC) pour déterminer les caractéristiques générales de la dégradation thermique de ces copolymères. On a séparé et analysé des fractions de produits comprenant des gaz permanents, des produits volatiles à 20°, des fragments de chaîne du produit et le résidu. On discute les différentes étapes de la réaction et l'ensemble des résultats est intégré dans un mécanisme de réaction global.

Sommario—Si sono preparati 10 copolimeri di butadiene e acrilonitrile per la gamma di composizioni 100–25 mole % butadiene. I rapporti di reattività sono: $r_{\text{butadiene}} = 0{,}50$, $r_{\text{acrilonitrile}} = 0{,}07$. Si sono applicate le tecniche di analisi termica (TVA, TGA e DSC) per determinare le caratteristiche generali della degradazione termica di tali copolimeri. Si sono separate ed analizzate le frazioni di prodotti compresi gas permanenti, prodotti volatili a 20°, frammenti di catena e residui. Si sono discusse le parti costituenti della reazione complessiva e il tutto rappresentato sotto forma di meccanismo di reazione integrato.

Zusammenfassung—Hergestellt wurden 10 verschiedene Copolymere aus Butadien und Acrylnitril im Bereich der Copolymerzusammensetzung von 100 bis 25 Mol-% Butadien. Die r-Parameter für die Copolymerisation sind $r_{\text{Butadien}} = 0{,}50$, $r_{\text{Acrylnitril}} = 0{,}07$. Verschiedene thermische Untersuchungsmethoden (TVA, TGA und DSC) wurden angewandt, um das allgemeine Verhalten der Copolymeren beim thermischen Abbau zu untersuchen. Die dabei aufretenden Spaltprodukte bestehend aus Gasen, bei 20° flüchtigen Produkten, Kettenspaltprodukte und Rückstände wurden getrennt und analysiert. Aufgrund der Informationen aus diesen Spaltprodukten wird ein Mechanismus für den Abbaumechanismus des Copolymeren aufgestellt.