

PYROLYSIS-GAS CHROMATOGRAPHY OF BUTADIENE CO-POLYMERS

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SUMMARY

Pyrolysis-gas chromatographic investigations have been carried out on five kinds of butadiene (BD) co-polymers with a Curie-point pyrolyzer. In the pyrolysates, the yield of vinylcyclohexene (VCH) formed from successive BD units in the co-polymer shows the different sequential structures of these co-polymers. Assuming that the probability of the BD unit in the center of each triad degrading to products other than BD and VCH is constant, the VCH/BD molar ratio, Q , is related to the run number, R , and the BD mole%, X , in the equation $Q = [k_1(X - R/2)^2 + k_2R(X - R/2)] / [(1 - k_1)(X - R/2)^2 + (1 - k_2)R(X - R/2) + R^2/4]$. The run number of each co-polymer is then calculated by means of Q and X obtained from the pyrogram.

With progress in polymerization techniques, many polymers having controlled sequential structures have been produced. Some of these polymers have specific properties resulting from their unique microstructures. Typical examples are the alternating vinyl co-polymers. The alternating isobutylene-alkyl acrylate co-polymer is superior to acrylic rubbers in its resistance to hydrolysis and heat [1]. Further, the alternating styrene-acrylonitrile co-polymer has a high softening point and excellent mechanical properties compared with the random co-polymers [2]. It is therefore important to investigate the microstructures of polymers. Pyrolysis-gas chromatography (p.g.c.) is one of the most powerful methods for the investigation of microstructures; p.g.c. has been applied successfully to the analysis of chain branching in polyethylene or poly(vinyl chloride) and shown to be an effective method of determining the short-chain branch content [3, 4].

The pyrolysis-gas chromatographic behaviours of polybutadienes [5] and butadiene-acrylonitrile [6] co-polymers have been reported. In this work, the relationships between the pyrolysis products and the microstructures for butadiene co-polymers (co-monomer = acrylonitrile, methacrylonitrile, methyl methacrylate, methyl acrylate, and methyl vinyl ketone) were investigated by p.g.c. and the run number of each co-polymer was evaluated.

EXPERIMENTAL

Materials

Alternating co-polymers of butadiene (BD) with methyl methacrylate (MMA) [7], methyl vinyl ketone (MVK) [8], methyl acrylate (MA) [9],

methacrylonitrile (MAN) [10] , and acrylonitrile (AN) [10] were synthesized by complexed co-polymerization with Lewis acids. Random co-polymers with different composition were prepared in low yield by radical polymerization with azobisisobutyronitrile as initiator.

Table 1 shows the co-polymer compositions calculated from elemental analysis.

Apparatus

A Curie-point pyrolyzer (Nippon Bunseki Kogyo JHP-2) was coupled directly to a gas chromatograph (Shimazu GC-4BM) equipped with a dual flame-ionization detector. Samples of 30-60 μ g and a stainless steel column (2 m X 3 mm i.d.) packed with 20% DOP on 60-80 mesh Celite 545 support were used. The column temperature was 80 . The flow rate of nitrogen was 40 ml min⁻¹; the hydrogen and air pressures were 0.5 kg cm⁻² and 1.0 kg cm⁻², respectively. A column (5 cm X 3 mm i.d.) packed with a mixture of K₂CO₃ and Diasolid H (60-80 mesh, 1 + 2, w/w) was placed between the pyrolyzer and the separation column to precut acidic products from nitrile co-polymers.

The peak areas were measured by a digital integrator (Shimazu ITG-4A). Identification of the peaks was carried out by comparison with the retention data of known substances.

TABLE 1

Composition of BD co-polymers
(A: alternating co-polymer, R: random co-polymer.)

Co-polymer	Co-monomer of BD (mole %)				
	MMA-BD	MVK-BD	MA-BD	MAN-BD	AN-BD
A	50.1	53.6	53.0	48.6	50.5
R ₁	5.8	17.8	19.4	26.6	28.0
R ₂	19.3	43.7	24.1	33.0	37.3
R ₃	28.2	51.0	47.2	37.5	42.2
R ₄	30.4	51.5	57.1	41.3	47.3
R ₅	54.8	67.7	61.3	41.4	56.0
R ₆	80.6	92.3		47.6	59.4
R ₇				70.0	
R ₈				71.2	

RESULTS AND DISCUSSION

The BD monomer and the cyclic BD dimer, 4-vinylcyclohexene (VCH), obtained from successive 1,4-BD units are well known as the main pyrolysis products of polybutadienes; the BD units are mostly linked 1,4 in polybutadienes prepared by conventional radical polymerization. The relationship

between the pyrolysis products (mainly VCH, BD, and co-monomer of BD) and the monomer sequence distribution in some co-polymers is reported in this paper.

Pyrogram and composition

Figure 1 shows the pyrograms of MMA-BD co-polymers at the pyrolysis temperature of 590 °C. Under the p.g.c. conditions used, lower hydrocarbons, BD, MMA, and VCH were the main pyrolysis products. There is a difference between the pyrograms of alternating and random co-polymers; the VCH peak is barely detectable in the pyrogram of the alternating co-polymer. Most of the MMA units in MMA-BD co-polymers pyrolyze into MMA monomer as in poly(methyl methacrylate). The yield of MMA at 590 °C was plotted against the MMA content of the co-polymer, where the yield is taken as the MMA mole fraction in the pyrolysis products, i.e., $\text{MMA}/(\text{MMA} + \text{BD} + 2\text{VCH})$ as one mole of VCH corresponds to two moles of BD. A very good linear relationship was obtained; this MMA yield therefore indicates the composition of MMA-BD co-polymers, including the alternating one. From least-squares regression analysis, the regression line of the MMA content of co-polymer (y) on the MMA yield described above (x) was $y = 1.06x - 9.93$, and the error variance (V_{yx}) was 7.02.

The pyrolysis-gas chromatographic behaviour of MAN-BD and MMA-BD co-polymers are closely similar. The yield of MAN, $\text{MAN}/(\text{MAN} + \text{BD} + 2\text{VCH})$, indicated the composition of the co-polymers. In MVK-BD co-polymers, a small quantity of acetone was formed in addition to lower hydrocarbons, BD, MVK, and VCH.

Polyacrylonitrile exhibits complicated pyrolytic reactions, i.e., elimination of hydrogen cyanide or cyclization involving the C-N group. Large quantities

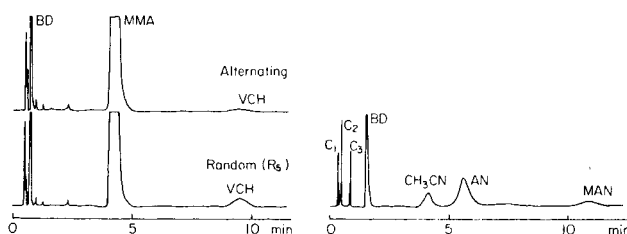


Fig. 1. Pyrograms of MMA-BD co-polymer at 590°C.

Fig. 2. Pyrogram of alternating AN-BD co-polymer with Porapak N column.

of both acetonitrile and lower hydrocarbons and quantities of the monomers were formed on the pyrolysis of AN-BD co-polymers. Figure 2 shows the pyrogram of the alternating AN-BD co-polymer at 590 °C. Porapak N was used as a column packing, because the separation of AN from acetonitrile was impossible with the DOP column. The mole fraction $(AN + acetonitrile) / (AN + acetonitrile + BD + 2VCH)$ in the degradation products indicated the composition of these AN-BD co-polymers.

MA-BD co-polymers gave the monomers, and also a great deal of methanol from scission of the side-chain. This phenomenon is especially notable at the low pyrolysis temperature. Figure 3 gives the pyrograms of the alternating MA-BD co-polymer pyrolyzed at 590 and 710 °C. The production of methanol decreased greatly at 710 °C; the yield $MA / (MA + BD + 2VCH)$ at 710 °C indicated the composition of both the alternating and the random MA-BD co-polymers.

Table 2 shows the results of regression analysis for five BD co-polymers, where y is a co-monomer content of BD co-polymer and x is a co-monomer yield on pyrolysis. It is reasonable that the MA-BD co-polymer, with the high tendency to undergo side-chain scission, has the large error variance, V_{yx}

VCH/BD molar ratio and run number

Figure 4 shows the VCH/BD molar ratio in the degradation products of each MMA-BD co-polymer pyrolyzed at 386, 590, and 710 °C. The other four BD co-polymers also gave the same tendency as the MMA-BD co-polymer. The VCH/BD molar ratio changes with the pyrolysis temperature and the co-polymer composition in the case of random co-polymers. The fact that in the case of the alternating co-polymers the values of the VCH/BD

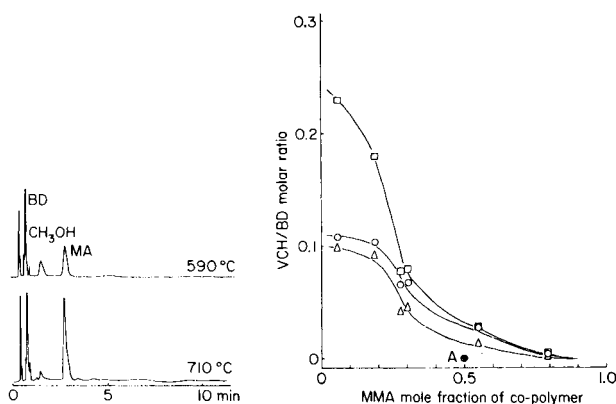


Fig. 3. Pyrograms of alternating MA-BD co-polymer at 590 and 710°C.

Fig. 4. VCH/BD molar ratio of MMA-BD co-polymers. □ 386°C; ○ 590°C; △ 710°C.

TABLE 2

Regression analysis for co-monomer-content (y) and -yield (x) at the pyrolysis temperature of 590°C

Co-polymer	a^a	b^a	V_{yx}
MMA-BD	1.06	-9.93	7.02
MVK-BD	1.19	3.87	10.3
MA-BD ^b	0.875	0.83	18.4
MAN-BD	0.862	-0.44	2.09
AN-BD	1.11	2.88	0.968

^a $y = ax + b$. ^bPyrolyzed at 710°C.

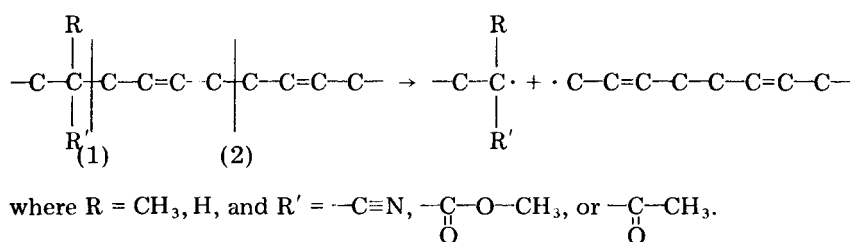
molar ratio are nearly zero may be interpreted as follows. The pyrolysis temperature dependence of the VCH/BD molar ratio results from the number of sites where a random chain scission occurs. The number of random chain scissions increases with increase in pyrolysis temperature. Consequently, the higher the pyrolysis temperature, the smaller the probability of VCH production. The dependence on the co-polymer composition is a result of the difference in BD sequence distribution. Because the number of successive BD units decreases with decreased BD content in the random co-polymer, the lower the BD content, the smaller the probability of VCH production. The alternating co-polymer contains only BD-co-monomer units in its chain, and has a VCH/BD ratio of nearly zero.

The relationship between this VCH/BD molar ratio and the BD sequence distribution was further investigated. Let P_{BBB}, P_{BBM}, P_{MBB}, and P_{MBM} represent the probabilities of a BD unit in the center of triads BD-BD-BD, BDMBD-M, M-BD-BD, and M-BD-M, respectively, where M is a co-monomer. If the probability of the BD unit in the center of each triad degrading to products other than BD and VCH is constant, and if the BD units in the center of BD-BD-BD, BD-BD-M, and M-BD-BD triads degrade to VCH and BD in the ratio $k_1/(1 - k_1)$, $k_2/(1 - k_2)$, and $k_2/(1 - k_2)$, respectively, the VCH/BD molar ratio, Q , can be given as

$$Q = \frac{[k_1 P_{BBB} + k_2 (P_{BBM} + P_{MBB})]}{[(1 - k_1) P_{BBB} + (1 - k_2) (P_{BBM} + P_{MBB}) + P_{MBM}]} \quad (1)$$

In this equation, each P value is calculated from the monomer reactivity ratios shown in Table 3 and the monomer feed ratio [11], and Q is estimated from the pyrograms. The values of k_1 and k_2 can therefore be calculated. For the pyrolysis of MMA-BD co-polymers at 590 °C, the calculated Q values when $k_1 = 0.11$ and $k_2 = 0.067$ in eqn. (1) agreed very well with the Q values obtained from the pyrograms; the correlation coefficient was 0.997. Table 3 gives the values of k_1 and k_2 for five BD co-polymers. All the k_1 values are nearly 0.1, as is k_1 for polybutadiene obtained by conventional radical polymerization. The value of k_2 decreases in the order MMA-BD >

MAN-BD > AN--BD > MVK-BD > MA-BD; this order may result from the stability of the radical produced after chain scission at position (1) shown below.



The tertiary radical is produced in the cases of MMA- and MAN-BD co-polymers (R = CH₃) and the secondary radical in the other three co-polymers (R = H). Therefore, the scission at this position is easier in the former and the k₂ Values (the probability of the dimer formation) become larger than in the latter.

The run number is a parameter [12] for characterizing sequence distribution in co-polymers. The run number is 1 for a homopolymer and 100 for a completely alternating co-polymer; eqn. (1) can be rewritten as

$$Q = \frac{k_1(X - R/2)^2 + k_2R(X - R/2)}{(1 - k_1)(X - R/2)^2 + (1 - k_2)R(X - R/2) + R^2/4} \quad (2)$$

where R = run number, and X = BD mole%. When the values of k₁ and k₂ are known in eqn. (2), the run number of a BD co-polymer can be calculated by using the values of Q and X obtained from the pyrogram. The run numbers of five BD co-polymers are shown in Table 4. Each alternating co-polymer has an R value near 100 and the alternating sequential structure of each is confirmed; the difference between the alternating co-polymer and the random one with the composition of ca. 50 mole% is obvious.

As described above, the VCH/BD molar ratio in the pyrolysis products of BD co-polymers indicates the sequence distribution of co-polymers, and the run number can be determined from it; the run numbers obtained were reasonable for the co-polymers studied.

TABLE 3

k₁ and k₂ values for BD co-polymers
(r is a monomer reactivity ratio)

Co-polymer	k ₁	k ₂	r _{BD}	r _M
MMA-BD	0.11	0.067	0.60	0.17
MVK-BD	0.10	0.012	0.30	0.14
MA-BD	0.12	0.0090	2.2	0.13
MAN-BD	0.092	0.028	0.50	0.20
AN-BD	0.11	0.013	0.51	0.072

TABLE 4

Run numbers of BD co-polymers

Co-polymer	MMA-BD	MVK-BD	MA-BD	MAN-BD	AN-BD
A	99	94	95	96	99
R ₁	10	25	32	57	45
R ₂	35	31	43	68	62
R ₃	54	65	74	66	75
R ₄	52	64	69	79	84
R ₅	71	64	65	78	85
R ₆	38	16		81	81
R ₇				60	
R ₈				58	

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