THERMAL DEGRADATION OF LINEAR
AND CYCLIZED POLYMERS AS WELL AS CYCLOPOLYMERS
OF CONJUGATED DIENES

J.DAŇHELKA and I.KÖSSLER

Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2

Thermal degradation of linear, cyclized and cyclopolymers of conjugated dienes *in vacuo* produces beside gaseous low molecular products also liquid and solid products whose average number molecular weight ranges from 400 to 600 depending upon the experimental conditions. These products were fractionated, molecular weight and infrared spectra measured for each fraction. The analysis of pyrolytic products of fractions has shown that in the case of polymers containing cyclic units the linear segments undergo chain scission preferably. An average length of cyclic segments in the original polymer could thus be estimated from the shape of pyrolytic products distribution curves. The data thus obtained have facilitated the elucidation of some reactions proceeding during thermal degradation.

The thermal degradation of linear polymers of dienes (polyisoprenes, polybutadienes *etc.*) has been studied by several authors[1-9]. In most cases gaseous products of pyrolysis were analyzed[1,7,10]. It has been shown that these products contain a great number of various compounds. According to their character and distribution conclusions have been drawn as to the mechanism of polymer chain scission at higher temperatures both in the absence and presence of oxygen.

The purpose of this work was to degrade linear, cyclized and cyclopolymers of conjugated dienes, resp, *in vacuo* and to analyze the fractions of liquid products whose molecular weight was higher than 300. It was intended to confirm and enhance the knowledge about the mechanism of chain scission of these polymers which was obtained by analyzing the gaseous products. In our previous work[11] the mass-spectrometric analysis of pyrolytic products fractions has shown that these products are a very complex mixture of compounds. The attempts to achieve a better separation were thus connected with great difficulties. We thus attempted to elucidate the mechanism of chain scission both from the shape of pyrolytic products distribution curve and from the types of newly formed end groups. Moreover, the formation or diminution of various functional groups was examined in dependence on the molecular weight of fragments.

EXPERIMENTAL

Polymers

cis-1,4-Poly(1,3-butadiene) was a commercial Ameripole CB sample. *cis*-1,4-Polyisoprene was natural rubber *Hevea*. 3,4-Polyisoprene was prepared through ionic polymerization using phenylmagnesium bromide catalyst in *p*-xylene at 100°C (ref.[12]).

Cyclized 1,4-polyisoprene was obtained by cyclization of natural rubber by reacting it with sulfuric acid in toluene at temperature of boiling for ten hours[13]. The samples contained 20% double bonds determined by the iodine monochloride method. This value is usually observed in the case of samples containing 2—4 cycles[14]. Cyclized 3,4-polyisoprene was prepared in a similar way, the time of cyclization being five hours[13].

Cyclopolybutadiene was prepared in heptane medium using a $C_2H_5AlCl_2$–$TiCl_4$ catalytic system (Al/Ti = 50/15) at 25°C (ref.[15]). Cyclopolyisoprenes were prepared at 25°C using a $C_2H_5AlCl_2$–$TiCl_4$ system in benzene[16] (Al/Ti = 1/2) (samples Cl, C2) and a $(C_2H_5)_2AlBr$–$TiCl_4$ system in heptane (sample C3). Sample C4 was prepared by employing an AlBr–$TiCl_4$ system (Al/Ti = 3/4) in heptane[17].

Pyrolytic Decomposition

On the basis of the temperature dependence of the pressure increase[18] the temperature between 360°C—450°C was selected for experiments. The decomposition was carried out in a vacuum apparatus (Fig. 1). Both A and B apparatuses were used (dimensions in mm): pyrolytic flask, $d = 80$ (160), $\varnothing$ 40 (50); collection flask, $d = 60$ (65), $\varnothing$ 15 (35); connecting tubes, $\varnothing$ 8 (10).

Pyrolytic flask 1 was filled to one half (5 to 20 g of sample). The rubber-like samples were cut to small pieces (0·1 cm³), powdered samples were mixed with methylalcohol and pressed to pellets $d = 30$ mm, $\varnothing = 15$ mm and dried. The filling tube 2 was then sealed and the apparatus was evacuated for 4—5 hours under simultaneous heating of active charcoal-containing ampoules 6 to 300°C. The apparatus was then cut off from the vacuum pump 8 by closing the stopcock 7. By cooling the ampoules 6 down (finally by liquid nitrogen) the vacuum of 10^{-2}–10^{-3} Torr was achieved inside the apparatus. Pyrolytic flask was first heated up to 300°C for approximately an hour. The ocluded gases were thus removed and remaining water and solvent are evaporated. These compounds are trapped in collection flask 4 cooled in a liquid nitrogen bath. The sample was then heated up to 360—450°C for 1 to 3 hours while the condensates were collected in flask 3. The products which are gaseous at ambient temperature were thus liquefied in a cooled flask 4 with the exception of hydrogen, methane and other volatile hydrocarbons which were trapped in active charcoal-containing ampoules. The pyrolytic unit was, after the end of pyrolysis, disconnected from vacuum part by closing tap 5 and flask 3 was sealed off under vacuum.

Analysis of Decomposition Products

The hydrogenation of some pyrolysates (0·2 g) was carried out in etylacetate at normal pressure using a PtO_2 catalyst. The iodinemonochloride method was used for double bond assay.

Infrared spectra were measured within the 400—3800 cm⁻¹ region using a Zeiss UR-10 instrument. The samples were either in form of potassium bromide pellets or in carbon disulphide solution or in form of a film placed between two KBr plates. The quantitative analysis of individual atomic groups was determined in carbon disulphide solution from the value of $(1/cd) \log (I_0/I)$,

the symbols having their usual meaning. The concentration is expressed in g/100 g (of solution), the pathlength being in cm units. In the case of tablets the value of $(F/a) \log (I_p/I)$ was employed for calculation where F denotes the tablet area, a being the sample weight and I_p represents the intensity at the wave number chosen in such a way that the losses due to scattering and reflections were eliminated.

Molecular weights were measured ebulliometrically using a differential method and apparatus already described[19].

Column fractionation on a solid support has already been described[11]. The pyrolytic product from natural rubber (Bn), which could not been prepared in form of a film, was fractionated on a chromatographic column packed with Al_2O_3, 1 m long, o. d. 35 mm. The packing was 750 mm high, the solvent flow rate was 3 ml/min, benzene being used as a mobile phase.

RESULTS

Polymer types that were pyrolyzed are presented in Table I. The main thermal decomposition product (liquid fraction) contained fragments whose number molecular weight ranged from 400 to 600. This product represented $70-85\%$ w/w of the original sample weight. This value is in agreement with the published results[20]. The differences between the infrared spectra of pyrolytic products that were fractionated and those corresponding to individual fractions and to original polymers, resp., are presented in Tables II – V.
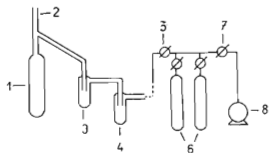

Fig. 1

Apparatus for Pyrolytic Decomposition

1 Pyrolytic flask, 2 filling tube, 3, 4 collecting flasks, 5, 7 vacuum stopcocks, 6 active charcoal ampoule, 8 vacuum pump.
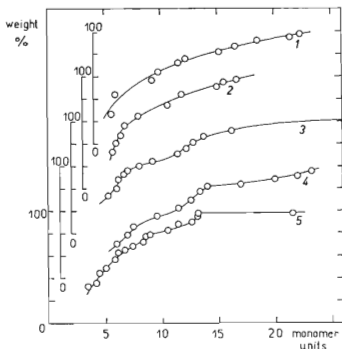
Fig. 2

Integral Distribution Curves of Pyrolytic Products

Samples (Table I): 1 An, 2 Cn, 3 Bc, 4 A, 5 C3.

The hydrogenation of the pyrolytic product of cis-1,4-poly(1,3-butadiene) leads to the disappearance of the 1,2 form (912 and 995 cm^{-1} bands) while the $trans$-1,4 form (970 cm^{-1}) only partially diminished. The 745 cm^{-1} band corresponding to cis-1,4 form did not disappear completely. Also the bands in the 3 000 cm^{-1} region indicated the presence of a non-hydrogenated product (cis-1,4 form). It can thus be concluded that cis-1,4 and $trans$-1,4 forms were not hydrogenated completely. The pronounced band at 730 cm^{-1} seen in the spectra together with an 802 cm^{-1} band might correspond to the $(-CH_2-)_n$ rocking vibration. In the case of cis-1,4 poly-isoprene pyrolytic products the increase of intensity of a 1 155 cm^{-1} band was not due to the isomerization to $trans$-1,4 form only since the absorption intensity of 600 and 1 330 cm^{-1} bands was not changed correspondingly. This increase is connected with the oxidation of the sample (the spectrum of the pyrolysate exhibits an intense band at 1 712 cm^{-1}) during which process the absorption intensity of the 1 155 cm^{-1} band is increased. A partial oxidation of the sample cannot be avoided since it takes place during the pyrolysis as a consequence of absorbed oxygen presence. The hydro-genation of the pyrolysate (sample Bn) proceeded much easier in comparison with the pyrolysate of cis-1,4-poly(1,3-butadiene) (sample An). Absorption bands due to the cis-1,4 form disappeared completely (the band at 1 315 cm^{-1} remained). Also bands at 890, 915, 1 650 and 3 065 cm^{-1} diminished. New bands appeared at 738 cm^{-1} (rocking $(-CH_2-)_3$), 920 cm^{-1} and a broad band at 1 165 cm^{-1}. The shape changes of absorption bands were observed in the region from 1 350 to 1 380 cm^{-1}. Geminal methyl groups manifested by the 1 380 cm^{-1} band splitting to 1 375 and 1 385 cm^{-1}

Table I

List of Pyrolysed Polymers

Polymer	Sample	$\overline{M}_n$ (u) of pyrolysates	Apparatus	Temperature of pyrolysis, °C
cis-1,4-Polybutadiene	An	419 (7·75)	B	420
cis-1,4-Polyisoprene	Bn	458 (6·75)	B	380
3,4-Polyisoprene	Cn	543 (7·98)	B	400
Cyclised cis-1,4-polyisoprene	Bc 1	379 (5·58)	A	440
Cyclised cis-1,4-polyisoprene	Bc 2	593 (8·72)	B	380
Cyclised 3,4-polyisoprene	Cc	595 (8·75)	B	360
Cyclopolybutadiene	A	515 (9·54)	B	380
Cyclopolyisoprene[a]	C 1	435 (6·39)	A	450
Cyclopolyisoprene[a]	C 2	375 (5·52)	A	450
Cyclopolyisoprene[b]	C 3	450 (6·62)	B	420
Cyclopolyisoprene[b]	C 4	404 (5·94)	A	440

Reaction medium: [a] benzene, [b] heptane.

are, in the case of pyrolysate fractions of cyclized 3,4-polyisoprene, preserved. The intensity of a 1 380 cm^{-1} band increases (26, 38 and 40) with the increasing molecular weight (fractions 1,4 and 8) whereas intensities of bands at 700 and 760 cm^{-1} decrease (17, 16, 10 and 9, 7, 4 resp.).

The results of fractionation of cyclopolybutadiene and cyclopolyisoprene pyrolysates are presented in Tables III and V and in Fig. 2, resp.

DISCUSSION

Molecular Weights of Pyrolysates and Fractionation

Average molecular weight of pyrolytic products formed depends upon the pyrolytic conditions where the pressure gradient between the ampoule with active charcoal and heated pyrolytic flask is established. Products whose boiling point is lower or just corresponding to the established pressure will distil from the flask. The pressure established inside the apparatus is dependent both upon the pumping rate and the rate of sample heating. At larger diameter of the apparatus tubing and lower output of the heater, the pumping rate being constant, the established pressure will be lower and products of higher molecular weight will distil off. The distilling products further interact and still higher molecular weight products are formed. If units of certain molecular weight will break preferably it is to be expected that molecular weights of products formed in consecutive reactions will be a multiple of initial molecular weight of these units.

The molecular weight distribution of these pyrolytic products can be seen from "integral distribution curves" of the latter (Fig. 2). From the comparison of curves it follows that, in the case of linear polymers, a series of products is formed whose molecular weight corresponds to 22 monomer units in the chain. In the case cyclised polymers and cyclopolymers resp. it can be assumed, judging from the curves, that products will preferably be formed whose molecular weight is a multiple of the basic unit molecular weight. Thus in the case of cyclopolyisoprene (sample C 3) a considerable amount of pyrolytic products is formed whose molecular weight can be expressed as a 4·5, 9 and 13th multiple of the monomer unit molecular weight. It can thus be assumed that the original polymer contained cyclic units consisting of three cycles (four units) in average. The units break down less readily that linear chain. Similarly, the prominent products of samples C 1, A, Bc 2 and Cn consist of 7, 7 and 13, 6 and 12·5, and 6 units respectively.

cis-1,4-Poly(1,3-butadiene)

Isomerisation in a considerable extent was observed during pyrolysis (increased intensity of 970 cm^{-1} absorption). New vinyl groups were formed during chain scission (band 912, 959, 1 645 and 3 065 cm^{-1}). From the comparison of relative

Table II

Changes in Infrared Spectra of Pyrolytic Products with Regard to Original Polymers

ν̃, cm⁻¹	Assignment	Change[a]	ν̃, cm⁻¹	Assignment	Change[a]	ν̃, cm⁻¹	Assignment	Change[a]
	cis-1,4-poly(1,3-butadiene)			3,4-polyisoprene			cyclopolybutadiene	
702, 725, 745	(triplet) —CH=CH—CH₃	++	567	3,4 form	—	720	broad band	
885	—CH=CH₂	+	890	3,4 form	—	779		+
912	—CH=CH₂	+	702	phenyl	+	818		+
959	=CH₂	+	760	phenyl	+	880, 890	=CH₂	+
970	trans-1,4 form	+	3067	3,4 form	—	912	—CH=CH₂	¦
995	—CH=CH₂	++		cyclised cis-1,4-polyisoprene		970	trans-1,4 form	—
1380	—CH₃	++	883	>C=CH₂	+	1580	C=C, C=O	+
1612	conjug. C=C	++	912	—CH=CH₂	+	1610	C=C	+
1645		++	1040	—C—O—	+	1640	C=C	+
3065	=CH₂	++	1100		+	1768	C=O	+
	cis-1,4-polyisoprene		1178		+	1715	C=O	+
572	cis-1,4 form	—	1200		+	1750	=CH₂	+
742	cis-1,4 form	—		cyclised 3,4-polyisoprene			cyclopolyisoprene[b]	
802	cis-1,4 form	++				700	(C 1, C 2)	+
840	cis-1,4 form	++				745	(C 1—C 3)	—
890	>C=CH₂	++				760	(C 1, C 2)	—
1600, 1700	shift to 1 672	—				809	(C 1, C 2)	
1655	cis-1,4 form	—						
1720	cis-1,4 form	++						
3000		++						

TABLE II
(Continued)

Wavenumber	Change	Assignment	Wavenumber	Change	Assignment	Wavenumber	Change	Samples[b]
912	++	—CH=CH₂	702	++	phenyl	820	—	(C 1—C 4)
975	++		760	++	phenyl	889	—	(C 3, C 4)
990	++	—CH=CH₂	810	++	C=C	912	—	(C 1, C 2, C 4)
1 040	—	cis-1,4 form	870	—		970	++	(C 3, C4)
1 130	—	cis-1,4 form	1 200	—		1 035	-|-	
1 155	+	trans-1,4 form	1 380	+	—CH₃	1 085	+	(C 1, C 2)
1 315	—	cis-1,4 form	1 605	—	} C=C	1 098		(C 3, C 4)
1 650	++	>C=CH₂	1 671	++		1 165	++	(C 3, C 4)
1 665	—	cis-1,4 form	1 700	—	} C=O	3 065		(C 1—C 4)
1 712	++	C=O	1 765	++				
3 070	++	>C=CH₂						

[a] ++ formation, + increase, -- disappearance, — decrease. [b] Samples numbers given in parentheses (Table I).

TABLE III
Fractionation of Pyrolytic Products

|	cis-1,4-Poly(1,3-butadiene)						cis-1,4-Polyisoprene				3,4-Polyisoprene					
Fraction	$\dfrac{m}{\%\ w/w}$	$\overline{M}_n$	u	$\log\dfrac{E(912)}{E(820)}$	$\log\dfrac{E(912)}{E(885)}$	$\dfrac{C{=}C}{\%}$	$\dfrac{m}{\%\ w/w}$	$\overline{M}_n$	u	$\dfrac{C{=}C}{\%}$	$\dfrac{m}{\%\ w/w}$	$\overline{M}_n$	u	$E(890)$	$E(702)$	$\dfrac{C{=}C}{\%}$
Gaseous	19·00						35·00				28·00					
Liquid[a]	81·00	419	7·75	5·60	13·64	37	65·00	458	6·75	60[b]	72·00	543	7·98	216·0	15·0	32[c]
1	15·15	306	5·67	7·16	26·00	44	8·38	636	9·34		7·71	386	5·68	257·7	59·8	36
2	19·52	318	5·88	9·35	20·92		33·02	490	7·21		10·80	403	5·94	218·7	54·8	
3	7·46	500	9·25	6·55	10·23		20·22	460	6·76		4·65	435	6·40	281·0	57·1	30[d]
4	6·23	521	9·65	6·74	10·68	30	3·38	397	5·82		7·99	454	6·67	312·0	51·2	
5	5·79	610	11·60	—	6·92						11·55	543	8·00	320·0	50·8	
6	5·85	655	12·13	3·82	6·61						9·39	714	10·50	249·0	36·5	26
7	5·39	820	15·15	1·77	5·40						10·16	807	11·85	133·5	21·9	
8	6·22	890	16·50	2·15	5·40						5·38	1 011	14·90	82·0	12·6	
9	4·50	990	18·65	1·67	2·82						3·43	1 050	15·45	53·3	11·2	
10	2·96	1 160	21·45	1·89	1·88						0·93	1 114	16·75	75·5	9·5	
11	1·93	1 208	22·35	2·39	3·64											
Σ	81·00	453	8·40	—	—		65·00	495	7·26		72·00	547	8·00	—	—	

[a] Nonfractionated. [b] 82% of hydrogenation. [c] In the case of non pyrolysed sample E(1450)/E(1380) = 1·55 (KBr pellet), E(1 450)/E(1 380) = 1·71 (film), [d] 19·2% of hydrogenation.

intensities of 912, 885 and 820 cm^{-1} bands for various fractions (Table III) it follows that with the increasing number of units in fragments the content of either exo-methylenic groups (band at 885 cm^{-1}) increases or the vinyl groups content decreases (band at 912 cm^{-1}) or both. The same holds for the band at 820 cm^{-1} which might be assigned to a trisubstituted double bond in the cyclic unit. The formation of methyl groups (1 380 cm^{-1}), CH_3—CH=CH— (triplet 702, 725 and 745 cm^{-1}) and conjugated double bonds C=C (1 612 cm^{-1}) was confirmed spectroscopically.

The formation of certain atomic groups is initiated in the primary reaction of the chain scission.

$$\sim CH_2—CH_2—CH=CH—CH_2 \overset{\cdot}{\mid} CH_2—CH=CH—CH_2—CH_2\sim \ \rightarrow$$
$$\rightarrow \ \sim CH_2—CH_2—CH=CH - \overset{\cdot}{C}H_2 + \overset{\cdot}{C}H_2—CH=CH—CH_2—CH_2\sim \qquad (A)$$
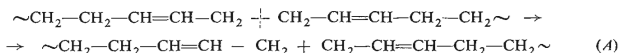
If the recombination of radicals does not take place the products will be formed through the reaction whose mechanism is analogous to the disproportionation mode of termination of radical polymerizations

$$\sim CH_2—CH=CH—CH=CH_2 + CH_3—CH=CH—CH_2\sim \qquad (B)$$
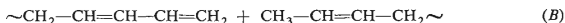
Madorsky assumes (in the case of polyisoprene)[10] that hydrogen transfer might proceed simultaneously with the bond scission. It follows from the decrease of overall number of double bonds that cyclisation takes place in considerable extent during pyrolysis. The radicals formed *via* reaction (A) can relatively easily form six-membered rings *e.g.* by reaction

$$\sim CH_2—CH=CH—CH_2—CH_2—CH=CH—\overset{\cdot}{C}H_2 \ \rightarrow \ \sim \overset{\cdot}{C}H\text{—}\hexagon \qquad (C)$$
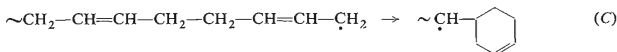
Reactions of intramolecular transfer followed by radical cyclisation also lead to the formation of rings

$$(D)$$
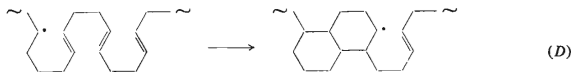
The products formed in reaction (A) can, after having undegone the intramolecular hydrogen transfer, give up low molecular products and form methyl end-groups and cojugated double bonds.

The chain scission of polymer containing cyclic segments will lead to the formation of end double bonds as it will be seen on the case of cyclopolybutadiene described lower. The longer the fragment the greater number of exomethylenic groups it

contains. This may be accounted for by the presence of greater number of cyclic units which break less readily than the linear ones. The cyclic units will thus be present in higher molecular weight fragments. This was further confirmed by analysis of double bonds content, the higher fractions having lower double bond content. During the formation and disappearance of radicals also the *cis-trans* isomerisation reaction takes place.

cis-1,4-*Polyisoprene* (Hevea)

Thermal degradation of *cis*-1,4-polyisoprene yielded, besides gaseous products, also the liquid ones, completely soluble in methyl alcohol, whose average molecular weight was found to be 458 which corresponds to 6·75 monomer units. On the other hand, the pyrolysate obtained from *cis*-1,4-polybutadiene was a viscous liquid not quite soluble in methanol. Molecular weight was measured to be 419 which corresponds to 7·75 monomer units. The pyrolysate prepared by pyrolysis of 3,4-polyisoprene was still more viscous and its molecular weight was 543 *i.e.* 7·98 monomer units. These results, together with the observation of double bond content decrease in a series 3,4-polyisoprene, *cis*-1,4-poly(1,3-butadiene) and *cis*-1,4-polyisoprene, leads to the conclusion that after the initiation of the cyclisation process the longest

TABLE IV
Fractionation of Pyrolytic Products of Cyclized *cis*-1,4-Polyisoprene Bc 2

Fraction	m, % w/w	$\overline{M}_n$	u	E (883)	E (912)
Gaseous	31·00				
Liquid[a]	69·00	593	8·73	36·3[b]	19·5[b]
1	2·69	455	6·70	29·1	20·3
2	5·18	467	6·86	29·4	27·6
3	6·13	353	5·20	22·3	17·3
4	5·44	416	6·10	31·2	20·1
5	7·31	411	6·05	22·9	29·2
6	4·81	548	8·05	31·8	33·6
7	4·86	630	9·25	44·6	23·8
8	4·05	885	12·85	45·6	17·3
9	4·24	830	12·20	39·9	14·6
10	5·19	1 100	16·20	47·2	15·8
11	5·95	3 770	56·20	44·3	11·8
12	8·23	778	11·40	54·2	8·3
13	4·92	940	13·80	46·1	9·1
Σ	69·00	588	8·66		

[a] Non fractionated. [b] Original polymer E (883) = 137·6, E (912) = 33·9.

cyclic segments are formed in 3,4-polyisoprene, shorter ones in *cis*-1,4-polybutadiene and the shortest ones in *cis*-1,4-polyisoprene, the conditions of experiment being constant in all cases. It follows from the spectra that a partial isomerisation to

SCHEME 1

trans-1,4-form (1 155 cm^{-1} band) has taken place but in a lesser extent than in the case of *cis*-1,4 polybutadiene. Vinyl groups were formed in a small extent too (bands at 912 and 990 cm^{-1}). A considerable amount of vinylidene or exomethylene groups C=CH$_2$ (890, 1 650, 3 070 cm^{-1}) has been formed. A partial cyclisation has occurred (decrease of C=C bond concentration, the change in the value of E (1 450)/E (1 380) ratio from 1·71 to 1·55).

Assuming that *cis*-1,4-polyisoprene breaks preferably in the β-position with regard to a double bond[21] then on the basis of infrared spectra of high molecular weight products of pyrolysis one can put forward a reaction mechanism (Schema 1) consisting of the most likely reactions. The intramolecular hydrogen transfer operating on radical *II* might yield a molecule containing two CH$_3$ groups attached to one carbon atom. The alternative way is the isomerisation of radical *II* giving structure *IV*.

TABLE V

Fractionation of Pyrolytic Products of Cyclopolymers

Fraction	Cyclopolybutadiene			Cyclopolyisoprene C 1			Cyclopolyisoprene C 3			
	m, % w/w	$\overline{M}_n$	u	m, % w/w	$\overline{M}_n$	u	m, % w/w	$\overline{M}_n$	u	E(889)
Gaseous	25·00			31·00			30·00			
Liquid[a]	75·00	515	9·54	69·00	435	6·39	70·00	450	6·62	41·2
1	11·74	408	7·57	11·31	385	5·68	2·72	342	5·02	68·6
2	10·47	331	6·14	12·23	359	5·32	4·24	233	3·42	72·2
3	5·35	378	7·00	7·60	472	6·95	5·10	388	5·70	73·7
4	8·19	514	9·53	6·61	496	7·30	6·56	316	4·60	65·8
5	7·96	628	11·63	10·25	531	7·82	6·74	285	4·19	64·8
6	8·54	685	12·70	9·90	597	8·75	4·28	402	5·91	70·2
7	4·46	717	13·28	2·82	614	9·10	3·02	425	6·25	54·8
8	2·75	752	13·93	6·60	826	12·10	3·05	460	6·76	47·8
9	5·09	1 103	20·41	1·68	1 140	16·75	3·08	515	7·57	44·3
10	4·39	1 255	23·20				3·76	579	8·51	46·8
11	3·22	920	17·00				3·99	577	8·48	44·5
12	2·84	1 195	22·10				4·19	609	8·95	33·3
13							4·52	727	10·69	26·8
14							4·69	868	12·76	27·1
15							3·83	892	13·11	25·5
16							3·06	891	13·10	18·8
17							2·41	790	11·61	20·5
18							0·76	1 470	21·70	—
Σ	75·00	526	9·54	69·00	484	7·10	70·00	444	6·53	—

Nonfractionated.

These reactions, however, do not take place since the products after hydrogenation would have to contain geminal methyl groups. Also the cleavage connected with hydrogen transfer as suggested by Madorsky[10] seems to be improbable from the same reason. The formation of five-membered or six-membered rings on the chain end *i.e.* structures *IVa*, *V* and *VI* resp. are more likely reactions in this case.

Radical *III* can isomerise giving structure *VII* from which conjugated structures *VIII* and *IX* may be derived; cyclisation would give structure *VIIb*. Conjugation as well as vinyl and isopropenyl group formation were confirmed by infrared spectra. Radical *III* can also give a six-membered ring on the end of polymer chain (*X*, *XI*, *XII* and *XIII*, resp.).

The reaction scheme presented here accounts for the observed decrease of methyl groups preserving the multiple of molecular weight of basic unit,

$$VII \rightarrow IX, X \rightarrow XII \quad \text{and} \quad VII \rightarrow VIIa \rightarrow VIIb.$$
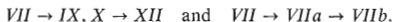
The macroradicals formed can eliminate low molecular gaseous products in a similar way as described in the case of polybutadiene. The methyl groups of *cis*-1,4-polyisoprene will control the bond cleavage in such a way that fragments whose molecular weight is an integer multiple of a monomer unit weight are formed preferably. In the case of *cis*-1,4-poly(1,3-butadiene) more fragments are formed whose molecular weight is not an integer multiple of molecular weight of monomer unit. This finding is in accordance with the results of gas chromatographic analysis of gaseous pyrolytic products[22] and mass spectrometric analysis[11], resp.

3,4-Polyisoprene

The original polymer was already partially cyclised (low C=C content). About 40% of linear units were during pyrolysis either cyclised or the elimination of isopropenyl took place. This follows from the C=C bonds concentration decrease from 55 to 32% (*i.e.* 42% conversion) as well as from the isopropenyl bonds concentration decrease from E (890) = 333 to E (890) = 216 (*i.e.* 35% drop).

The main chain scission *I* giving two radicals *II* and *III* is the primary process which takes place during thermal degradation. The cyclisation by a radical mechanism then proceeds. This will lead to the formation of cyclic species containing five- and six-membered rings *IV* and *V* (Scheme 2). The cyclisation proceeds relatively easy giving condensed rings. The process is stopped by structural irregularities *e.g,* by bonded phenyl which had been built in the chain during the polymerisation. At the site where the phenyl is built in bond cleavage proceeds easily. This is why the phenyl content in pyrolytic products increases with the decreasing molecular weight (Table III).

The isopropylene groups increase, caused by the reaction leading to structure V, is lower than the decrease caused by cyclisation; the result being that the isopropylene groups content decreases with the increasing molecular weight of the fraction.
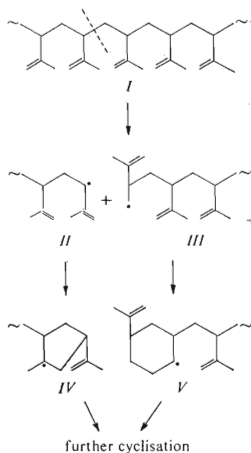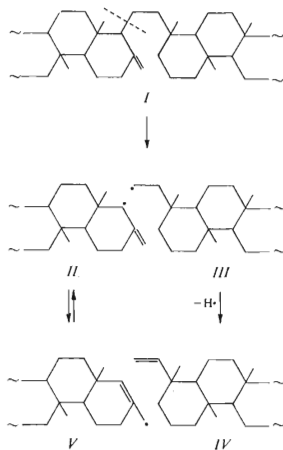

SCHEME 2

Cyclized cis-1,4-*Polyisoprene*

The thermal degradation of *cis*-1,4 polyisoprene which was cyclized by sulphuric acid treatment leads to disapperance of functional groups seen in infrared spectra at 1040, 1178 and 1200 cm^{-1}. These bands do not correspond to *cis*-1,4 units of the initial linear polymer. The absorptions might be ascribed either to RO—SO$_3$H (ref.[23]) groups or to —CH groups of linear units connecting cyclic segments which are, however, of a different type than the original monomer units. The bond cleavage will very likely occur exclusively on linear segments. This is corroborated by the fact that unlike linear polyisoprene no monomer units[23] are formed during pyrolysis. Moreover, the infrared spectra of pyrolysate obtained from slightly cyclised *cis*-1,4-polyisoprene are very simple and similar to those obtained from a highly cyclized polymer. According to the analysis of the distribution curve the average number of monomer units in cyclic segments is equal to six, which is in accordance with the

structure suggested for the cyclized polymer on the basis of the solution properties measurements which indicate the presence of two to six units in one cyclic segment[14].

Exomethylene groups having absorption at 833 cm^{-1} (ref.[24]) are also seen in pyrolytic products. Their concentration, however, is lower than in the case of initial cyclized product (Table IV). The presence of —CH$_2$—C (=CH$_2$) —CH$_2$—CH$_2$ units formed by the isomerisation of *cis*-1,4 structure cannot be excluded although this seems rather unlikely. The concentration of a vinyl group, to which an absorption band at 912 cm^{-1} corresponds, increases with the decreasing molecular weight (Table IV). This indicates that these groups are formed during main chain scissions. Their concentration, however, does not correspond to double bond content determined by the iodine monochloride method. This fact, together with the observation of 1600 cm^{-1} absorption bands, suggests that also other double bonds of the di-substituted (*trans*) type or tri- or even tetrasubstituted type are formed. The CH$_3$ groups content decreases in the process of pyrolysis as it is seen from the comparison of spectra in the 3000 cm^{-1} region. Here, the transformation to exomethylene groups or the elimination takes place.

In Scheme 3 the likely primary steps of chain scission are presented. It follows from the spectra of individual fractions that the ability to oxidise decreases with the increasing molecular weight (bands at 1720 and 1100 cm^{-1}). This is in agreement
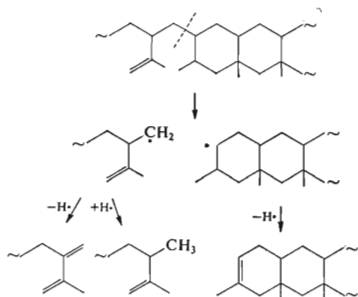

SCHEME 3

with the observations concerning the oxidative behaviour of polymers containing cycles in the main chain[25].

Cyclized 3,4-Polyisoprene

The polymer contains geminal methyl groups (1 375 and 1 345 cm^{-1}) formed through a cyclisation process carried out in the presence of protonic acids[20,22]. Linear units cleavage is predominant during the pyrolysis of this polymer. New CH_3 groups are formed in this process (intensity increase at 1 380 cm^{-1} band). Unlike the pyrolysis of cyclized 1,4-polyisoprenes the double bond content (870 cm^{-1} band) increases during the pyrolysis in this case. The initial steps of bond scission can thus be described by Scheme 4.

SCHEME 4

Monomer units are not eliminated during pyrolysis. The increase of phenyl groups content with the decreasing molecular weight is due to the same reason as described for the linear 3,4-polyisoprene.

Cyclopolybutadiene

There is only a small difference between infrared spectra of pyrolytic products and those of initial polymer. In spite of this it is clear that degradation of linear units had taken place (band at 912 and 970 cm^{-1}). Apart from a prominent band at 1 580 cm^{-1}, which is present in spectra of certain fractions and which disappears upon hydrogenation, only very weak bands are seen which indicate the presence of new types of double bonds. According to the analysis of distribution curves the cyclic segment in the original polymer consists of 6·5 monomer units.

Cyclopolyisoprene

The cyclopolyisoprene molecule is believed to consist of condensed five- and six-membered rings[26,27] into which solvent fragments may be incorporated[24]. The pyrolysis of polymer gives, besides gaseous products, also liquid products which, unlike the cyclised polyizoprene, possess more complicated structure than the original polymer. The great similarity between the spectra of pyrolytic products of cyclised cis-1,4-polyisoprene and those of cyclopolyisoprene indicates that in both cases similar condensed rings are present in the polymer. This was assumed in previous papers[26,27] as well. There is, however, a slight difference in the spectra. It is a presence of 883 cm^{-1} bands in the case of cyclized polyisoprene pyrolysate and 889 cm^{-1} bands observed in spectra of cyclopolyisoprene pyrolysate.

The scission of cyclopolyisoprene chain proceeds in such a way that 50% of fragments from liquid and solid products contains multiples of monomer unit starting from a pentamer up to a 21-mer as it was proven by mass spectrometry[11]. Other very frequently occurring fragments are lighter by C_3H_6 (propylene) group. Besides these the predominating fragments are heavier or lighter by H_2 unit. The primary step might be visualised as a scission of single bonds connecting cyclic segments.
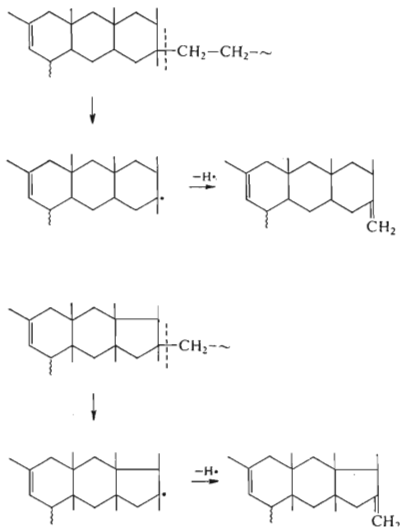
By comparing the spectra of pyrolysates of cyclopolyisoprene samples it is possible to distinguish the differences in initial structures of individual samples (Table II). Not only the structure of cyclic segments is dependent on the way of preparation of cyclopolymers but also the length of these segments; the distribution curve of pyrolytic products of sample C 3 shows the presence of compounds containing 4, 5, 9, and 13 monomer units in the molecule whereas in the case of sample C 1 7 units are present. When linear units connecting cyclic segments are broken new exomethylen groups are formed together with the conjugated double bonds. This is accompanied by the decrease in methyl group concentration. The initial steps may be described by following reactions if suggested structures[28] are accepted.

REFERENCES

1. Williams C. G.: Phil. Trans. *150*, 241 (1860).
2. Staudinger H., Fritschi J.: Helv. Chim. Acta *5*, 785 (1922).
3. Staudinger H., Geiger E.: Helv. Chim. Acta *9*, 549 (1926).
4. Midgley T., Henne A. L., jr: J. Am. Chem. Soc. *51*, 1215 (1929).
5. Basset H. L., Williams H. G.: J. Chem. Soc. *2324* (1932).
6. Boonstra B. S. T., Van Amerongen G. J.: Ind. Eng. Chem. *41*, 161 (1949).
7. Madorsky S. L., Straus S., Thompson D., Williamson L. W.: J. Res. Natl. Bur. Std. *42*, 499 (1949).
8. Straus S., Madorsky S. L.: J. Res. Natl. Bur. Std. *50*, 165 (1953).
9. Straus S., Madorsky S. L.: Ind. Eng. Chem. *48*, 1212 (1956).
10. Madorsky S. L.: *Thermal Degradation of Organic Polymers*, Interscience, New York 1964.
11. Daňhelka J., Poláček J., Kössler I.: This Journal *34*, 2833 (1969).
12. Štolka M., Vodehňal J., Kössler I.: This Journal *28*, 1535 (1963).
13. Štolka M., Vodehnal J., Kössler I.: J. Polymer Sci. *A2*, 3987 (1964).
14. Vohlídal J., Boháčková V., Matyska B.: Preprints, Symposium Helsinki, III-477, 1972, J. Polymer Sci., C in print.
15. Štolka M.: Unpublished results.
16. Kössler I.: Unpublished results.
17. Krauserová H., Mach K., Matyska B., Kössler I.: J. Polymer Sci. *C16*, 469 (1967).
18. Schütz A.: Unpublished results.
19. Daňhelka J., Schulz L., Kössler I.: Chem. listy, in press.
20. Angelo R. J.: Chem. Eng. News 41 (*50*), 44 (1963).
21. Midgley T., Henne A. L.: J. Am. Chem. Soc. *53*, 203 (1931).
22. Petrusová L.: Unpublished results.
23. Štolka M., Vodehnal J., Kössler I.: J. Polymer Sci. *A2*, 3987 (1964).
24. Kössler I., Vodehnal J., Štolka M.: J. Polymer Sci. *A3*, 2081 (1965).
25. Dvořák J., Matyska B., Vodehnal J., Kössler I.: This Journal *32*, 1561 (1967).
26. Gaylord N. G., Kössler I., Štolka M., Vodehnal J.: Polymer Sci. *A2*, 3969 (1964).
27. Kössler I., Štolka M., Mach K.: J. Polymer Sci. *C4*, 977 (1964).
28. Drahorádová E., Doskočilová D., Matyska B.: This Journal *36*, 1301 (1971).

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