

THERMAL DEGRADATION OF *trans*-POLYPENTENAMERJ. ZACHOVAL^a, J. KÁLAL^a, J. KUBÁT^b and J. MITERA^c^a Polymer Department,^b Department of Coke and Gas Technology and^c Department of Petroleum and Petrochemistry,

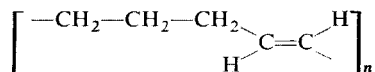
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The analysis of IR and NMR spectra has revealed that the thermal degradation of *trans*-polypentenamer leads to the *trans-cis* isomerization of the double bonds and to cyclization. Butadiene, pentadiene, cyclopentane, ethylidenecyclopentene and vinylcyclopentene were identified as the main volatile decomposition products.

The thermal degradation of diene polymers and natural rubber, 1,4-polyisoprene and 1,4-polybutadiene in the first place, was studied in a number of papers¹⁻³. The majority of papers about the thermal degradation of diene polymers were dealing only with the analysis of volatile products of pyrolysis; a lesser attention was devoted to the change in the microstructure of the polymer. An exception to this are papers by Tkáč and coworkers⁴, and Golub and Gargiuli⁵ who investigated changes in the microstructure of the polymer occurring during the thermal degradation of 1,4-polyisoprene and 1,4-polybutadiene *in vacuo* at ~300°C and found that the thermal degradation of these polymers is accompanied by cyclization.

Trans-polypentenamer, which represents a new type of elastomer, is obtained by the polymerization of cyclopentene *via* the "methathesis" mechanism in presence of a complex catalyst, $WCl_6-C_2H_5AlCl_2-C_2H_5OH$ (ref.⁶), and contains in its chain the basic structure repeat unit



This basic unit differs from polybutadiene (polybutenamer) by the presence of one more $-CH_2-$ group. With respect to this structure it was interesting to study processes occurring in the thermal degradation of *trans*-polypentenamer and to try to describe them from the standpoint of similar changes taking place in the thermal degradation of 1,4-polyisoprene and 1,4-polybutadiene.

EXPERIMENTAL

A sample of *trans*-polypentenamer (Farbenfabriken Bayer A.G., FRG) was purified by repeated precipitation from benzene solution with methanol; the solvent residue was removed by drying

at 40°C/4 Torr to constant weight. The rate and temperature of degradation were determined by thermogravimetric analysis (TGA) with a programmed rate of heating of 7°C/min, using 100 mg of the sample; the data also confirmed that the sample did not contain any solvent residues. The 40–50 mg samples were also subjected to isothermal degradation at 200° and 350°C and a pressure of 0.005 Torr. The infrared analysis of products after degradation to various degrees was performed by using the KBr technique with a Specord apparatus (Zeiss, Jena). NMR spectra of soluble fractions were recorded in a C₆D₆ solution with a Varian HA-100 apparatus. A Chrom IV (manufactured by Laboratorní přístroje) apparatus with a flame ionization detection and a Curie Point (Pye) pyrolyser were used for pyrolysis chromatography, the temperatures being 480, 510, and 610°C; the column was 4 m long, 3 mm in diameter, packed with 10% of silicone rubber, Merck, on Chromaton NAW. The determination was carried out with a nitrogen flow rate 20 ml/min, hydrogen flow rate 20 ml/min, and air flow rate 300 ml/min. The products of pyrolysis were analyzed in combination with a mass spectrometer on a column 6 m long, 3 mm in diameter, packed with 10% of silicone rubber, Merck, on Chromaton NAW with helium as the carrier gas. The energy of bombarding electrons during recording of the spectrum was 70 eV.

RESULTS AND DISCUSSION

A record of the thermogravimetric analysis of *trans*-polypentenamer is shown in Fig. 1. A perceivable weight loss occurs at temperatures about 200°C. From an equation derived by Fuoss and coworkers⁷

$$E^+ = E/n = -RT^2/W_i \cdot (dW/dT)_i, \quad (1)$$

where E is the activation energy, R is the gas constant, W_i is the weight of the sample at the point of inflexion, $(dW/dT)_i$ is the derivative of the TGA record at the point

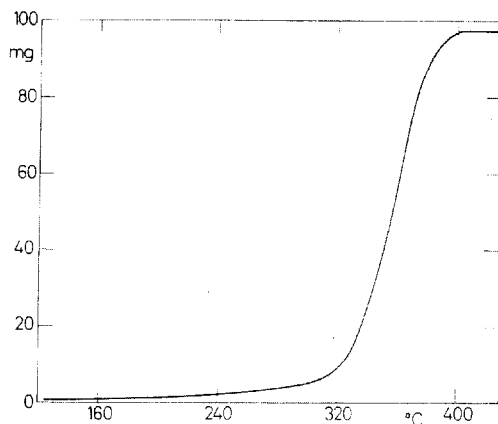


FIG. 1

Thermogravimetric Analysis of *trans*-Polypentenamer

of inflexion, T is the absolute temperature and n is the reaction order, the unit activation energy (E^+) 21.6 kcal/mol was calculated. The reaction order (2.02) was read off from a nomogram suggested by Klimeš⁸, so that the activation energy of the thermal degradation of *trans*-polypentenamer determined by the TGA method is 43.6 ± 4 kcal/mol. This value varies within the limits given for the thermal degradation of 1,4-polyisoprene (42-56 kcal/mol, ref.^{2,3}); the activation energy given for 1,4-polybutadiene is 62 kcal/mol (ref.²), as determined by isothermal measurements.

The infrared spectra of *trans*-polypentenamer before thermal degradation and after degradation for various weight losses (Table I) are shown in Fig. 2. At 200°C (Fig. 2b), when the onset of decomposition was observed, a decrease in the content of the *trans*-double bonds can be seen in the infrared spectrum (absorbancy at 970 cm^{-1}), as well as an increase in the content of the *cis*-double bonds (at 1404 cm^{-1} and 724

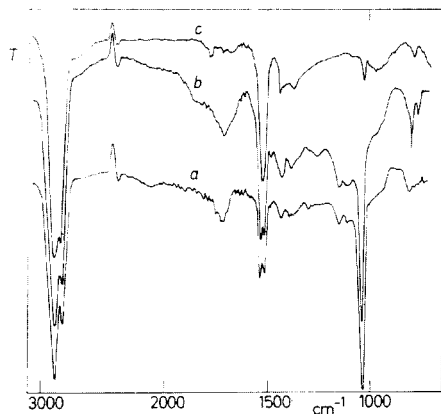


FIG. 2
Infrared Spectra of *trans*-Polypentenamer
after Thermal Degradation
a) Original sample; b) sample degraded at
200°C, loss 5%; c) sample degraded at 350°C,
loss 50.0%.

TABLE I
Dependence of the Weight Loss on Temperature and Time of Degradation

Temperature °C	Time h	Loss %	Temperature °C	Time h	Loss %
200	6	2.0	350	3	21.5
200	12	5.0	350	5	46.1
350	1	4.8	350	6.5	50.0
350	2	12.3	350	6.5	51.1
			350	8	55.4

cm^{-1}); the thermal degradation at 200°C is also accompanied by the crosslinking of the polymer. More pronounced changes in the infrared spectra occur in samples at 350°C (Fig. 2c); the weight loss in these samples varied from 4.8–55% (Table I). With increasing time of thermal degradation at 350°C the content of the *trans*-double bonds (at 970 cm^{-1}) decreases; up to the weight loss $<21.5\%$ the intensity of bands at 724 cm^{-1} and 1404 cm^{-1} increases while for samples undergoing higher degradation the intensities of these bands decrease again. A new band at 910 cm^{-1} appears in the spectra, probably corresponding to the presence of the vinyl groups $-\text{CH}=\text{CH}_2$. The intensity of this band, similarly to that of bands at 724 cm^{-1} and 1404 cm^{-1} , decreases with the weight loss $>21.5\%$. This suggests that the *trans*-polypentenamer is subjected to the thermal *trans-cis* isomerization proceeding with an activation energy only a little lower than that of the pyrolytic and cyclization processes. The isomerization process is masked by a fast degradation reaction, mainly at elevated temperatures. In this respect there exists an analogy with the thermal degradation of 1,4-polyisoprene and 1,4-polybutadiene⁶. The *cis*- and *trans*-double bonds also participate in the cyclization process, so that at a later stage of degradation (weight loss $>21.5\%$) the content of the *cis*-double bonds arising by the isomerization of the primary *trans*-double bonds is gradually decreased. The presence of vinyl double bonds can be a consequence of the isomerization process of the primary radicals formed by the thermal cleavage of polymer chains:

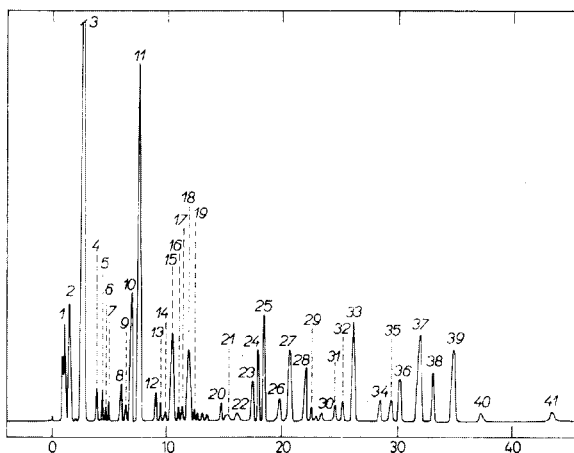


FIG. 3

Pyrolysis Chromatogram of *trans*-Polypentenamer at 510°C

1 Butadiene, 2 pentadiene, 3 cyclopentene, 10 ethylidenecyclopentane, 11 vinylcyclopentane.



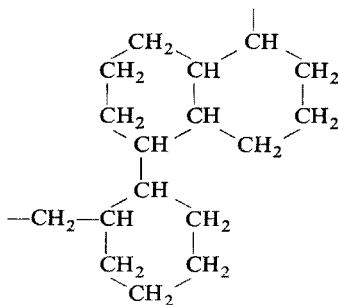
In the NMR spectrum the band at 4.60τ ($-\text{CH}=\text{CH}-$) disappears almost completely; the band at 8.00τ ($-\text{CH}_2-\text{C}=\overset{|}{\text{C}}$) is also eliminated while a broad characteristic resonance with a maximum at 8.72 appears on the other side. The NMR spectrum provided a proof of the presence of the $\text{CH}_3-\overset{|}{\text{C}}$ groups (band at 9.13τ); the possibility of the presence of the $\text{CH}_3-\text{C}=\overset{|}{\text{C}}$ groups (band at 8.30τ) is not excluded either. The NMR spectrum, similarly to the infrared spectra, gives a supplementary proof of the course of the cyclization reaction during the thermal degradation of *trans*-polypentenamer.

The probability of the cyclization process during the thermal degradation of *trans*-polypentenamer is also indicated by the finding that the infrared spectra of the thermally degraded products and the samples intentionally cyclized by treating a solution of *trans*-polypentenamer in xylene with H_2SO_4 and $\text{BF}_3 \cdot \text{OEt}_2$ at 140°C (ref.⁹) are similar.

A broad chromatographic record is also characteristic of the pyrolytic decomposition of *trans*-polypentenamer (Fig. 3). The intensity of the individual bands and their qualitative participation within the temperature range of $480-610^\circ\text{C}$ does not essentially depend on the pyrolysis temperature. A typical feature is the presence of the five main products of pyrolysis, *viz.*, butadiene, pentadiene, cyclopentane, ethylenecyclopentene and vinylcyclopentane which at a pyrolysis temperature of 480°C are present in a ratio $13 : 19 : 100 : 20 : 52$ for the case that the band of cyclopentene is 100. Consequently, cyclopentene is the product that is most markedly represented in the pyrolysis products. The chromatographic record differs somewhat in the intensity of the individual bands during the pyrolysis of products cyclized with H_2SO_4 from that obtained by the pyrolysis of polypentenamer alone⁹. It is quite likely that the change in the quantitative participation of the individual components is due to the fact that pyrolysis occurring at the beginning concerns noncyclized polypentenamer chains in which the participation of the individual products differs from their participation in the pyrolysis of the almost completely cyclized portion at the final stage of degradation.

At the present state of knowledge existing about the process of thermal degradation of *trans*-polypentenamer it would be rather too early to discuss the mechanism of this process in detail. If one rules out the possibility of the formation of cycles containing five, seven and more members, it seems quite probable that unlike the formation of condensed cycles with a degree of cyclization approx. 3 for cyclized 1,4-polyisoprenes and 1,4-polybutadienes the cyclization of *trans*-polypentenamer will be prevalingly accompanied by the formation of 1,5-disubstituted decahydronaphthalene

cycles and 1,2-disubstituted cyclohexane cycles:



At present, a detailed investigation of problems of the thermal degradation and cyclization of *trans*-polypentenamer is underway.

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