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THERMOOXIDATIVE DEGRADATION OF POLYACROLEIN

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Thermooxidative degradation of polyacrolein has been investigated with a derivatograph. It was found that up to 80° a physical process occurs — the evaporation of traces of water and monomer acrolein trapped by the polymer. Exothermic process of dehydration of hydrated aldehyde groups of polyacrolein takes place from 80 to 130°. A very pronounced exothermic process from 130 to 180° with a sharp weight loss is caused by the degradation of ring structures with $n < 3$. The presence of ring structures with $n > 3$ in the polymer shifts the DTA and DTG peaks by 20° to lower temperatures. At temperatures of about 250° and higher side carbonyl groups are thermally oxidized and decarboxylated with a considerable weight loss. All these suggestions were confirmed by infrared spectroscopy.

Up to the present only three papers dealing with the thermal degradation of polyacrolein have been published [1–3], and only one of these is concerned with thermooxidative degradation [3]. Our investigations of the thermooxidative degradation of samples of polyacrolein, in combination with investigations of infrared spectra of these samples yielded additional information on the structure of polyacrolein and its thermooxidative degradation.

Experimental

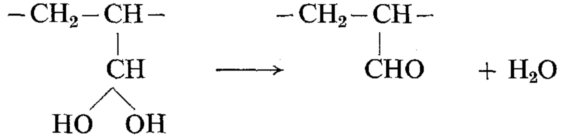
TG, DTG and DTA were carried out with a MOM derivatograph (Hungary). The sample weight was 50 mg, the heating rate 6°/min, air flow rate 50 ml/min. Ceramic crucible was used.

Infrared spectra were made with a Nippon-Bunko Model LS-301 spectrophotometer using KBr pellets. The results are shown in Figs 1–4.

Discussion of results

The endothermic process occurring with a slight weight loss up to 80° is not caused by chemical changes, but by the physical process of evaporation of traces of water and monomeric acrolein trapped by the polymer. Infrared spectra of a sample of polyacrolein heated to 80° (Fig. 1b) do not show any changes compared to the spectra of the initial polyacrolein (Fig. 1a).

The following stage, from 80 to 130°, i.e. up to the beginning of an abrupt exothermic peak on the DTA curve (Fig. 2b – I), is caused by the exothermic process of dehydration of hydrated aldehyde groups of polyacrolein:



$$\underset{\substack{| \\ \mathrm{CH} \\ \diagup\ \diagdown \\ \mathrm{HO}\quad\mathrm{OH}}}{-\mathrm{CH_2}-\mathrm{CH}-} \longrightarrow \underset{\substack{| \\ \mathrm{CHO}}}{-\mathrm{CH_2}-\mathrm{CH}-} + \mathrm{H_2O} \qquad (1)$$

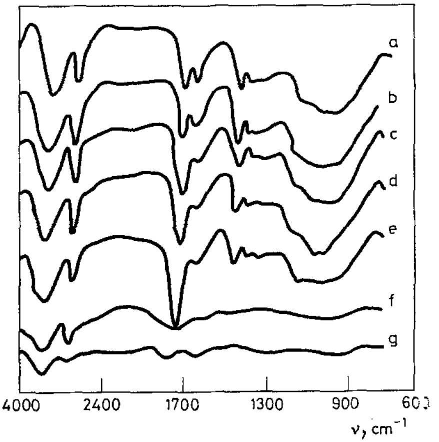
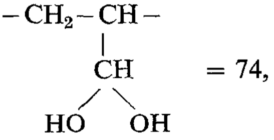


Fig. 1. Infrared spectra of polyacrolein samples heated to different temperatures: a initial sample, b 80, c 130, d 150, e 190, f 250, g 350°

as is confirmed by the infrared spectrum of a polyacrolein sample heated up to 130° at a rate of 3°/min. Fig. 1c shows a decrease in the absorption band at 1640 cm^{-1} ($-O-H$ bonds) and an increase in the intensity of absorption at 1725 cm^{-1} ($-CHO$ groups). A broad band from 950 to 1150 cm^{-1}, characterizing the $-C-O-C-$ bonds of cyclized aldehyde, does not exhibit any changes. The TG curve (Fig. 3 – I) can be used to determine the weight per cent of the water lost from 80 to 130°. The conversion to hydrated polyacrolein units, made according to the equation:

$$\frac{M_a \cdot W}{18}$$

where M_a is the molecular weight of the polyacrolein unit



$$\underset{\substack{| \\ \mathrm{CH} \\ \diagup\ \diagdown \\ \mathrm{HO}\quad\mathrm{OH}}}{-\mathrm{CH_2}-\mathrm{CH}-} = 74,$$

W is the difference between the weight loss up to 130° and the weight loss up to 80°, and 18 is the molecular weight of water, gives the content of hydrated aldehyde groups in the polymer, which amounts to 12%.

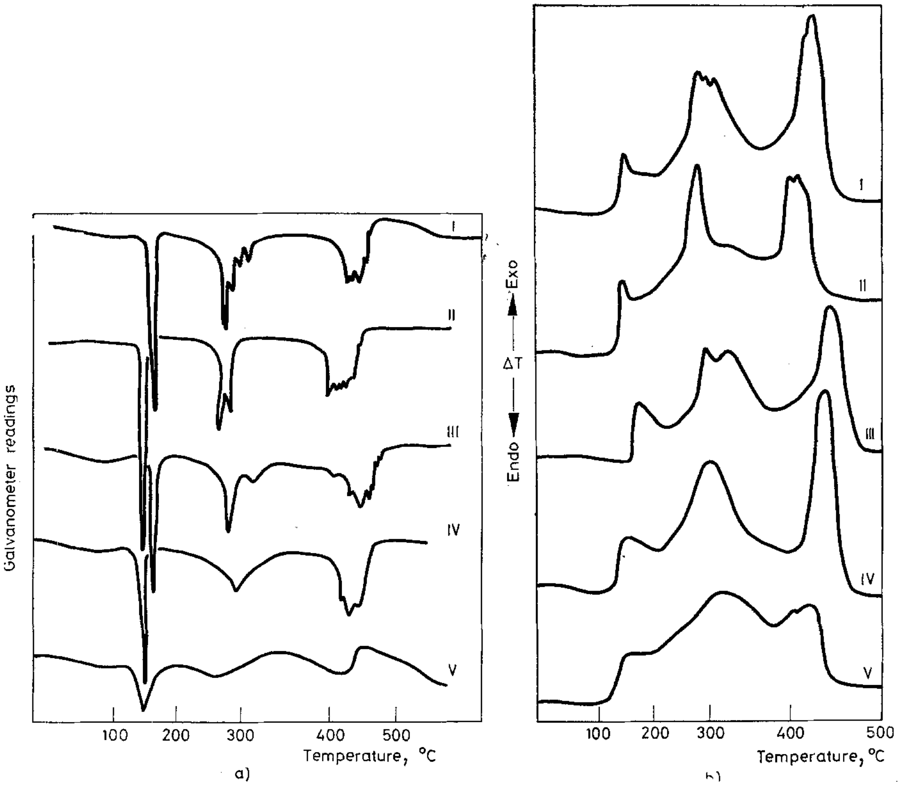
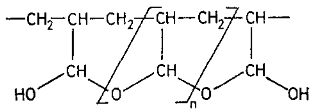


Fig. 2. DTG (a) and DTA (b) curves for samples of polyacrolein obtained by different methods

I. Polyacrolein obtained by a static method (ring structures with $n < 3$) [7]
II. Polyacrolein obtained by a static method with preliminary acidification of the reaction medium to pH 1.9 (ring structures with $n > 3$) [7]
III. Polyacrolein obtained in an aqueous suspension (ring structures with $n < 3$) [8]
IV. Polyacrolein obtained by the method of Schultz and co-workers (ring structures with $n > 3$) [9]
V. Sample I in an atmosphere of helium

A pronounced exothermic process at 130–180° (Fig. 2a, b–I), with a drastic weight loss, is caused by the degradation of ring structures in the polyacrolein sample with $n < 3$:



Infrared spectra of polyacrolein samples heated up to 150° show a small decrease in the intensity of absorption over a wide range from 950 to 1150 cm^{-1}, and a considerable decrease up to 190° (Figs 1d and 1e). The absence of peaks in the DTG and DTA curves at this temperature (130–180°) of samples of modified polyacrolein (Fig. 4) in which ring structures with $n < 3$ are absent, confirms reaction 2.

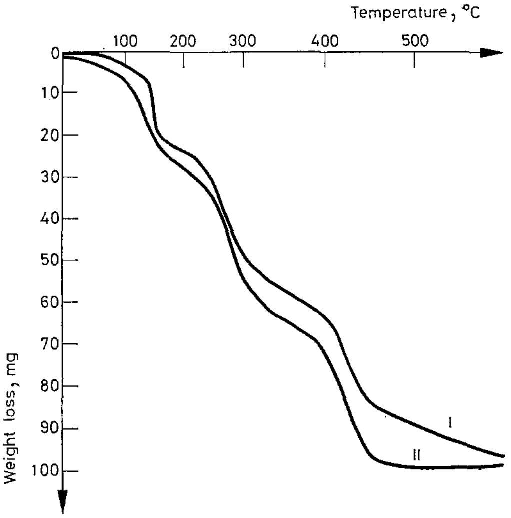


Fig. 3. TG curve of samples of polyacroleins (conditions are the same as in Fig. 2)

An increase in the extent of cyclization of polyacrolein ($n > 3$) is accompanied by a shift of the above exothermic effect to temperatures lower by 20° (Figs 2–II and 2–IV). This is caused by the fact that the so-called "small" blocks ($n < 3$) in the polyacrolein chains exhibit higher thermal stability than "large" blocks ($n > 3$).

At a temperature of approximately 250° carbonyl side groups undergo thermal oxidation and decarboxylation with a considerable weight loss (Fig. 2–I); subsequently the main carbon chain degrades (350°). Infrared spectra of polyacrolein samples heated to 250 and 350° (Figs 1f and 1g) differ appreciably from the preceding samples, but virtually do not differ from each other. The effect of the oxidation process on the change in the polyacrolein structure becomes apparent if we compare the DTA and DTG curves of polyacrolein samples obtained in an atmosphere of helium and in air (Fig. 2–I–IV). Clear exothermic effects of oxidation over the range of temperature 270–320° disappear when polyacrolein is heated in an atmosphere of helium.

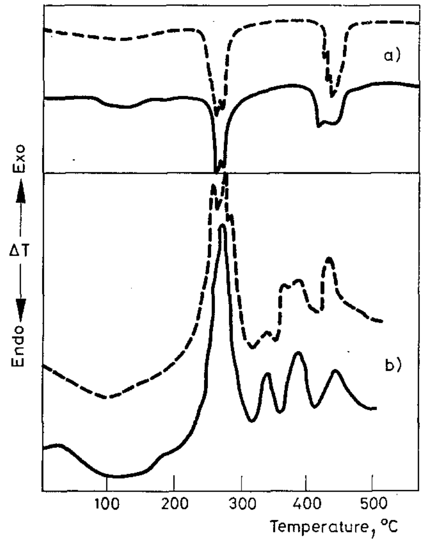
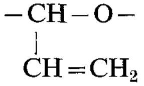


Fig. 4. DTG (a) and DTA (b) curves for samples of polyacrolein modified according to the Cannizzaro reaction (dashed line) and according to the cross Cannizzaro reaction (full line) [10]

It is interesting to note that over the same range of temperature the shapes of the DTG and DTA curves of polymers prepared by different methods are different (Fig. 2–I–IV). Evidently, this results from peculiarities of the structure of the main polyacrolein chain. It may be suggested that the redox polymerization of acrolein does not always proceed by the mechanism of vinyl polymerization [4]. Calculation of the electron structure of monomeric acrolein [5] shows that the index of free valency, characterizing the ability of an atom to undergo homolytic addition, is comparatively high even at the third carbon atom, i.e. at the carbon of the carbonyl group (the numbering is made by analogy with butadiene):

$$\begin{array}{cccc} 0.707 & 0.158 & 0.588 & \\ \uparrow & \uparrow & \uparrow & \\ \mathrm{CH_2}= & \mathrm{CH}- & \mathrm{CH}= & \mathrm{O} \\ 1 & 2 & 3 & 4 \end{array} \tag{3}$$

Hence, the formation of the following units in polyacrolein is possible:



$$\underset{\displaystyle CH=CH_2}{-\overset{|}{CH}}-O- \qquad (4)$$

In this case the cross-linking of the chains may occur not only at the $-C-O-C-$ bonds, but also with the opening of the side vinyl bond in the 4th unit.

The vinyl bond is known to have a band at 1615 cm^{-1}, but this band is overlapped by the absorption of the $-O-H$ groups at 1640 cm^{-1}. Infrared spectra of polyacrolein samples heated at high temperatures (Fig. 1) always show an absorption band of low intensity at 1610–1640 cm^{-1}. Even at 190° a shoulder remains in this region, which cannot be attributed to vibrations of the $-O-H$ group; hence, it should be assigned to vinyl bonds.

Moreover, according to Filkenshtein and co-workers [6], the $-C-O-C-$ bonds of structure 2 are characterized by absorption bands in the regions of 1075 cm^{-1} and 1140–1150 cm^{-1}. They may also be distinguished in our spectrum of the sample of the initial polyacrolein (Fig. 1a). It is of interest that the absorption band at 1150 cm^{-1} does not become weaker when the polymer is heated (Figs 1d, 1e), whereas the intensity of the band at 1075 cm^{-1} decreases greatly.

It is quite possible that the appearance of several maxima in the DTG curve and accompanying thermal effects (Figs 2–I and III) for different polyacroleins in the region of approximately 300° is caused just by the presence of units 4 in the main chain of polyacrolein. The amount of these units and the dimensions of the blocks which they form depend on the method of preparation of the polymer. These factors affect to a great extent the processes of thermooxidative degradation over this temperature range, in which blocks of different thermal stability (which depends on the method of preparation of the polyacrolein) successively degrade.

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RÉSUMÉ — Etude de la dégradation thermique oxydante de la polyacroléine à l'aide d'un Derivatograph. On montre qu'un processus physique se produit jusqu'à 80°: l'évaporation des traces d'eau et de l'acroléine monomère encagée dans le polymère. La déshydratation des groupes aldéhydes hydratés de la polyacroléine se produit exothermiquement entre 80 et 130°. Un processus exothermique très prononcé entre 130 et 180°, accompagné d'une brusque perte de poids résulte de la dégradation de la structure annulaire lorsque $n < 3$. La présence dans le polymère de structures annulaires avec $n > 3$ déplace les pics ATD et TGD de 20° vers les températures inférieures. Aux températures d'environ 250° ou plus, on observe l'oxydation thermique et la décarboxylation des groupes carbonyles latéraux, accompagnée d'une perte de poids considérable. Cette interprétation est confirmée par spectroscopie infrarouge.

ZUSAMMENFASSUNG — Die thermooxidative Zersetzung von Polyacrolein wurde mit einem Derivatographen untersucht. Es wurde gefunden, daß bis zu 80° ein physikalischer Vorgang stattfindet — die Verdampfung von Wasserspuren und von im Polymer eingeschlossenem monomerem Acrolein. Der exotherme Vorgang der Dehydratisierung hydratisierter Aldehydgruppen des Polyacroleins vollzieht sich von 80 bis 130°. Ein sehr stark exothermer Vorgang zwischen 130 und 180°, mit scharf ausgeprägtem Gewichtsverlust, wird durch die Zersetzung von Ringstrukturen mit $n < 3$ verursacht. Die Gegenwart von Ringstrukturen mit $n > 3$ im Polymer verschiebt die DTA- und DTG-Peaks um 20° in Richtung der niedrigeren Temperaturen. Bei etwa 250° oder höher liegenden Temperaturen werden Seiten-Carbonylgruppen thermisch oxidiert und decarboxyliert, und zwar unter bedeutendem Gewichtsverlust. All diese Annahmen wurden durch infrarotspektroskopische Untersuchungen unterstützt.

Резюме — Изучена термоокислительная деструкция полиакролеина на «Дериватографе» фирмы МОМ (Венгрия). Найдено, что до 80° происходит физический процесс испарения захваченных полимером следов воды и мономерного акролеина. От 80 до 130° проходит экзотермический процесс дегидратации гидратированных альдегидных групп полиакролеина. Ярко выраженный экзотермический процесс при 130—180° с резкой потерей в весе объясняется деструкцией циклических структур с $n < 3$. Наличие в полимере циклических структур с $n > 3$ сдвигает пики DTA и DTG в область более низких температур на 20°. При температурах около 250° и выше происходит термическое окисление боковых карбонильных групп и их декарбоксилирование со значительной потерей в весе. Все высказанные положения подтверждены данными ИК-спектроскопии.