

Thermal Oxidative Degradation of Poyacroleinoximes

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Abstract

Thermal oxidative degradation of poyacroleinoximes that have been obtained by condensation of polyacroleins that contain as much as 80 % of aldehyde groups, with hydroxylamine has been studied. In response to differential thermal and isothermal analysis as well as to IR and mass spectrometry, it has been demonstrated that the process of thermal oxidative degradation of poyacroleinoximes to a large measure depends on their heating rate and to a lesser degree, on the molecular mass and on the structure of polymers. It has been found that dehydration of oxime groups and N-hydroxy piperidine cycles is observed in a temperature range from 120 to 250 °C at the heating rate up to 4 °C/min (on evidence of DTGA, as well as based on the results that have been received in the study of thermal oxidative and thermal degradation under the isothermal regime at 170 and 190 °C), which gives rise to acrylonitrile units in the macromolecules, these units being capable to intra- and intermolecular cross-linking. Thus, heat treatment of poyacroleinoximes at 190 °C under the isothermal regime may yield heat resistant polymers. With increased heating rates for poyacroleinoximes, being as large as 5 °C/min and higher, the destruction becomes complicated even at 170 °C due to oxidizing detachment of lateral groups that make up the macromolecules of polymers, probably, at the expense of a chain process initiated by nitroxyl radicals. This yields a hydrocarbon polymeric residue that contains conjugated $\text{C}=\text{C}$ bonds in the macrochain and that is burnt down in a temperature range of 400–600 °C.

INTRODUCTION

The emergence of papers into synthesis and study of the properties of poyacroleinoximes (PAO) falls on the 60s of the past century. Now, it has been known that polymeric reagents that involve oxime groups are of considerable importance in catalytic nucleophilic reactions of organic and bioorganic chemistry [1]. They show a higher than usual hydrolytic activity, particularly, in relation to toxic organophosphoric compounds [2–5]. In addition, PAO readily form complexes with metals [6] and cyanide anions [7], which ensures that they can be used for sewage treatment in gold mining. The structure of a PAO macromolecule that includes a various quantity of aldoxime units [8–10] has been studied. It was found that the composition of a polymer that has been produced by condensation of polyacroleins (PA) with hydrox-

ylamine includes various fragments (I–IV), the composition and quantity of which depend on the structure of the initial polymer (Scheme 1). The formation of oximes process has been reported and it is employed for the quantitative determination of aldehyde groups [11]. However, there are no insights in the literature on the behaviour of various PAO at elevated temperatures. Investigation of the processes of thermal oxidative degradation that occur in macromolecules will make it possible to recognize performance characteristics of PAO as well as the interrelation between the structure of the polymers under investigation and their properties.

EXPERIMENTAL

DTA and TG thermograms were recorded with derivatograph System: F. Paulik, L. Erdey

(Hungary) in air atmosphere in the range of temperatures 20–800 °C. Weighted specimens were of 0.1 g; the temperature changing rate was 4 and 5 °C/min; the sensitivity of DGA and DTG comprises 1 : 5. The reference substance was Al₂O₃. Isothermal study of polymers performed in a set-up made up of a pipe still heater that was equipped with a thermocouple. PAO heating was conducted in the air atmosphere or in argon with the rate of temperature rise of 4 and ≥5 °C/min, depending on the task in view. Samples were let to stand at the temperatures of 170 or 190 °C from 30 to 240 min. Monitoring the processes that occurred in the samples under investigation was performed every 30 min with IR spectroscopy. IR spectra of polymers were registered with a Specord IR-75 spectrometer in tablets with KBr. Mass spectrometer studies were conducted in chromatomass spectrometer MAT-212 (Finnigan) using a system of direct introduction of the sample in the source of ions. Ionisation potential $V_{\text{ion}} = 70$ eV; the temperature of the ion source was 300 °C; the temperature of introduction was 100–120 °C.

Polymers (PAO) were synthesized through the modification of PA with hydroxylamine in aqueous medium. Polyacroleins were prepared by polymerisation of acrolein in various initiating systems: K₂S₂O₈/Fe²⁺ (PAO-1), NaNO₂/H₂O₂ (PAO-2).

RESULTS AND DISCUSSION

The present work gives the results of thermal oxidative degradation of PAO that have been obtained by modification of PA with hydroxylamine and that were different from one another not only in their content of oxime groups, but also in molecular mass (M) and in the structure of macromolecules (PAO-1 and PAO-2). The composition of these polymers [8, 10] has been investigated. Accordingly, the

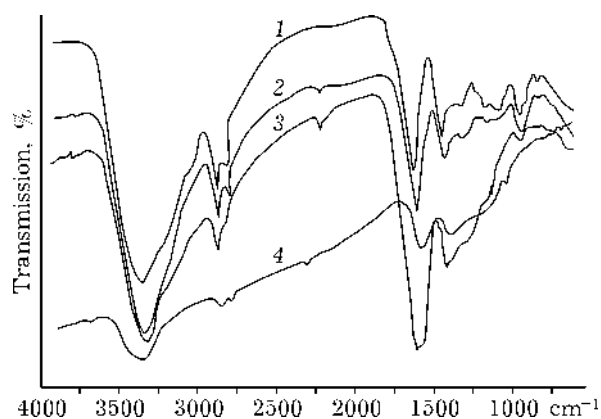
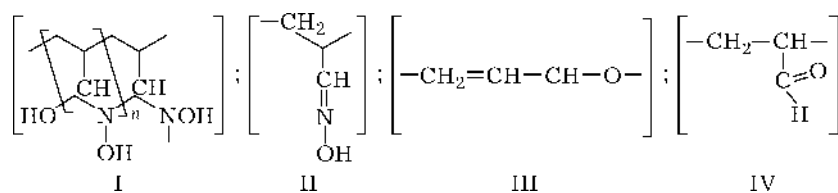


Fig. 1. IR spectra of PAO-1 samples: 1 – the initial sample, 2–4 – the sample processed at 170 (2, 4) and 190 °C (3); the temperature increase rate, °C: ≤4 (2, 3), ≥5 (4).

macromolecules PAO-1 with $M = 60\,000$ include structural fragments I and II that comprise 75–80 %, which corresponds to the mass fraction of nitrogen of 14–16 %. The structures III, IV are accounted for by 20–25 %. It has been found with EPR spectroscopy method that the composition of macromolecules includes nitroxyl radicals, and the concentration of paramagnetic centres in the polymers comprises 10^{18} – 10^{20} spin/g [8]. Computation has shown that one radical falls on 100 units of the macromolecular chain. Macromolecules of PAO-2 with $M = 5000$ are composed of structural fragments II (30–35 %) that contain free oxime groups (the mass fraction of nitrogen comprises 6–7 %) and III, IV (65–70 %) (see Scheme 1).

The bands at 3416, 2926 and 2859, 1158, 937 cm^{-1} in IR spectra of PAO-1 (Fig. 1) account for –OH, –CH₂–, –C–N–, –N–O– bonds, respectively. The wide band at 1642 cm^{-1} is attributable to the combined absorption of –C=C– and –C=N– bonds, and the small shoulder at 1710 cm^{-1} corresponds to –C=O– groups. The IR spectrum of PAO-2 is identical to the spectrum of PAO-1; however, there are no bands typical for –C–N– bonds.



Scheme 1.

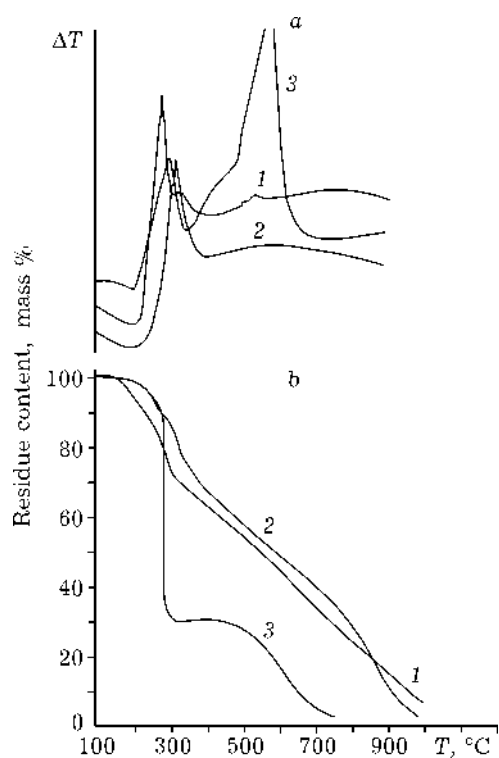
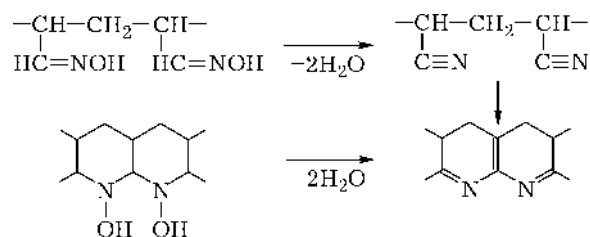


Fig. 2. Curves of DTA (a) and of thermogravimetric analysis (b): 1 - PAO-2; 2, 3 - PAO-1; heating rate, °C: 4 (1, 2), 5 (3).

Figure 2 presents data of the dynamic thermogravimetric analysis of thermal oxidative degradation of polymers. No endothermic effect that is typical for PA and that is responsible for the loss of sorption water (10 %) [12], is registered in the DTA curve that has been received when heating PAO-1 at the rate of 4 °C/min in the range of 50 to 120 °C. Such a mass loss for this polymer falls on 190 °C. Meanwhile, the low-molecular PAO-2 that contains for the most part free oxime groups in its macromolecules, shows the mass loss at a lower temperature and it is as large as 6 % at 100 °C. According to DTA, thermal oxidative degradation of PAO in temperature limits from 120 to 250 °C is accompanied by a rather appreciable exothermic effect that shows a greater intensity and comes 40–50 °C earlier for PAO-2, than for PAO-1. The mass loss at 250 °C

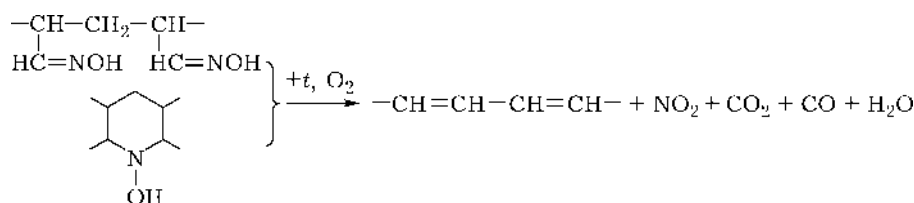


Scheme 2.

for both polymers comprises 27 %. Water has been found in volatile destruction products by the method of mass spectrometry ($m/e = 18$). The IR spectra of PAO-1 samples that were thermally processed both in air atmosphere and in an inert medium at 170 °C show a decreased intensity of the band at 1158 cm^{-1} that is typical for the ---C---N--- bond, and upon the subsequent heating, it dies out completely at 190 °C (see Fig. 1). At the same time, the spectra show a band at 2238 cm^{-1} that gives an indication of nitrile groups, and a band at 1642 cm^{-1} that is due to the ---C=N---OH group is displaced to 1652 cm^{-1} , which is indicative of ---C=N--- bonding in the cycle (Scheme 2).

No formation of acrylonitrile units was previously observed in macromolecules of polymers upon PAO exposure to dehydration agents, unlike low-molecular aldoximes, because of the structural feature of their macrochains [8, 10]. However, when heating PAO with initial rate of no more than 4 °C/min and when the isothermal regime is observed subsequently at 190 °C over the course of 3–4 h, this process could be realized virtually completely.

Upon increasing the heating rate for PAO-1 to reach 5 °C/min and higher, the destruction process adopts a spontaneous character and the mass loss at 170 °C comprises even 70 % (see Fig. 2). H_2O , C, CO_2 , and NO_2 ($m/e = 18, 28, 44$ and 46) have been detected almost in equal proportions in volatile products by the mass spectrometry method. The IR spectra of the



Scheme 3.

received black hydrocarbon residue show no absorption bands that would give an indication of various groups included into the PAO-1 macromolecule (see Fig. 1). However, a band at 1605 cm^{-1} that is typical for conjugated -C=C- bonds makes its appearance at the same time. Thus, thermal oxidative degradation at the increased heating rate occurs with an oxidizing detachment of lateral groups (Scheme 3).

According to DTA and thermogravimetric analysis, the resulting hydrocarbon residue is burnt down in a temperature range of 400 to $600\text{ }^{\circ}\text{C}$ (see Fig. 2).

In our opinion, with an increase in the heating rate of a substance, the process of thermal-oxidative degradation of PAO-1 adopts a chain character due to its initiation by nitroxyl radicals that can be generated in the polymer [8].

CONCLUSION

Hence this paper pioneers in presenting the data concerning thermal oxidative degradation of polyacroleinoximes. It was found that the nature of the process to a large measure depends on the heating rates and to a lesser degree, on its molecular weight and on the polymer structure. The processes that run in PAO during their heating at a rate of $4\text{ }^{\circ}\text{C}/\text{min}$ and less in the temperature range of $120\text{--}250\text{ }^{\circ}\text{C}$, lead to dehydration of oxime groups and to the formation of acrylonitrile units in macromole-

cules, the units being capable of intra- and intermolecular cross-linking. The resulting is that thermal resistance of the polymer increases. Upon an increase in the heating rate up to $5\text{ }^{\circ}\text{C}/\text{min}$ and higher, oxidizing detachment of lateral groups is evidenced even at $170\text{ }^{\circ}\text{C}$, which gives rise to a hydrocarbon residue with conjugated -C=C- bonds. The received studies made it possible to recognize temperature limits for the service of polyacroleinoximes that is up to $100\text{--}120\text{ }^{\circ}\text{C}$.

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