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THERMOANALYTICAL STUDIES OF 2,2,6,6-TETRAMETHYL-4-OXY-4-ETHYNYLPIPERIDIN-1-OXYL POLYMERIZATION

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The structure transition temperature, monomer melting point and critical temperatures of polymerization and decomposition of 2,2,6,6-tetramethyl-4-oxy-4-ethynylpiperidin-1-oxyl were determined by means of thermal analysis. Some features of the polymerization of the acetylenic monomer were studied via thermal analysis, and IR and ESR spectroscopy.

It was shown that, during non-isothermal temperature increase, the mass loss of the sample associated with the exothermic effect of polymerization occurred at the expense of the monoacetylene sublimation process (42%), a reagent explosion and decomposition of the reaction products formed (15%).

Keywords: ESR and IR spectroscopy, 2,2,6,6-tetramethyl-4-oxy-4-ethynylpiperidin-1-oxyl polymerization

Introduction

The solid-state thermopolymerization of disubstituted diacetylene with stable nitroxyl free radical pendant groups was recently carried out at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences and the Mendeleev Institute of Chemical Technology. The magnetic measurements performed at the Institute of Chemical Physics of the Academy of Sciences showed the polymers to be weak organic ferromagnets with T_c higher than 400 K [1]. It is of great interest to study the thermal transformations of various acetylenes with a stable nitroxyl free radical because of the potential for the creation of polymeric organic ferromagnets and high-spin polymeric photo- and thermostabilizers.

The aim of this paper was to use thermal analysis to study the reactivity of 2,2,6,6-tetramethyl-4-oxy-4-ethynylpiperidin-1-oxyl (TEOPO) at high temperatures, and in particular its ability to undergo thermopolymerization.

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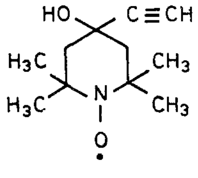
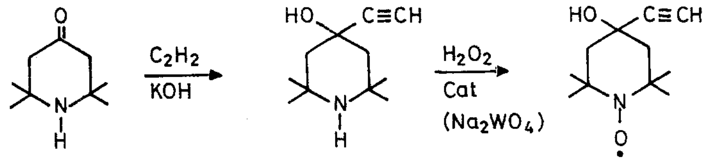
Experimental

The acetylenic monomer containing the stable nitroxyl free radical has the formula



This compound was synthesized as follows [2]:



Two TEOPO modifications were formed via recrystallization from different solvents. Either a crystalline sample with a cubic modification or thin needle crystals were obtained via recrystallization from methanol, ethanol, chloroform, acetone or dioxane, or from an alcohol solution in water (methanol, ethanol/water = 1:1).

The monomer crystalline structure is of some interest due to its reactivity in the polymerization process.

The X-ray analysis of TEOPO was carried out with the Hemer-Uogts automatic diffractometer (a graphite monochromator at a scanning rate of $\Theta / 2\Theta$, $2\Theta_{max} = 60$ °C). The structure was interpreted directly and defined more accurately through linear least square analysis in the non-isotropic approximation for non-hydrogen atoms [3].

Figure 1 presents the molecular packing scheme for TEOPO crystals. It is seen that the monomer molecule has the 'chair' conformation. Strong hydrogen-bonds between the nitroxyl oxygen atom and a hydroxyl hydrogen are unfavourable for topochemical polymerization since the acetylenic bonds are situated far from each other in the same plane and can not polymerize in the solid state [4].

It should be noted that the monoacetylene crystal does not change its colour during X-ray analysis, indicating that TEOPO is appropriately stable towards X-ray irradiation.

The monoacetylene crystal has a monoclinic structure. The nitrogen atom at the paramagnetic site is shifted by 0.207 Å out of the plane of the atoms bonded to the nitrogen. The N–O bond distance is 1.289 Å, and the N–C bond distances 1.487 and 1.493 Å. The monoacetylene molecules are connected in chains through O–H...O hydrogen-bonds. The minimum inter- molecular distance including acetylenic group atoms is 5.566 Å.

IR spectra were recorded with a Specord M-80 spectrometer, using KBr pellets.

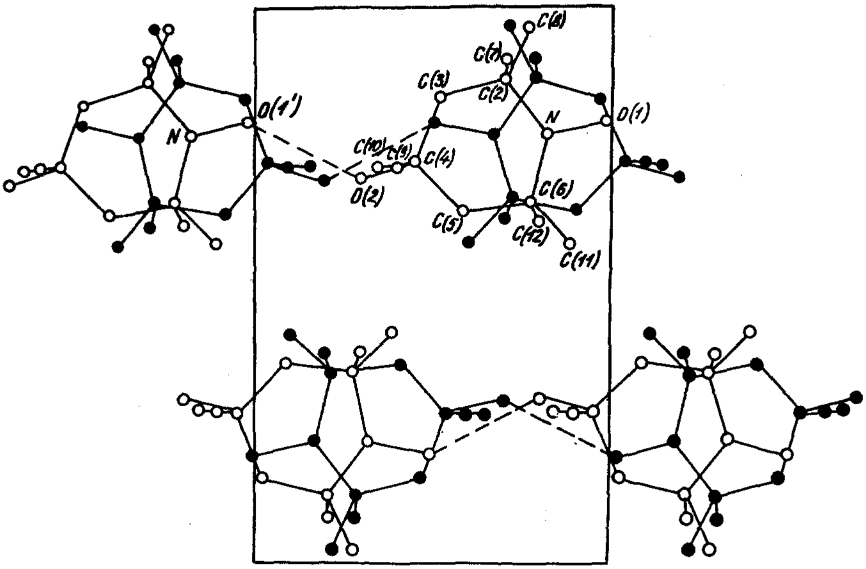


Fig. 1 A scheme of molecules packing in 2,2,6,6-tetramethyl-4-oxy-4-ethynylpiperidin-1-oxyl monomer crystal

ESR spectra were recorded with an ERS-200 spectrometer (Germany).

Thermal analysis was performed with a Derivatograph 1050°C (Hungary) under non-isothermal conditions in the temperature range 20°– 600°C in a flowing argon or air atmosphere. The experimental conditions were as follows: sample weight 100 mg; reference material annealed Al_2O_3; heating rate 3 deg/min; argon flow 50 ml/h. Some experiments were carried out in flowing argon under isothermal conditions at 130°C (heating rate 20 deg/min) prior to testing.

Results and discussion

The same thermal curves and IR spectra were found for both the cubic and the needle modifications of the monoacetylenic compound, and therefore the former was used for further investigation.

The TEOPO thermal curves obtained on heating in an argon flow are presented in Fig. 2. Two small square peaks corresponding to endothermic effects were observed in the DTA curve. The first effect, at 95°C, may be related to a structure transition process, and the second one, at 122°C, to the monoacetylene melting point.

The IR and ESR spectroscopic data confirmed the above explanation, since the same spectra were obtained for both the initial compound and those preheated up to 95° or 122°C. Consequently, no chemical conversion of the monomer takes place at or below these temperatures.

The heats were 3.78 and 5.04 kJ/mol for the structure transition process and the TEOPO melting point, respectively [5].

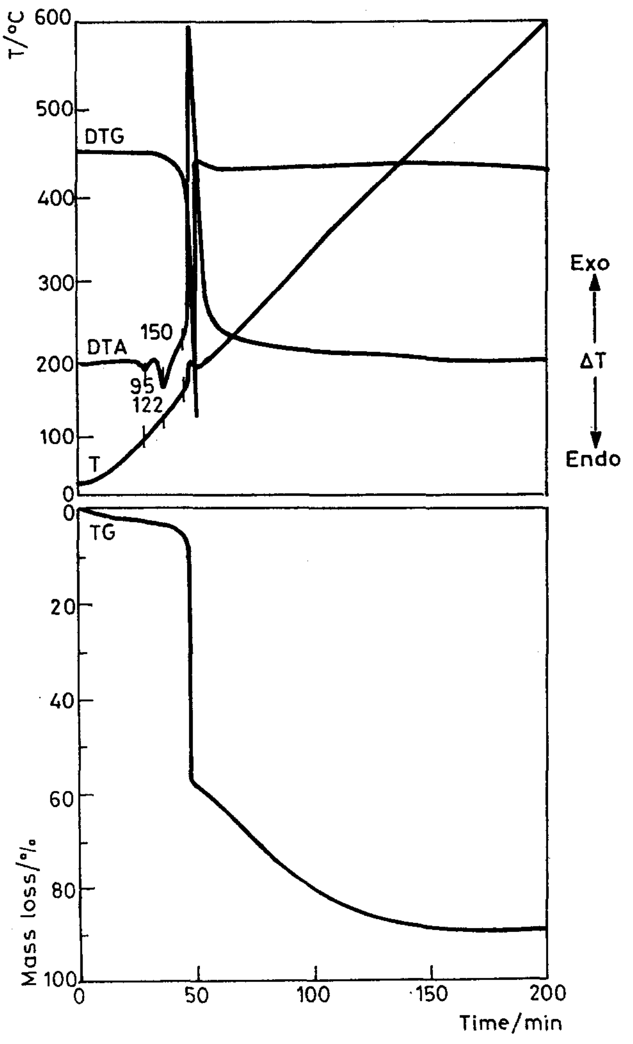


Fig. 2 Thermoanalytical curves of TEOPO obtained by heating in flow argon

TEOPO melting is accompanied by a small mass loss (3%) due to partial monomer sublimation. The IR and ESR spectroscopic data and chemical analysis indicate that the sublimed monomer retained the initial chemical composition.

Above 150°C an exothermal process started (t_{max} = 170°C), apparently corresponding to TEOPO polymerization, with a heat of 141 kJ/mol.

According to the thermoanalytical data, therefore, the monoacetylene polymerization took place efficiently in the melt state. The polymerization process occurred with both explosive development and monomer sublimation, the mass loss at 170°C being 57% (TG curve). After this, no effect was observed in the DTG and TG curves; the mass loss at 500°C was 90%.

It was also shown that aerial oxygen did not affect the polymerization process, since the TEOPO thermal curves exhibited the same characteristics on heating in air or in an argon flow. Above 300°C, a strong exothermic effect appeared, due to thermooxidative degradation of the monoacetylene conversion products.

If the sample was preheated up to 200°C, then cooled and heated again, practically no exothermic effect was observed in the DTA curve. This result indicates completion of the polymerization reaction at 150°– 170°C.

A polymer sample was purified by multiple precipitation with heptane from chloroform solution. The IR spectrum of the polymer differed strongly from that of the monomer. The absorption band relating to the triple bond was not present and a new absorption band characterizing a conjugated double bond was observed.

The intensity of the ESR spectroscopic signal of the polymer decreased significantly in the course of TEOPO thermopolymerization, and at the same time the singlet was split due to the high g factor anisotropy.

Series of experiments were performed under isothermal conditions in flowing argon for 200 min at 130°C, i.e. 20 deg below the appearance of the exothermic effect (Fig. 3).

For about 40 minutes after the beginning of heating, an exothermic peak associated with the polymerization process in the DTA curve was observed. However, in this case the process proceeded without explosive development. The mass loss at maximum effect occurrence was only 15%, and after 200 minutes it was 20%.

Under non-isothermal conditions the mass loss occurred at the expense of both partial reagent sublimation and polymerization product decomposition. The IR and ESR spectra of the sublimed product coincided with those of the initial TEOPO.

In order to study the polymerization process in detail, TEOPO samples were heated at 130°C under argon for 1–10 hrs and studied then by means of thermal analysis under non-isothermal conditions and by IR and ESR spectroscopy.

Significant differences in thermal characteristics were observed on comparison of the thermal curves of preheated and initial TEOPO samples.

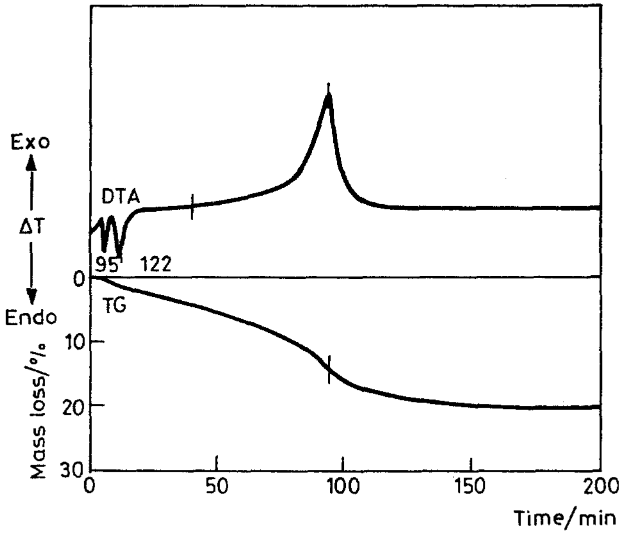


Fig. 3 Isothermal DTA and TG-curves at 130°C in flow argon

As may be seen in Fig. 4, the endothermic effect relating to the structure transition in the sample preheated at 130°C for 1 h is absent from the DTA curve. Moreover, the melting point of the monoacetylenic compound and the temperature of polymerization beginning are decreased (115° and 130°C, respectively). In spite of the explosive development of the polymerizaton process and the close values for the preheated monomer and the original sample, the mass loss at the effect maximum was only 25%, and this was followed by the much slower decomposition process.

The exothermic effect of the samples preheated for 2–10 hours was essentially changed and the explosive development of the polymerization was not observed. For example, the square of the exothermic peak decreased three-fold for the sample preheated for 4 hours.

IR and ESR spectroscopic data confirmed the monomer consumption. In fact, increase of the heating duration led to an intensity decrease for the carbon-carbon triple bond (2110–2120 cm^{-1}) and to the appearance of the double bond signal (1600 cm^{-1}) in the IR spectrum of the reaction mixture.

Figure 5 presents the ESR spectrum of the original TEOPO sample, as well as those of samples preheated for 1 or 4 hours. The intensity of the ESR spectrum decreased strongly with increase of the polymerization time.

The nitroxyl radicals decayed during polymerization. The spectrum was observed to split after 4 hours of polymerization. This result was typical of a radical marker and indicative of a small content of the radical species in the reaction mixture (~ 1%). The kinetics of the radical decay is plotted in Fig. 6. This dependence shows the monomer consumption in terms of the nitroxyl radical. It is seen that the decay process was completed after 4 hours under isothermal conditions at 130°C.

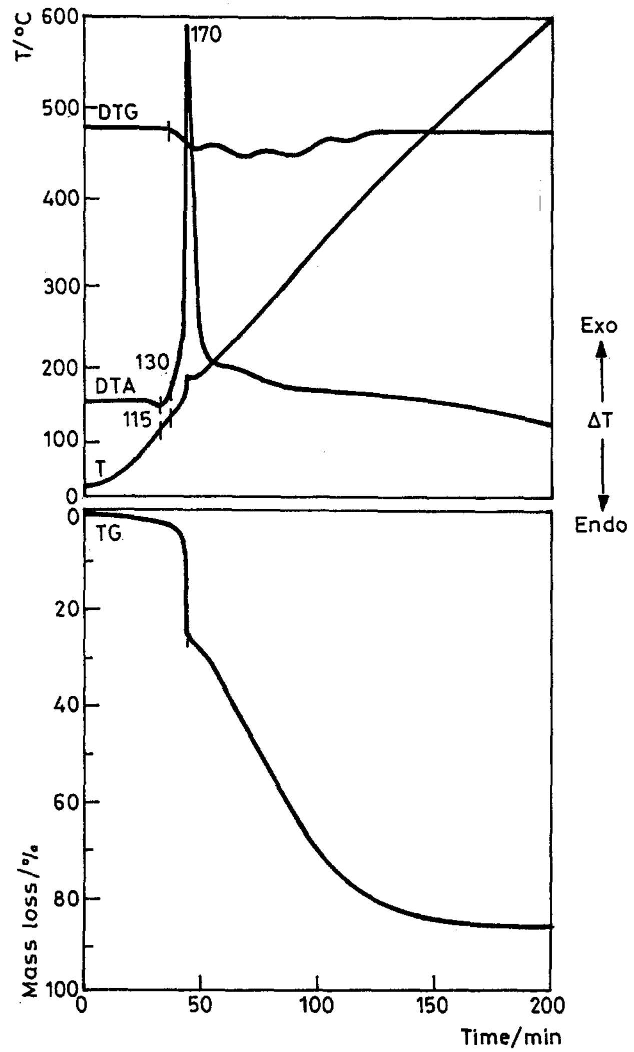


Fig. 4 Thermoanalytical curves of TEOPO preheated at 130°C for 1 hour in flow argon

The thermal curves of the sample preheated under non-isothermal heating in an argon flow revealed that the polymer samples differed in thermal stability, depending on the heating time.

The temperature corresponding to 10% mass loss was chosen as a thermal stability criterion.

The dependence of the temperature of 10% mass loss by the monoacetylene on the heating time is given below:

Time, h	:	1	2	4	6	8	10
Temperature, °C	:	170	180	185	185	190	195

These data showed that the thermal stability of the polymer sample preheated for 10 hours was 25 deg higher than that of the sample preheated for only 1 hour. Therefore, different thermodynamic non-equilibrium structures are formed as a result of either polymerization of the original monomer or preheating of the monomer for more than 2 hours.

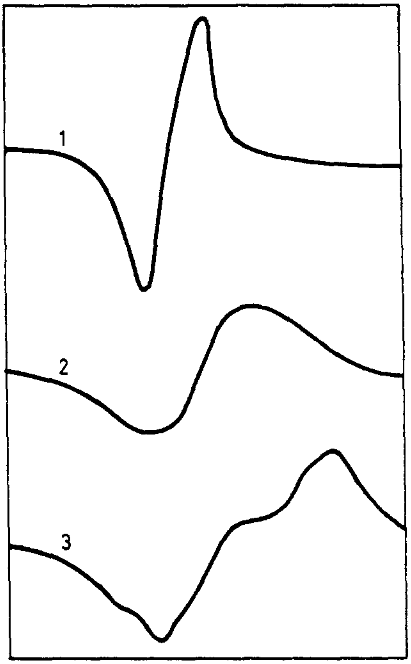


Fig. 5 ESR-spectra curves: 1 – TEOPO, 2 – preheated at 130°C 1 h, 3 – preheated at 130°C 4 h

The existence of a critical (threshold) polymerization temperature is of great interest. Under non-isothermal conditions, the polymerization reaction with explosive development proceeded at 150°C. The stable nitroxyl radicals are well known to be efficient inhibitors of free radical reactions [6]. Nevertheless, at high

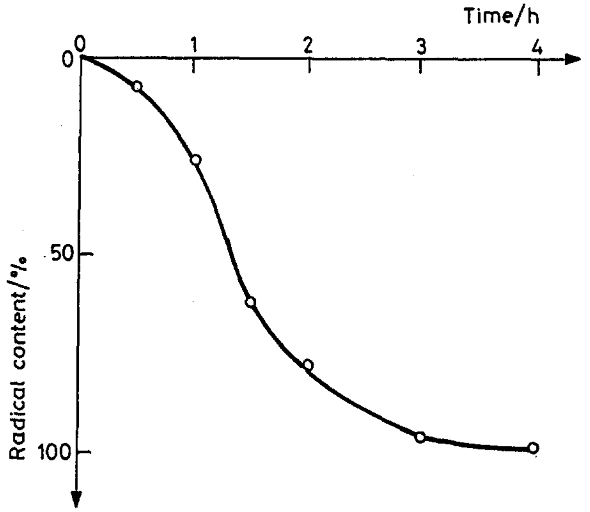


Fig. 6 Kinetics of radicals decay during in the course of thermopolymerization at 130°C

temperature they are able to join multiple C–C bonds and initiate a polymerization reaction, for example that of styrene [7].

A quiet course of polymerization under isothermal conditions below the critical temperature, and an explosive process at just that point, indicate energy transfer. This energy stimulates stable nitroxyl radicals and converts them from inhibitors to initiators of the spontaneous explosive polymerization.

The polymer composition depends on the heating time because of the occurrence of side-reactions, such as the transfer of active sites on methylene groups of the piperidine cycle due to hydrogen abstraction from methylene or hydroxyl groups by the nitroxyl radical. Further, the polymer can be cross-linked via double conjugated bonds.

Actually, the intensity of the absorption band of the conjugated double bonds in the polymer, at 1600 cm^{-1}, is less for TEOPO preheated at 130°C for 8–10 hours than for a sample preheated for 3–4 hours. ESR spectroscopic data confirmed the total consumption of the nitroxyl radicals during 4 hours of polymerization.

The appearance of the absorption band at 1735 cm^{-1} in the IR spectrum of the polymer, and also the decrease in peak intensity at 3380 cm^{-1}, characterizing the OH group valence vibration, showed the presence of carbonyl groups formed as a result of thermal transformation.

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Zusammenfassung — Mittels Thermoanalyse wurde die Strukturumwandlungstemperatur, der Monomerschmelzpunkt und die kritischen Temperaturen für Polymerisierung und Zersetzung von 2,2,6,6-Tetramethyl-4-oxy-4-ethynylpiperidin-1-oxyl bestimmt. Mit Hilfe von Thermo-analyse, IR- und ESR-Spektroskopie wurden einige Eigenschaften der Polymerisierung des Acethylen-Monomers untersucht.
Es wurde gezeigt, daß bei einem nichtisothermen Temperaturanstieg der Massenverlust der Probe zunimmt, verbunden mit einem exothermen Effekt der eingetretenen Polymerisierung auf Kosten des Monoacetylen-Sublimierungsprozesses [42%], der Explosion und der Zersetzung der gebildeten Reaktionsprodukte [15%].