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To cite this article: T I Kolesnikov *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **525** 012022

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Synthesis and study of the properties of thermoset oligoimides with propargyl fragment

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Abstract. A series of thermoplastic oligoimides with a propargyl substituent in the side chain was synthesized by the method of high-temperature catalytic copolycondensation in the melt of benzoic acid based on the monomer 5- (2-propyn-1-yloxy) benzene-1,3-diamine (PBD), 2,2-bis-[(3,4-di-carboxyphenoxy)phenyl]propane dianhydride (BPADA), 2,2-bis-[(4-aminophenoxy)phenyl]propane (BAPP) and phthalic anhydride (PA). The uncured imide oligomers showed good solubility (>20 wt% in N-methyl-2-pyrrolidone), wide temperature processing window (>50°C) and also flow well at 220°C. These imide oligomers were successfully converted to cross-linked structures after curing at 300°C. Cross-linked oligomers have a temperature of 5% weight loss >500°C and T_g>200°C.

1. Introduction

Aromatic polyimides (PI) have a complex of valuable properties: high thermal and heat resistance, good mechanical properties, chemical resistance, low moisture absorption, radiation resistance and performance in a wide temperature range. For the use of PI as matrix for polymer composites materials (PCM), prepolymer solutions are used — polyamic acids or imide-forming polymerization compositions of the PMR-15 type (polymerization of monomer reactants). In case of PMR-15, the solvent removal, the chain growth, imidization, and the formation of a three-dimensional network occur in a course of stepwise heating of the impregnated tissue to 350 °C for several hours. The disadvantage of these matrix for PCM is the difficulty of technological control during processing. It is necessary to carefully remove residual solvent and water, otherwise defects are formed, and the mechanical properties of PCM deteriorate. In this regard, the idea seems attractive of using the fully imidized oligomers with reaction groups capable to cure with formation of a three-dimensional network without release of volatile compounds [1].

In the 90s, Hughes (USA) [2] developed a series of Therimid oligoimides containing ethynyl end groups capable of cyclotrimerization with the formation of an aromatic cycle. Alkynyl groups are introduced using monofunctional alkyne-containing amines or anhydrides [3-5]. Also, oligoimide compositions based on 4-phenylethynylphthalic anhydride (PEPA) [6-8] are used, with the curing temperatures of about 380 °C. In oligomers of this type, the content of cross-linkable groups and the



chain length, which determines the rheological behavior, are rigidly connected to each other, which makes it difficult to tune properties. In this connection, another approach is promising of using (co)oligoimides containing monomer moieties with cross-linkable groups in a side chain, the content of the latter in chain and the main chain length chain can be varied independently.

In this work, we have prepared a new type of cross-linkable thermoplastic oligoimides (OI) based on a new monomer 5-(2-propyn-1-yloxy) benzene-1,3-diamine (PBD). Due to presence of alkynyl group in the side chain, these OI can crosslink via cyclotrimerization to form 3D network. To obtain OI, an advanced method of high-temperature catalytic polycondensation in molten benzoic acid (BA) [9], BA playing the role of a solvent, catalyst and reactivity regulator in this process.

2. Materials and methods

2.1. Materials

2,2-Propylidenebis(1,4-phenyleneoxy)diphthalic anhydride (BPADA) (Aldrich) was crystallized from acetic anhydride, $T_m=189^\circ\text{C}$. 2,2-bis-[(4-aminophenoxy)phenyl]propane (BAPP) was crystallized from isopropanol, $T_m=130^\circ\text{C}$. Phthalic anhydride (PA) (Aldrich) was sublimed in vacuo, $T_m=131^\circ\text{C}$. Benzoic acid (BA) was recrystallized from the mixture (ethanol/water) and dried in vacuo, $T_m=122^\circ\text{C}$. Diethyl ether, acetone and chloroform (Chimmed, Russia) were used without additional purification.

2.2. Measurements

IR spectra were recorded on FTIR spectrometer Bruker, mod. Equinox 55/S (Germany) in a range of $4000\text{--}400\text{ cm}^{-1}$. Samples were prepared in a form of CsI tablets with the substance content of 1%. NMR ^1H and ^{13}C were registered on Bruker AM-300 spectrometer at 300.13 and 75.47 MHz respectively. Chemical shifts are given with respect to signal of $\text{Si}(\text{Me})_4$.

DSC thermograms were recorded on DSC-500 device (Russia) at heating rate of $16^\circ\text{C min}^{-1}$. GPC measurements were executed on the device "Stayer" (Akvilon) at 60°C , with Phenogel column (2-70 kDa) and DMF as eluent ($1\text{ ml}\cdot\text{min}^{-1}$). Polystyrene standards were used.

Thermomechanical analysis was (the stock penetration mode) performed using the UIP-70 instrument (Sputnik, Russia) at a load of $2.8\text{ kg}\cdot\text{cm}^{-2}$ and a heating rate of 10°C/min . Polymer samples for TMA were obtained by hot pressing at $220\text{--}300^\circ\text{C}$.

Data of thermogravimetric analysis (TGA) were obtained using a PerkinElmer Pyris 1 TGA analyzer under a nitrogen flow of 100 mL/min at a heating rate 10°C/min in dynamic mode.

Determination of logarithmic viscosity was performed using a Ubbelode capillary viscometer for solutions of oligomers and polymers in chloroform with concentration 0.5 g/100 ml at 25°C .

2.3. Synthesis of 5-(2-propyn-1-yloxy) benzene-1,3-diamine (PBD)

To a solution of 2.22 g (0.01 m) 1,3-dinitro-5-(prop-2-en-1-yloxy)benzene [10] in 50 ml of dioxane at $10\text{--}15^\circ\text{C}$, a solution of 22.6 g (0.1 m) $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ in 55 ml of concentrated HCl was added dropwise and maintained for 3 hours. Then, it was neutralized with a concentrated aqueous solution of NaOH until the yellowish color disappears (pH 9-10), and extracted with CH_2Cl_2 ($4\times 100\text{ ml}$), dried with Na_2SO_4 , filtered through a layer of silica gel, and evaporated. To the residue 40 ml water and about 1 ml of concentrated HCl was added until positive acidic test, activated charcoal was added. Mixture was filtered and the filtrate basified to pH 8-9 with aqueous NaOH. The precipitate was filtered off, washed with water and dried to obtain 0.356 g . (22%). $T_m=88\text{--}89^\circ\text{C}$, NMR ^1H : 3.41 (s, 4h); 3.49 (s, 1H); 4.55 (s, 1H); 4.72 (s, 2H-); 5.46-5.49 (m, 2H); MS (m/z) = 162 M^+ ; IR spectrum (CsI): $3440, 3350\text{ cm}^{-1}$ (N-H), 3260 cm^{-1} (C-H acetyl), 3040 cm^{-1} (C-H ar), 2924 and 2870 cm^{-1} (CH_2), 2124 cm^{-1} ($\text{C}\equiv\text{C}$), 1620 cm^{-1} (N-H), 1600 and 1490 cm^{-1} (C-Car), 1170 cm^{-1} (C-O-C). ^1H NMR (300 MHz , DMSO-d_6): d 5.48 (d 1H), 5.43 (d 2H), 4.72 (s 4H), 4.52 (d 2H), 3.49 (t 1H). Elemental analysis: found, %: C, 66.48; H, 6.41; N, 17.11; calculated for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}$, % C, 66.65; H, 6.21; N, 17.27.

2.4. Synthesis of polyimide and oligoimides with propargyl groups (PI 9-10, OI 4-5, OI 9-10) in benzoic acid

Crystalline BA (9.0 g) and 0.57 g (0.20 mmol) of BPADA were loaded into a glass reactor equipped with a stirrer and an inert gas inlet. After inert gas was blown into the reactor, the mixture was heated up to 140°C, and 0.404 g (0.18 mmol) BAPP was added. The reaction mixture was stirred for half an hour at 140°C with slow blowing of inert gas. Then, to the reaction mixture, 0.026 g (0.02 mol) of PBD was added and the synthesis was carried out for another 1.5 hours. The final molar ratio of monomers for polyimide-1 (PI-1) was BPADA:BAPP:PBD:PA 10:9:1:0. After cooling, the solidified mixture was extracted with diethyl ether. Polymer residue was filtered and dried in vacuo.

Similarly, oligoimides were obtained (OI-1 and OI-2). For obtaining OI-1 BA (9.0 g) and 0.57 g (0.20 mmol) of BPADA were loaded. After addition of BAPP (0.404 g (0.18 mmol)), the reaction mixture was stirred for half an hour at 140°C with slow blowing of inert gas. Then, 0.026 g (0.04 mol) of PBD was added to the reaction mixture, and after 20 minutes 0.029 g (0.04 mol) of PA was added. Synthesis was carried out for one hour. The final molar ratio of monomers for OI-1 was BPADA:BAPP:PBD:PA 5:4:2:2 and for OI-2 was BPADA:BAPP:PBD:PA 10:9:2:2. After extracion with diethyl ether, was filtered and dried in vacuo.

3. Results and discussion

The syntheses of PI and OI-1, 2 were carried out according Figure 1. During the synthesis of OI-1,2, PA was introduced into the reaction system at the end of the process to close the terminal amino groups. To obtain propargyl-containing oligoimides with different degrees of polymerization, the ratio of initial monomers was changed (BPADA:BAPP:PBD:PA 5:4:2:2 for OI-1 and BPADA:BAPP:PBD:PA 10:9:2:2 for OI-2). Syntheses of all compounds were carried out in a homogeneous solution.

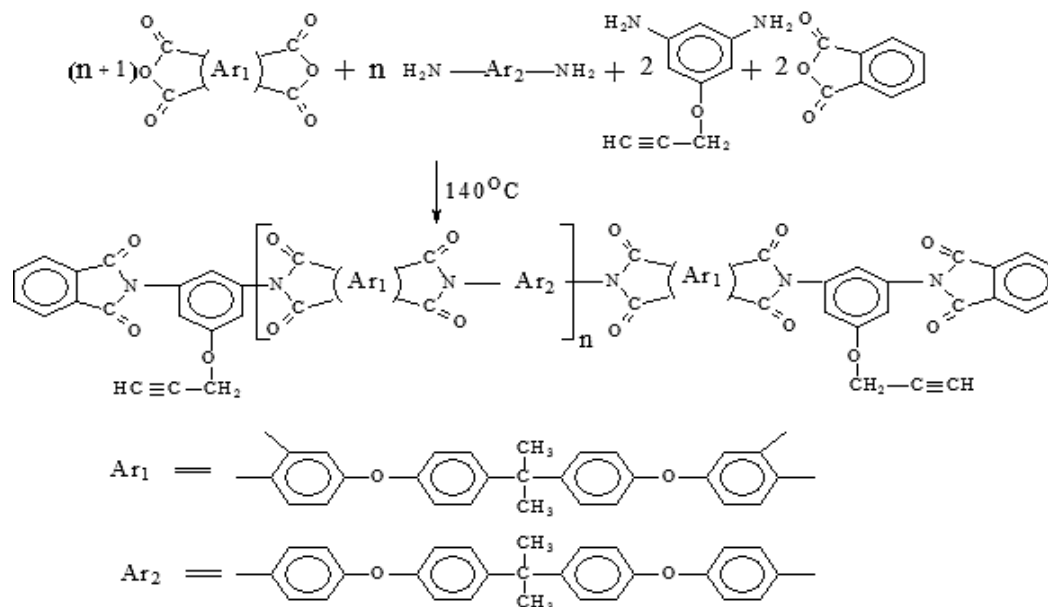


Figure 1. Scheme of synthesis of oligoimides ($n = 4, 9$ for OI-1, OI-2).

The resulting products were white powders or flakes, soluble in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF) and chloroform. By increasing the molar ratio of the BPADA / BAPP monomers in the initial mixture (OI-1, OI-2), the logarithmic viscosity increases 0.345, 0.641 dl/g, respectively. Molecular weight characteristics of OI-1 and OI-2 samples are present in Table 1.

Table 1. Molecular Mass Characteristics of OI-1, OI-2 (GPC).

Sample	M_w	M_n	M_w/M_n
OI-2	79700	36500	2.2
OI-1	54100	34200	1.6

For copolyimide (PI-1), obtained by stoichiometry 10-9-1-0, the logarithmic viscosity is $\eta_{\log} = 1.2$ dl/g. This value practically coincides with $\eta_{\log} = 1.22$ dl/g for homo polymer (10:10:0:0) obtained from BPADA and BAPP at the same conditions. So, it could be concluded that alkynyl fragment in PI-1 is stable at conditions of the synthesis.

All products of copolycondensation possess a film-forming ability. Transparent films were obtained from their chloroform solutions: brittle for OI-1, durable for OI-2 and PI-1. The presence of “polymeric behavior” of oligomers OI-1 and OI-2 is associated with the structure of the initial monomers (a large length of the elementary unit).

Figure 2 shows the IR spectrum of propargyl-containing polyimide PI-1. Absorption bands at 1720 and 1780 cm^{-1} were attributed respectively to the symmetric and asymmetric C=O vibrations in imide cycle. The intensity of absorption of 3288 cm^{-1} corresponds to the vibrations of the C–H bond of the ethynyl group. Such a spectrum indicates that copolycondensation proceeds to high conversion, and that the final reaction products contain ethynyl groups.

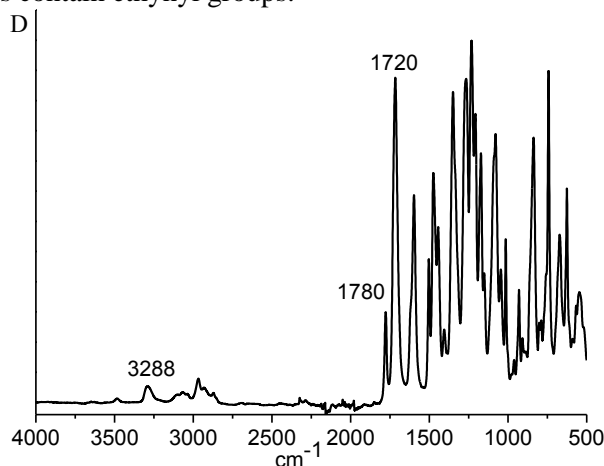
**Figure 2.** IR spectra of products of polycondensation PI-1.

Figure 3 shows the DSC thermograms of OI-1, OI-2 and PI-1. It is seen that all products demonstrate a jump in heat capacity in the region of 190–200°C corresponding to the glass transition temperature. In the higher-temperature region (270–330°C), an exothermic effect is observed corresponding to the cross-linking reaction of propargyl groups. The extremum of exothermic effect shifts to higher temperatures after heating which is apparently due to an increase in the effective activation energy of the cross-linking reaction (decrease in molecular mobility).

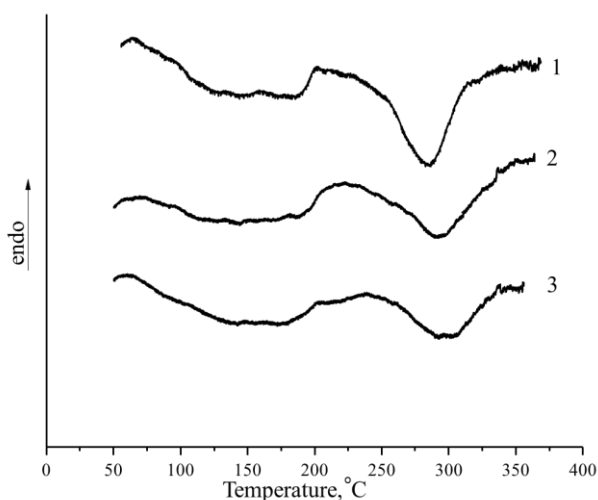


Figure 3. Thermograms DSC OI-1 (1), OI-2 (2) and PI-1 (3).

Curing of the synthesized samples was carried out in a hot press at different temperatures. Figure 4 presents the OI-1 thermograms with different degrees of curing. In the case of oligoimide curing at a temperature of 230°C (curve 3), the glass transition temperature does not change as compared with that of the uncured sample (curve 1). However, the shape of the exothermic peak of the compared samples is markedly different. Apparently, this is due to the partial cross-linking of the treated sample. The DSC data, as well as the fact that the treated sample remains thermoplastic and does not lose solubility, indicate that at 230°C only chain length increases, and a three-dimensional structure is not formed. Treatment at 300°C leads to loss of the solubility (curve 2) and disappearance of exothermic effect. Obviously, such changes are associated with the formation of a cross-linked polymer.

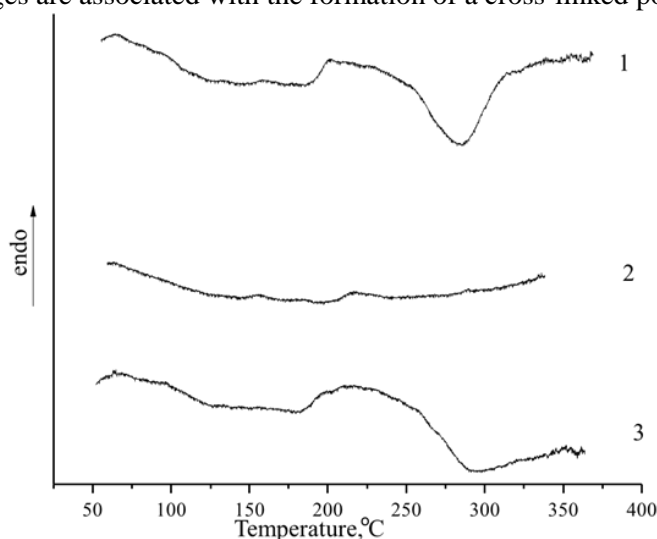


Figure 4. DSC thermograms of the initial oligoimide OI-1 (1), cured at 300 °C (2) and at 230 °C (3).

Cured propargyl containing compounds were investigated by IR spectroscopy. When comparing the IR spectra for the initial and for the cured polyimide PI-1 at a temperature of 300°C, it is shown Figure 5, you can see that characteristic absorption band of alkynyl group in the region of 3288 cm⁻¹ disappears, indicating consumption of propargyl unit.

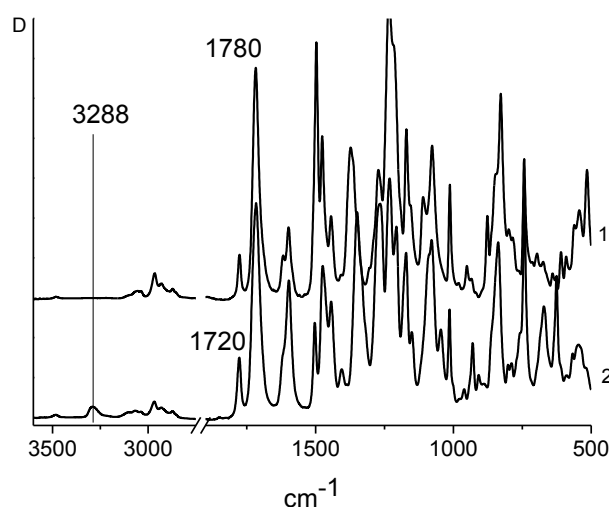


Figure 5. IR spectra of the initial PI-1 (2) and cured at a temperature of 300 °C for 20 minutes (1).

The results of the thermogravimetric analysis (TGA) of cured samples are shown in Figure 6 and Table 2. It can be seen that the obtained cross-linked products have excellent stability to thermal and thermal-oxidative degradation: $T_{5\%}$ are in the range of 500-518 °C in air, and the coke residue is about 50% in nitrogen atmosphere.

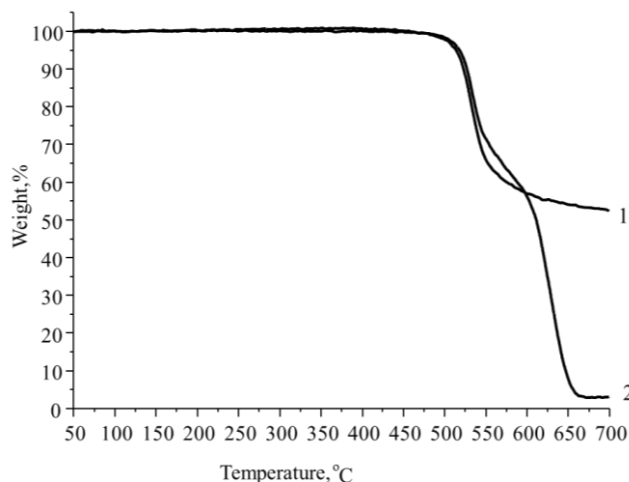


Figure 6. Thermograms of TGA of cured OI-2 in nitrogen atmosphere (1) and in air (2).

Table 2. The results of the TGA for cured polyimides.

Sample	$T_{5\%}$ in air (°C)	$T_{50\%}$ in air (°C)	Coke residue at 700 °C in N_2 , (%)
OI-1	505	600	50
OI-2	518	610	53
PI-1	516	608	50

The products were investigated by the method of thermomechanical analysis (TMA). In Fig. 7, TMA curves are shown of OI-1 sample heat treated for 20 minutes in hot press at 230°C (1) and at 300°C (2). From fig.7, it can be concluded that the sample heated at 300°C is cross-linked system, whereas samples heated at 230°C retains a viscous flow behavior at temperatures higher than 230°C. Similar behaviors was observed for OI-2 sample. Both samples heated at 230°C retain solubility in organic solved.

In Fig. 8, analogous TMA curves for high molecular polyimide sample PI-1 are shown. It is seen that in contrast to lower molecular weight samples, after heat treatment both at 300°C and at 230°C samples lose ability to flow at temperature above 230°C. This result indicates that some cross-linking *via* reaction of propargyl groups takes place even at 230°C. In a case of low lower molecular weight samples this effect is small, and this stage can be considered rather as chain elongation than cross-linking. But for a high molecular weight product, even small amount of crosslinks in a sample is enough to lose its ability to viscous flow and ability to melt processing.

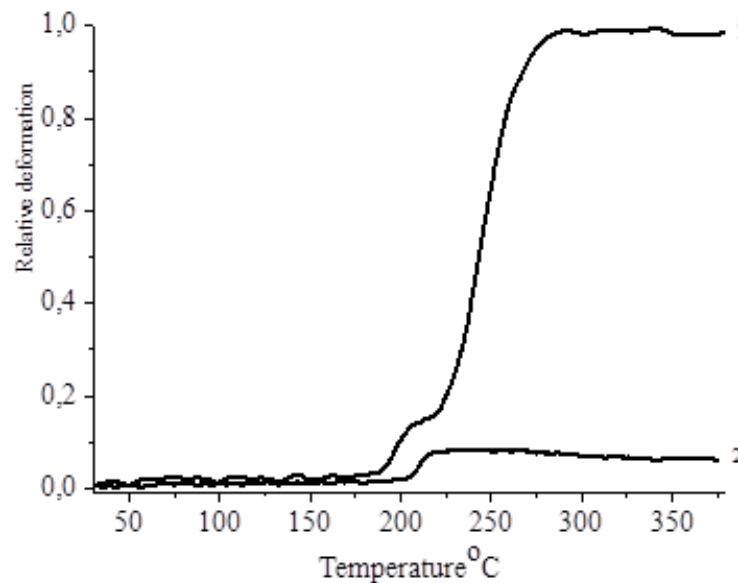


Figure 7. Thermograms TMA of OI-1 cured to 230 °C (1) and to 300 °C (2).

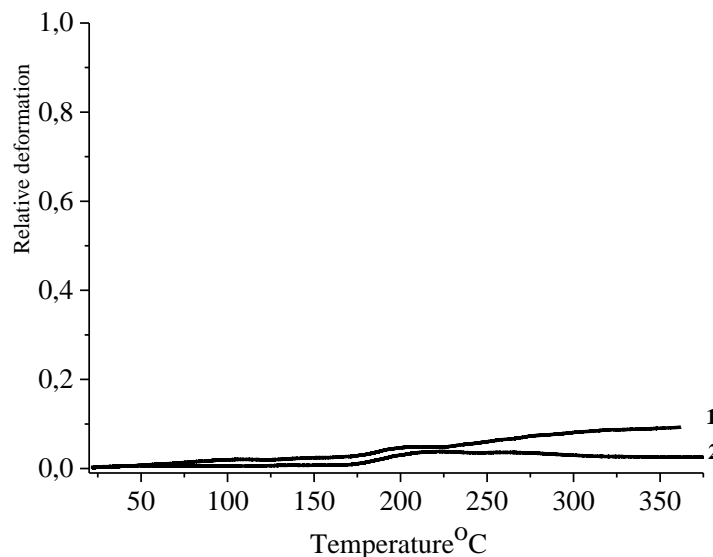


Figure 8. Thermograms TMA of PI-1 cured to 230 °C (1) and to 300 °C (2).

Thus, it was demonstrated that the obtained oligoimides have a “process window”, the range of which is about 100°C and is sufficient for molding PCM based on it.

4. Conclusions

In this work, new thermoplastic oligoimides of different molecular weights containing propargyl groups in the side chain were synthesized. It was shown that the synthesized oligomers are able to transfer into viscous flow state at 200–230°C and cross-linked with subsequent heating to 300°C. Such materials are of potential interest for use as thermoplastic binders.

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