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THE THERMAL TRANSFORMATION OF AN AROMATIC POLY(AMIDE), POLY(ORTHO-OXYAMIDE) AND POLY(BENZOXAZOLE)

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The thermal behaviour of three aromatic polymers, poly(3,3-dioxy-4,4-diphenylmethane) (POA), poly(2,2-m-phenylene-5,5-dibenzoxazolemethane) (PBO) and a commercial poly-(phenyleneisophthalamide) (Phenylon) was studied by thermal analysis, i.e. DSC and TG. PBO was formed by the progressive thermocyclization of POA. By transforming POA into PBO the thermal stability was increased proportionally to the degree of cyclization, due to the stiffening of the polymer chain. PBO was found to be more thermally stable than Phenylon. The activation energies of the desorption of moisture, cyclization and thermal degradation of the polymers in both nitrogen and air were determined from non-isothermal TG data.

Keywords: aromatic polymers, DSC-TG, kinetics, thermal degradation mechanism, thermal transformation

Introduction

The general strategy to improving the thermal stability of polymers has involved the design of polymers with increased chain interaction, greater crystallinity and/or restricted chain rotation [1]. Research has generally involved thermal stability investigations and the elucidation of the thermal degradation mechanism, as a route to polymer stabilization.

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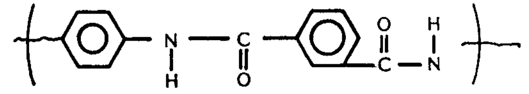
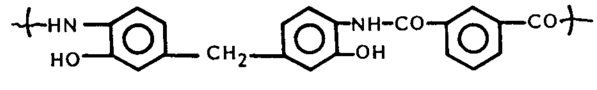
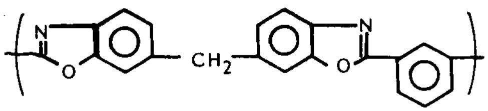
The goal of this study was to investigate the change in the thermal stability of poly(3,3-dioxy-4,4-diphenyl-methane) (POA) as it is transformed to poly(2,2-m-phenylene-5,5-dibenzoxazolemethane) (PBO), with increased stiffness of the polymer chain. The thermal stabilities of these two polymers were compared to that of a commercial poly(phenylene isophthalamide), trade name 'Phenylon'. The polymers can be represented by the following formulae:



Phenylon



POA



PBO

The study of the thermal degradation of aromatic poly(amides) was initiated by Atrushkevich and Korshak [2–4], but very few efforts were devoted to this field later. In our study thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were applied to investigate the behaviour of these polymers.

Experimental

POA was obtained by reacting 3,3-dioxy-4,4-diaminodiphenyl-methane with dichloroisophthalic acid in dimethylacetamide (DMAA) [5]. The limiting viscosity numbers (LVN) of POA, 332 ccm/g, Phenylon, 155 ccm/g, were determined in DMAA at 25°C. PBO was obtained by the thermal cyclization of powdered POA in vacuum under the following conditions: one hour at 100°C, followed by 30 min at 150°C and 30 min at 200°C. Three different samples were obtained by varying the final one hour cyclization temperature: 225°C for PBO-I, 250°C for PBO-II and 270°C for PBO-III.

The thermocyclization of POA into PBO was studied using a Perkin Elmer DSC-2 instrument. The measurements were performed under a nitrogen atmosphere in the range 30 to 450°C at heating rates of 10, 20 and 40 deg·min^{-1}. The kinetic parameters were determined according to the methods of Ozawa [6, 7] and Kissinger [8]. A Perkin Elmer TG-2 instrument was used for thermogravimetric measurements. Heating rates of 0.625, 2.5, 5, 10, 20 and 40 deg·min^{-1}, were applied under a nitrogen or air flow of 20 ccm/min. The kinetic parameters were calculated according to the Flynn-Wall method [9].

Results and discussion

Thermocyclization of POA into PBO

Typical DSC curves of POA are shown in Fig. 1. The presence of two exothermic peaks results from water evolution, the first lying between 60° and 100°C corresponding to physical desorption of adsorbed moisture from the hydrophilic polymer. The second peak, ranging from 300° to 340°C resulted from the water formed during the thermocyclization reaction. The peak areas increase with increasing heating rates, allowing a more precise determination of the enthalpies ΔH involved. Average enthalpies of 34 kJ/mol and 140 kJ/mol, respectively, for desorption and cyclization, were obtained by the method of Ozawa. The corresponding activation energies E_a were calculated according to both the Ozawa and the Kissinger method, yielding the same values, $E_a = 43$ kJ/mol for desorption and 156 kJ/mol for cyclization. The reaction order, n, can be determined according to the peak shape index [8], S; $n = 1.26\,S^{1/2}$. For cyclization $S = 0.63$, with a corresponding reaction order $n = 1$, indicating that the cyclization in this case is first order.

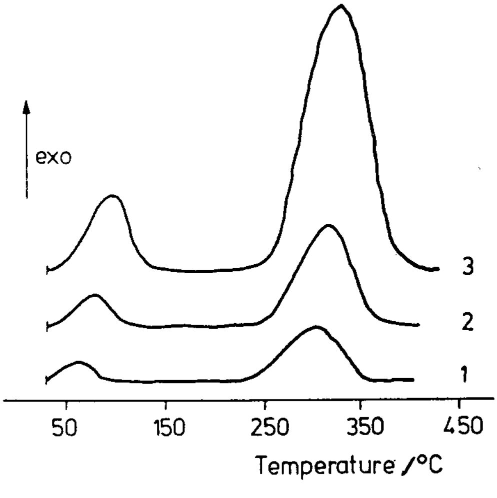


Fig. 1 DSC curves of POA in nitrogen, heating rates 10(1), 20(2) and 40 deg·min^{-1} (3)

The percentage of non-cyclized oxyamide groups can be determined by DSC if the cyclization enthalpy of POA, $\Delta H = 140$ kJ/mol is taken as 100%.

According to this estimation, the contents of non-cyclized groups are 33, 16 and 8% for PBO-I, PBO-II and PBO-III, respectively.

Non-oxidative TG

The TG and DTG curves of Phenylon, POA and PBO-III, obtained at a heating rate of 5 deg·min^{-1} are presented in Fig. 2. The slope of the heating curve was not dependent on the heating rate. A slight mass loss of 3–5% is observed in the range 50°–70°C in the case of Phenylon and POA, as a result of the expected evolution of adsorbed moisture.

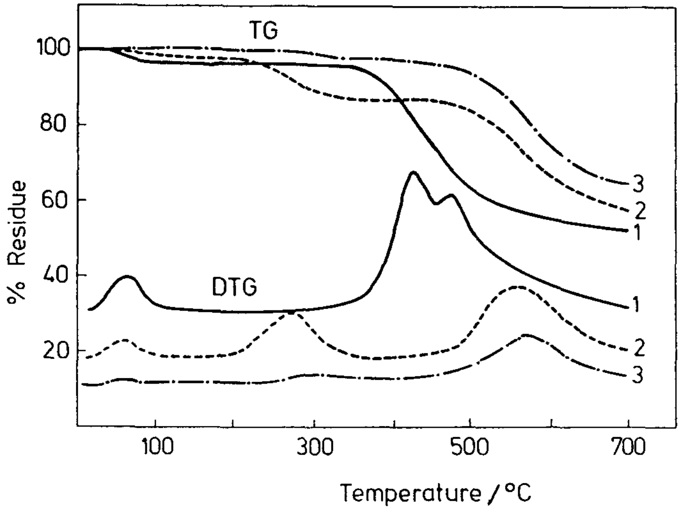


Fig. 2 Non-isothermal TG and DTG curves of Phenylon(1), POA(2) and PBO-III(3) in nitrogen, heating rate 5 deg·min^{-1}

In the case of POA a 10% mass loss was observed in the interval 200°–350°C resulting from the cyclization of POA. A mass loss of only 3% was observed in the same temperature interval for PBO-III. This mass loss indicated the presence of non-cyclized repeat units in the PBO-III chain due to the incomplete cyclization of POA in the course of its synthesis at 270°C. Characteristic mass loss temperatures, the amounts of carbonaceous residue and the temperatures of DTG maxima are given in Table 1. The shapes and positions of the DTG peaks of Phenylon and PBO vary considerably, indicating differences in thermolysis mechanisms.

Comparison of the TG curves showed that PBO-III was thermally more stable than Phenylon, while the thermal stability of POA was considerably lower due to the affinity towards cyclization. The overall activation energies, E_a, of the processes occurring in these polymers, presented in Table 2, confirmed the above conclusions. The obtained E_a values of water desorption in all the polymers agreed very well within experimental error, as did the values for cyclization in the case of POA and PBO-I. The E_a's of the thermal degradation stage were found to increase with conversion, especially in the case of POA and PBO-I, resulting in a larger deviation of the mean E_a values.

Table 1 Characteristic temperatures in °C for the heat resistance of the polymers investigated, TG heating rate deg·min^{-1}

	Degradation in nitrogen/ °C			Degradation in air/ °C		
	Phenylon	POA	PBO-III	Phenylon	POA	PBO-III
mass loss/%						
5	390	242	520	380	268	400
20	450	529	600	450	450	480
100	–	–	–	580	550	550
residue at 700°C/%	52	58	64	0	0	0
DTG max/°C						
first max.	67	62	57	54	56	
second	426	269	302	390	338*	
third	474	557	569	510	509	

*Centre of plateau

As expected, the thermal stability of the PBO samples increased with the degree of cyclization (Fig. 3). The more non-cyclized oxyamide fragments present, the less stable the polymer. The stabilities increase in the sequence:

PBO-I < PBO-II < PBO-III

Oxidative TG

The corresponding TG curves of Phenylon, POA and PBO-III in air, obtained at a heating rate of 5 deg·min^{-1}, are presented in Fig. 4. The slopes of the Phenylon TG curves were heating rate dependent, while those of POA and PBO-III were not. The evolution of adsorbed moisture was also observed in this case, not affected by the surrounding atmosphere. Very small mass uptakes were observed in the initial stages of thermooxidation. On the basis of the characteristic mass loss temperatures, Table 1, the resistance to thermooxidation can be arranged in the following series:

PBO-III > Phenylon > POA

Table 2 Kinetic parameters of the degradation of the polymers investigated in nitrogen and air

Polymer	Degradation in nitrogen				Degradation in air			
	Mass loss range/ %	Process	E_a/ kJ·mol^{-1}	A/ s^{-1}	Mass loss range/ %	Process	E_a/ kJ·mol^{-1}	A/ s^{-1}
Phenylon	1–4	desorption	65± 14	$1.0\cdot10^{9}$				
	10–12	therm. degr.	193± 14	$1.1\cdot10^{14}$	10–12	thermoox. degr.	209± 21	$3.7\cdot10^{15}$
	25–45	therm. degr.	258± 13	$5.0\cdot10^{16}$	25–90	thermoox. degr.	141± 17	$5.3\cdot10^{8}$
POA	1–2	desorption	67± 14	$1.0\cdot10^{9}$				
	3–12	cyclization	131± 18	$2.9\cdot10^{11}$	10–30	cyclization	138± 7	1.7·109
	15–43	therm. degr.	436±16	–	40–90	thermoox. degr.	173± 6	$2.1\cdot10^{10}$
PBO-I	1–2	desroption	52± 1	$1.0\cdot10^{8}$				
	5–12	cyclization	138± 7	$1.0\cdot10^{11}$				
	15–40	therm. degr.	406± 86	–				
PBO-III					5–15	cyclization	142± 4	$8.0\cdot10^{14}$
					10–90	thermoox. degr.	186± 6	$1.1\cdot10^{14}$

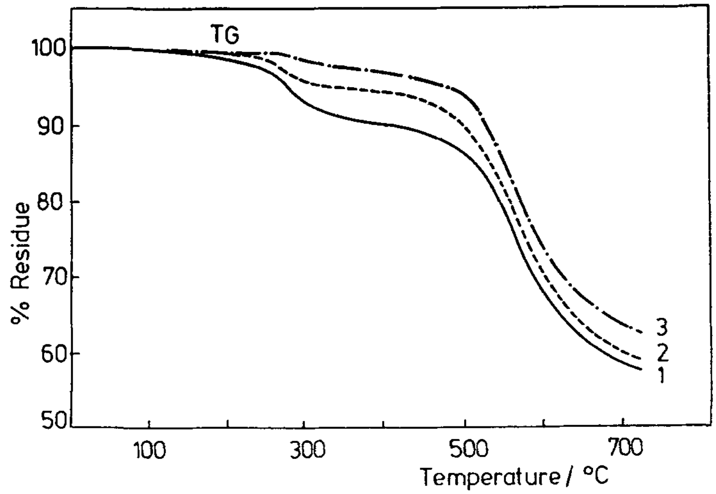


Fig. 3 Non-isothermal TG curves of PBO-I(1), PBO-II(2) and PBO-III(3) in nitrogen, heating rate 5 deg·min^{-1}

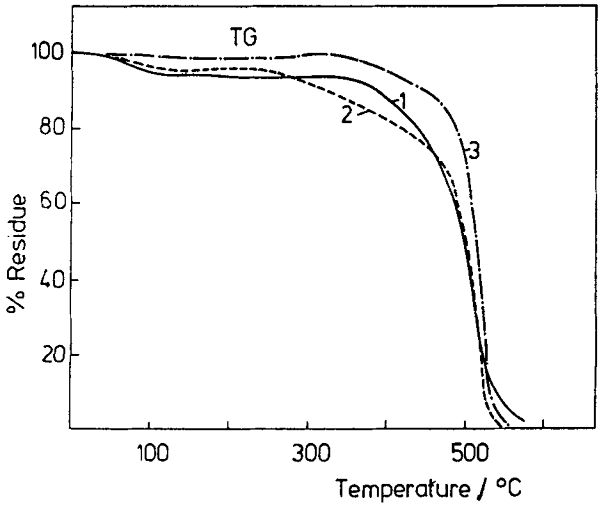


Fig. 4 Non-isothermal TG curves of Phenylon(1), POA(2) and PBO-III(3) in air, heating rate 5 deg·min^{-1}

The thermal decomposition of POA involved two stages: thermocyclization and thermooxidation. The mean activation energy of cyclization (Table 2) did not seem to be affected by the surrounding atmosphere. Phenylon and PBO-III also decomposed in two stages, as evidenced by the change in the slopes of the TG curves and the shape of the DTG peaks. The positions of the DTG maxima of POA and PBO were shifted to lower temperatures as compared to the non-oxidative case; whilst the major oxidative DTG peak of Phenylon was shifted to a higher temperature (Table 1). At mass losses above 40%, rapid mass loss occurred in all three polymers. The thermooxidation activation energy of Phenylon decreases with increasing conversion, while the value of POA and PBO-III are independent of conversion. The overall oxidative thermal degradation E_a of all three polymers were found to be lower than the non-oxidative values (Table 2). The oxidative thermal stability of the PBO-samples also depends on the degree of cyclization, as shown in Fig. 3. The initial mass loss differed significantly, however, at higher conversion the thermal behaviour was similar.

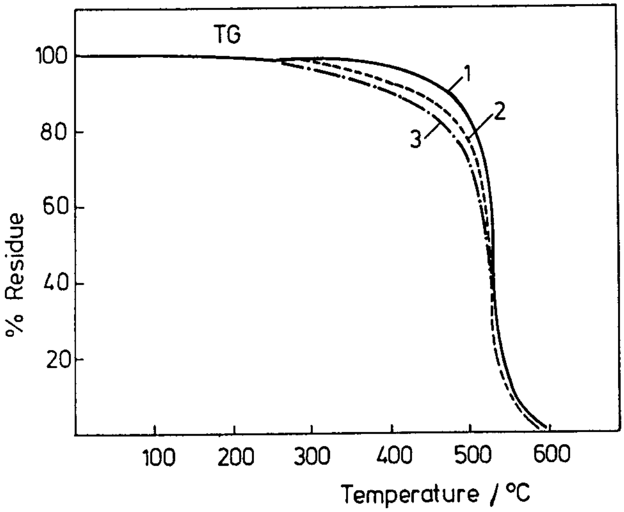


Fig. 5 Non-isothermal TG curves of PBO-I(3) PBO-II(2) and PBO-III(1) in air, heating rate 5 deg·min^{-1}

The proposal of the mechanism of the thermal cyclization of POA into PBO is given in Fig. 6. On the basis of the results presented, it was demonstrated that even under the most severe reaction conditions applied, i.e. at 270°C, 100% cyclization of POA was not achieved. The remaining non-cyclized oxyamide units decrease the thermal stability of PBO.

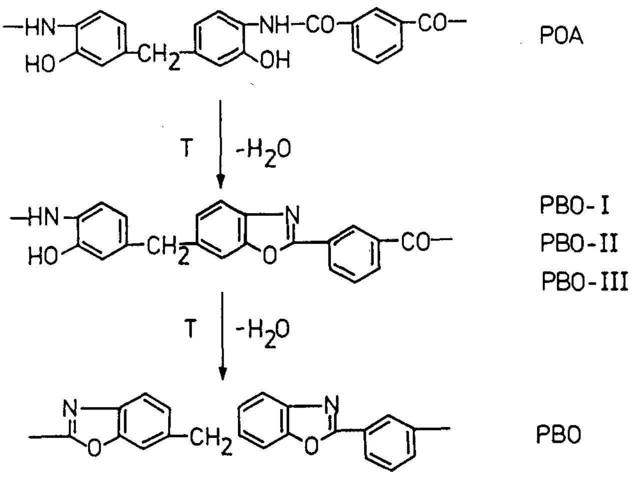


Fig. 6 Proposed cyclization mechanism of POA into PBO

Conclusions

The reaction conditions for obtaining PBO with a very low amount of noncyclized oxyamide groups were established. PBO was thermally more stable than Phenylon, as expected, due to greater chain stiffness.

* * *

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Zusammenfassung — Mittels DSC und TG wurde das thermische Verhalten von drei aromatischen Polymeren untersucht: Poly(3,3-dioxy-4,4-diphenylmethan) (POA), Poly(2,2-m-Phenylen-5,5-dibenzoxazolmethan) (PBO) und handelsübliches Poly(phenylen-isophthalamid) (Phenylon). PBO wird durch fortschreitende Thermocyclisierung von POA gebildet. Bei der Umwandlung von POA in PBO erhöht sich wegen der Versteifung der Polymerketten die thermische Stabilität proportional zum Cyclisierungsgrad. PBO ist thermisch stabiler als Phenylon. Anhand der nichtisothermen TG-Daten wurden sowohl in Stickstoff als auch in Luft die Aktivierungsenergien von Feuchtigkeitsdesorption, Cyclisierung und thermischem Abbau der Polymere ermittelt.