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STUDY OF THERMOCHEMICAL CONVERSIONS OF ALICYCLIC POLYIMIDES

B. A. Zhubanov, M. B. Leonova and *G. M. Mirkarimova*

INSTITUTE OF CHEMICAL SCIENCES, ACADEMY OF SCIENCES OF THE KAZAKH S.S.R.,
ALMA-ATA, U.S.S.R.

The thermochemical conversions of certain polyimides obtained by the polycondensation of dianhydrides of alicyclic tetracarboxylic acids and 4,4-diaminodiphenyl oxide were studied by different methods of thermal analysis (thermogravimetry, mass-spectrometric evolved gas analysis, and pyrolytic gas chromatography). The thermal dissociation of dianhydride fragments according to the reverse reaction of retrodiene synthesis is the basic reaction that determines the thermal stabilities of the polymers studied. It is shown that the absence of endoethylene bonding or its substitution by oxygen in the dianhydride fragments leads to increases in the thermal stabilities of alicyclic polyimides.

The development of new thermally stable alicyclic polymers offering valuable physicochemical properties [1] has led to the wide use of methods of thermal analysis for the study of their thermal stabilities.

This paper reports a study of the thermal destruction of certain polyimides based on dianhydrides of alicyclic tetracarboxylic acids and aromatic diamines. Pecularities of the decomposition mechanism of these polymers are discussed and the influence of the chemical nature of the anhydride component on the thermal stabilities of the alicyclic polyimides is shown.

Experimental

Materials

Polyimides based on dianhydrides of tricyclo [4,2,2,$0^{2,5}$]dec-7-ene-3,4,9,10-(PI I), tricyclo[4,2,2,$0^{2,5}$]dec-7-ene-7-isopropyl-3,4,9,10-(PI II), trycyclo [4,2,2,$0^{2,5}$] dec-7-ene-chloro 3,4,9,10-(PI III), bicyclo [2,2,2] octane-2,3,5,6-(PI IV), and 7-oxotricyclo [4,2,2,$0^{2,5}$]nonane-3,4,9,10-(PI V) tetracarboxylic acids with 4,4'-diamiodiphenyl oxide were prepared by a two-stage method of polycondensation in solvents of amide type [2–5]. Polymer characteristics are given in Table 1.

Table 1 Characteristics of polyimides based on dianhydrides of alicyclic tetracarboxylic acids and diaminodiphenyl oxide

Polyimides	Viscosity $[\eta]\cdot 10^{-1}$, m^3/kg H_2SO_4	Analysis found,% C	H	N	calculated,% C	H	N
PI I	0.65	71.3	4.6	6.3	71.2	4.1	6.4
PI II	0.38	72.8	5.0	6.1	72.5	5.0	5.8
PI III	0.47	65.9	4.1	5.6	66.0	3.6	5.9
PI IV	0.52	65.2	4.1	6.7	67.2	3.7	6.5
PI V	0.68	63.5	3.5	5.0	62.7	2.3	4.6

Methods

Thermogravimetric analysis of polymers was carried out in a MOM derivatograph in an air flow (50 ml min^{-1}) or in helium in a dynamic regime at a heating rate of 5 deg min^{-1} over the temperature range 20–600°.

Qualitative analysis of the polymer decomposition products was performed with an MX–1320 mass-spectrometer, with direct introduction of the sample into the ion source [6]. Gaseous products formed during polymer pyrolysis on dynamic heating at 5 deg min^{-1} were analysed, and the results were recorded as mass-spectra in the region 15–250 m/e with intervals of 1–3 min.

Quantitative analysis of volatile products of decomposition was carried out by pyrolytic gas chromatography. Pyrolysis was conducted in a flow-type pyrolytic cell coupled with a Chrom-5 chromatograph, equipped with a katharometer as detector.

Volatile products of polymer decomposition were separated on a column filled with Porapak QS, with a programmed temperature increase in the thermostat from 40 to 200° at a rate of 15 deg min^{-1}.

Discussion

The thermal stabilities of the polymers were evaluated by means of TG (Table 2). It is seen from this Table that according to the criterion T_5 the thermal stabilities of the alicyclic polymers cover the range 300–475°. Polyimide PI V with end-oxa bonding in the dianhydride component, has higher thermal stability than the polyimides containing endo-ethylene bonds, which are close in thermal stability.

Table 2 Thermal characteristics of alicyclic polyimides

Polymer	Thermal destruction temperature, °C			E, kJ/mol	Thermooxidative destruction temperature, °C			E, kJ/mol
	T_0	T_5	T_{50}		T_0	T_5	T_{50}	
PI I	355	415	605	147.8	300	360	500	121.4
PI II	355	400	610	141.1	290	350	505	135.7
PI III	360	415	575	154.5	325	390	525	136.5
PI IV	370	450	635	173.8	320	370	510	154.9
PI V	340	475	665	191.3	320	415	570	149.1

T_0, T_5 and T_{50} are the temperatures relating to 0, 5 and 50% weight loss during measurement in air and in a flow of inert gas.

The activation energy of thermal and thermooxidative decomposition of polymers, calculated according to the technique in [7], from the section 300–500° of the TG curve, varies from 120 to 190 kJ/mol and depends on the chemical structure of the dianhydride component. The mass-spectrometric study of polymer pyrolysis showed that the main products of decomposition of all samples were carbon oxides, water, benzene, phenol and aniline. Polymer PI I decomposes in two stages. In the first stage, intensive evolution of benezen is observed, with the maximum at around 360° connected with the thermal dissociation of tricyclodecene fragments according to the reverse Diels-Alder reaction [8]. The second stage is characterized by the appearance of CO, CO_2 and H_2O, with maximum evolution in the range 430–450° in the mass-spectra of all polymers studied. Carbon oxides are formed in the decomposition of the imide ring, and at such temperatures water can be formed by the interaction of end amine groups with heterocyclic carbonyl.

A thermodestruction study of the N,N.diphenylimide of tricyclodecenetetracarboxylic acid, modelling the fundamental unit of PI I, supported the proposed degradation scheme for the alicyclic polyimide, since qualitative and quantitative composition of the volatiles (Table 3) and also the temperature range of decomposition of model compounds have proved analogous to those for the PI I decomposition pattern.

Table 3 Volatile products (mol/base mol) of thermal destruction of alicyclic poliimides, according to results of pyrolytic gas chromatography (exposure time 30 sec)

Polyimide	Volatile products	Pyrolysis temperature, °C					
		350	400	450	500	550	600
model	C_6H_6	0.06	1.16	1.18	1.18	1.18	1.18
	C_6H_6	0.08	0.54	0.95	1.02	1.03	1.04
PI I	CO	–	0.01	0.08	0.41	0.77	1.12
	CO_2	0.01	0.03	0.10	0.28	0.48	0.69
	H_2O	0.18	0.25	0.25	0.35	0.56	0.73
	$C_6H_5CH(CH_3)_2$	0.05	0.27	0.65	0.70	0.69	0.53
	C_6H_6	–	0.01	0.01	0.01	0.02	0.03
PI II	CO	–	traces	0.16	0.48	0.85	1.22
	CO_2	0.01	0.10	0.24	0.39	0.53	0.67
	H_2O	–	0.27	0.32	0.43	0.55	0.62
	furan	–	–	traces	traces	0.03	0.06
	C_6H_6	traces	0.01	0.01	0.01	0.01	0.02
PI V	CO	–	traces	0.04	0.40	0.86	1.31
	CO_2	traces	0.02	0.09	0.03	0.58	0.83
	H_2O	0.18	0.22	0.29	0.53	0.81	1.08
	C_6H_6	–	traces	0.08	0.29	0.50	0.70
PI IV	CO	–	traces	0.03	0.36	0.86	1.36
	CO_2	0.01	0.02	0.06	0.42	0.90	1.38
	H_2O	0.18	0.18	0.18	0.47	0.50	0.50

During the pyrolysis of polymides PI II and PI III, decomposition of the tricyclic fragment also takes place, accompanied by evolution of the corresponding hydrocarbon. Thus, during the thermal decomposition of PI II, isopropylbenezen is evolved, with maximum at 380°, the greatest quantity being 0.7 mol/base mol. During the thermal decomposition of polyimide PI III, cholobenezene appears in the mass-spectra of the decomposition products, with maximum at 370°.

Decomposition of the bicyclooctane fragment during the pyrolysis of polyimide PI IV is accompanied by the evolution of benzene and cyclohexadiene, with maximum at 415°.

Polymer PI V decomposition begins with rupture of the imide ring and is accompanied by the evolution of CO and CO_2, with maximum at 440°. The appearance of furan at temperatures above 500° suggests the slight decomposition of the tricyclononane fragment.

Thus, the absence of endoethylene bonding or its substitution by oxygen in the anhydride structures used to prepare alicyclic polyimides leads to an increase in thermal stability. The stabilities of these polymers decrease in the sequence: PI V $>$ PI IV $>$ PI II $\geqslant$ PI III $\geqslant$ PI I

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Zusammenfassung – Thermochemische Umwandlungen einiger Polyimide, die durch Polykondensation der Dianhydride alicyclischer Tetracarbonsäuren mit 4,4'-Diaminodiphenyloxid dargestellt waren, wurden durch verschiedene thermoanalytische Methoden (TG, massenspektrometrische EGA und Pyrolyse-Gaschromatographie) untersucht. Die thermische Spaltung der Dianhydrid-Komponente nach einer Retro-Diensynthese ist die Hauptreaktion, die die thermische Stabilität der Polymeren bestimmt. Bei Abwesenheit der endo-Ethylen-Bindung in der Dianhydrid-Komponente oder Substitution durch eine Etherbindung wird die thermische Stabilität von Polyimiden mit alicyclischen Baugruppen erhöht.

РЕЗЮМЕ — Термическими методами анализа, масс-спектрометрическим АВГ и пиролизной газовой хроматографией изучены термохимические превращения полиимидов, полученных реакцией поликонденсации диангидридов алициклических тетракарбоновых кислот и 4,4-диаминодифенилоксида. Термическая диссоциация диангидридных фрагментов, соответствующая обратной реакции ретродиенового синтеза, является основной реакцией определяющей термоустойчивость изученных полимеров. Показано, что отсутствие эндо-этиленовой связи или замещение ее кислородом в диангидридных фрагментах, приволит к увеличению термоустойчивости полиимидов.