Polymer 40 (1999) 2419–2428

New semiladder polymers. Part II: Synthesis and properties of new poly(amideimidazopyrrolones)

D. Sęk*, E. Schab-Balcerzak, E. Grabiec

Centre of Polymer Chemistry, Zabrze, Poland

Received 19 May 1998; accepted 11 June 1998

Abstract

A series of polymers from new diamidedianhydrides of arylene-di(benzene-5-amido-1,2-dicarboxylic) anhydride type and aromatic tetraamines (3,3′-diaminobenzidine and 3,3′,4,4′-tetraaminodiphenylether) were synthesized using one step high temperature polycondensation in *m*-cresol and *p*-chlorophenol at 180°C and low temperature polycondensation. The polymers had a semiladder structure. The influence of the monomer structure and polycondensation method on the polymer properties has been investigated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Thermostable polymers; Semiladder polymers; Polybenzoilenobenzimidazoles

1. Introduction

Polyimidazopyrrolones, being a group of ladder polymers synthesized from aromatic tetraamines and aromatic dianhydrides, exhibit excellent thermal and dielectrical properties [1], [2]. The major limitation for the versatile applications of the ladder polymers is their hard solubility in organic solvents [3].

Introduction to the single-chain segments of some flexible groups such as amide, ether or ester between ladder segments should improve the solubility of the polymers. On the other hand, this modification may influence the thermal stability of such semiladder polymers.

In our previous work, we described the synthesis and properties of poly(esterimidazopyrrolones) [4]. They were soluble in *m*-cresol and *p*-chlorophenol but had lower thermal stability than some ladder polymers.

In this work, we have synthesized a series of new semiladder poly(amideimidazopyrrolones) from diamidedianhydrides and tetraamines (3,3′-diaminobenzidine and 3,3′,4,4′-tetraaminodiphenylether) and the proper model compounds.

2. Experimental

2.1. Materials

Trimellitic anhydride acid chloride (Aldrich) was used without further purification. 1,4-Phenylenediamine (Aldrich), 1,3-phenylenediamine (Aldrich), 4,4′-diamino-diphenylether (Aldrich), 4,4′-diamino-diphenylmethane (Aldrich), 4,4′-diamino-benzophenone (Aldrich), 3,3′-dimethoxybenzidine (Aldrich), *o*-tolidine (Aldrich), and 4,4′-diamino-biphenyl (Aldrich) were used as laboratory reagents without further purification.

2.1.1. Purification of amines

1,2-Phenylenediamine was recrystallized several times from chloroform in the presence of decolorizing charcoal (m.p. 102°C).

3,3′-Diaminobenzidine was recrystallized from boiling water in the presence of charcoal (m.p. 179–180°C).

3,3′,4,4′-Tetraaminodiphenylether was obtained using the reported method [5] (m.p. 150–151°C).

Pyridine was dried and distilled.

2.1.2. Purification of solvents

m-Cresol was distilled in the usual manner. Acetone was dried and distilled in the usual manner, *p*-chlorophenol (Aldrich) was used without further purification, and *N*,*N*-dimethylacetamide (Aldrich) was distilled over the calcium hydrate.

---

* Corresponding author: Polish Academy of Sciences, Centre of Polymer Chemistry, ul Marii-Curi-Sklodowskiej 34, 41-800 Zabrze, Poland.

PII: S0032-3861(98)00447-9

2.2. Measurements

For elemental analysis, a 24°C Perkin–Elmer analyzer was used. Melting points were determined on a DSC DuPont 1090B apparatus at a heating rate of 10°C min^{-1}. Thermogravimetric analysis was performed on a Paulik–Erdey apparatus at a heating rate of 10°C min^{-1} in argon. Viscosity was measured in *m*-cresol at 25°C or in *p*-chlorophenol at 50°C using an Ubbelohde viscometer. Molecular masses of the diamidedianhydrides were determined using electron ionization on an AMD-604 spectrometer. Infrared spectra were acquired on a BIO-RAD FTS 40 A spectrometer in the region of 4000–700 cm^{-1} at a resolution of 2 cm^{-1} and with 32 scans.

2.3. Synthesis of diamidedianhydrides

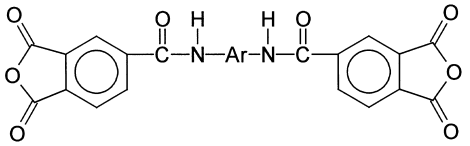
All new diamidedianhydrides were synthesized according to the following method. In a 100 ml flask with a condenser, magnetic stirrer and dropping funnel, 2.2 mmol of trimellitic anhydride acid chloride and 22 ml of dry acetone were placed under an argon atmosphere. After the mixture was heated under reflux, a solution of 1 mmol of a proper diamine and 28 mmol of dry pyridine in 22 ml of acetone were added slowly over a period of 15 min. The mixture was stirred and heated under reflux for 15 min. During the synthesis, the product precipitated. After cooling to room temperature, the product was filtered and than was washed several times with dry acetone and dried in a vacuum oven at 50°C. The crude product was crystallized from acetic anhydride or washed with hot acetic anhydride and dried in a vacuum at 200°C.

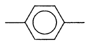
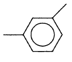
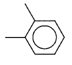
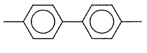
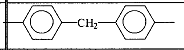
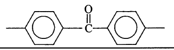
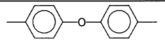
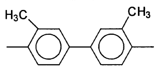
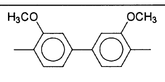
The structure and characteristics of the diamidedianhydrides are listed in Table 1. The structures of these dianhydrides were confirmed by FTIR spectra (characteristic bands at 1868 cm^{-1}, 1846 cm^{-1}, 1783 cm^{-1} for =C=O in anhydride, at 1648 cm^{-1} for amide group).

2.4. Synthesis of model compounds

Diamidedianhydride (1 mmol) and 2 mmol of 1,2-phenylenediamine in 10 ml of solvent (*m*-cresol or *p*-chlorophenol) were put into a pot equipped with a stirrer, condenser and argon inlet and heated at 180°C for 5 h. When the reaction was carried out in *m*-cresol, benzoic acid (2 mmol) was used as the catalyst. Model compounds were precipitated with 150 ml of ethanol, filtered, washed with ethanol and dried at 80°C.

Table 1
Structure and analysis of diamidedianhydrides



No.	Ar	M. p. ^{0}C	Carbon % Found	Carbon % Calcd	Hydrogen % Found	Hydrogen % Calcd	Nitrogen % Found	Nitrogen % Calcd	M. w. (MS)	Yield** %
1		-*	62.38	63.17	2.65	2.65	6.40	6.14	456	92 (62)
2		325	63.05	63.17	2.65	2.65	6.13	6.14	456	95 (78)
3		243	63.18	63.17	2.55	2.65	6.46	6.14	456	98 (74)
4		-*	66.11	67.62	3.23	3.03	5.40	5.26	532	98 (74)
5		344	67.63	68.13	3.39	3.32	5.27	5.13	546	82 (61)
6		326	66.13	66.43	2.85	2.88	4.97	5.00	560	71 (52)
7		351	64.78	65.70	3.01	2.94	5.17	5.12	548	91 (70)
8		328	68.50	68.57	3.77	3.60	5.12	5.0	560	90 (69)
9		360	64.15	64.87	3.34	3.04	4.63	4.73	592	91 (69)

*doesn't melt to 400^{0}C

** crude (after purification)

2.5. Polymer synthesis

For synthesis of the polymers, two methods were used, i.e. low and high temperature polycondensation.

2.5.1. High temperature polycondensation

The stoichiometric amount of a given diamidedianhydride (1 mmol) and a tetraamine (1 mmol) in *m*-cresol (10 ml) in the presence of benzoic acid (2 mmol) or in *p*-chlorophenol (10 ml) were stirred at 180°C under nitrogen for 10 h. The reaction mixture was poured into ethanol and the resulting precipitate was filtered, extracted with boiling ethanol and dried. For foil preparation, the reaction mixture (without polymer precipitation) was poured onto a glass plate and heated at 200°C in vacuum for 8 h.

2.5.2. Low temperature polycondensation

Tetraamine (1 mmol) was dissolved in dry DMA (10 ml) and the stoichiometric amount of a given diamidedianhydride (1 mmol) was added slowly to avoid gelation. The reaction was carried out at room temperature for 3 h. The reaction mixture was poured into ethanol and the resulting precipitate was filtered, extracted with boiling ethanol and dried. For foil preparation, the precipitated polymer (polyamide amino acid) was dissolved in DMA and poured onto a glass plate and heated at 200°C in vacuum for 8 h.

3. Results and discussion

3.1. Characterization of model compounds

Condensation of diamidedianhydrides with 1,2-phenylenediamine leads to the formation of model compounds as shown in Fig. 1.

In the first step of the reaction, after opening an anhydride ring, an amide–amino acid structure is formed which easily evolves water to form aminoimide. In the next step of the reaction, the second ring closure takes place and the imidazopyrrolone structure is formed.

The structures of the compounds obtained in the reaction were detected by FTIR spectroscopy. The absorption band at 1756 cm^{-1}, which is characteristic for carbonyl group –C(=O)–N= in fused rings, confirms the imidazopyrrolone structure along with the absorption band at 1618 cm^{-1} which is characteristic of –C=N– [6]. The presence of the aminoimide structure confirms the absorption band at 1720 cm^{-1} as characteristic of the imide carbonyl group. The absorption band at 1634 cm^{-1}, characteristic of the presence of an amine group in the aminoimide structure, is not seen clearly, being overlapped by the amide carbonyl group absorption of diamidedianhydride. Also, the absorption in the range at about 3000 cm^{-1} was not taken into consideration to detect the presence of an amine group because this region is also characteristic of –NH– in the amide group.

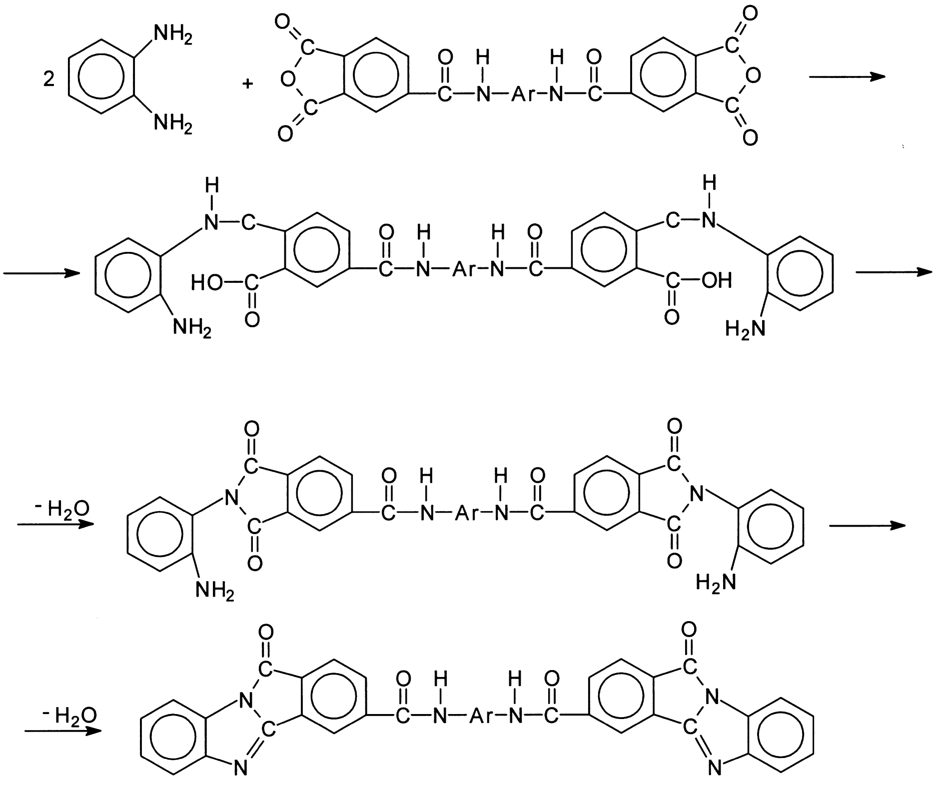


Fig. 1. Scheme of condensation of diamidodianhydrides with 1,2-phenylenediamine.

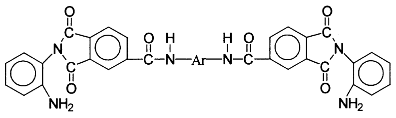
According to FTIR measurements during reaction of the diamidedianhydrides with 1,2-phenylenediamine in the conditions used, the formation of the aminoimide or imidazopyrrolone structure or a mixture of both was observed. The type of structure depended on the solvent used and also on the structure of diamidedianhydrides. The results are presented in Table 2.

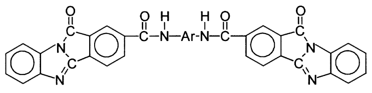
It can be seen that the solvent influences the closure of the second ring and imidazopyrrolone structure formation. It seems also that the cyclization is easier in solution and takes place at a lower temperature (180°C reaction temperature) than in the solid state. In most cases, the models obtained in *p*-chlorophenol exhibited a higher ratio of cyclization than obtained in *m*-cresol, except for the two compounds when, in the dianhydride structure, there are amides from 4,4′-diaminobenzophenone and 3,3′-dimethoxybenzidine. Prolongation of the time of reaction in which model compounds were obtained did not influence the structure formed.

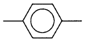
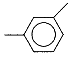
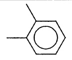
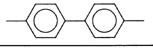
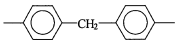
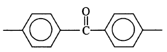
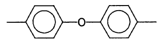
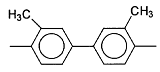
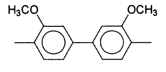
All compounds, which had aminoimide structure, were additionally thermally cyclized. The process of cyclization was detected by FTIR spectroscopy. Precipitated model compounds were heated from 200 to 320°C in the following way: the sample was heated during a few minutes to the desired temperature, kept for 1 h and then a spectrum was acquired. After that the sample was further heated during a few minutes to the temperature 20°C higher and treatment was repeated. Changes between the absorption band at 1756 cm^{-1} along with the absorption band at 1618 cm^{-1} and the absorption band at 1720 cm^{-1} were observed. In Table 2, the temperatures of full cyclization, confirmed by the disappearance of the imide absorption band at 1720 cm^{-1} at dynamical heating, are presented. The closure of the second ring being the result of the reaction of the amino group with oxygen from the carbonyl group in the imide ring depends on the dianhydride structure.

Fig. 2 shows the FTIR spectra of the model from 1,4-[phenylene-di(benzene-5-amido-1,2-dicarboxylic)] anhydride obtained in *m*-cresol after thermal cyclization, as an example. The strong absorption band at 1756 cm^{-1} and the decrease of the band at 1720 cm^{-1} confirm the

Table 2
Dependence of model compound structure on solvent and diamidedianhydride structure


aminoimide structure


imidazopyrrolone structure

No.	Ar	Structure of the model compounds after reaction in different solvents at 180^{0}C		Temperature of full cyclization [^{0}C]*(solid state)
		m-cresol	p-chlorophenol	
1		aminoimide	imidazopyrrolone	320
2		aminoimide	imidazopyrrolone	300
3		imidazopyrrolone	imidazopyrrolone	-
4		aminoimide	aminoimide	300
5		aminoimide	mixture	200
6		mixture	aminoimide	300
7		mixture	imidazopyrrolone	310
8		aminoimide	mixture	320
9		imidazopyrrolone	mixture	200

*the model compounds obtained in m-cresol except the model No. 9

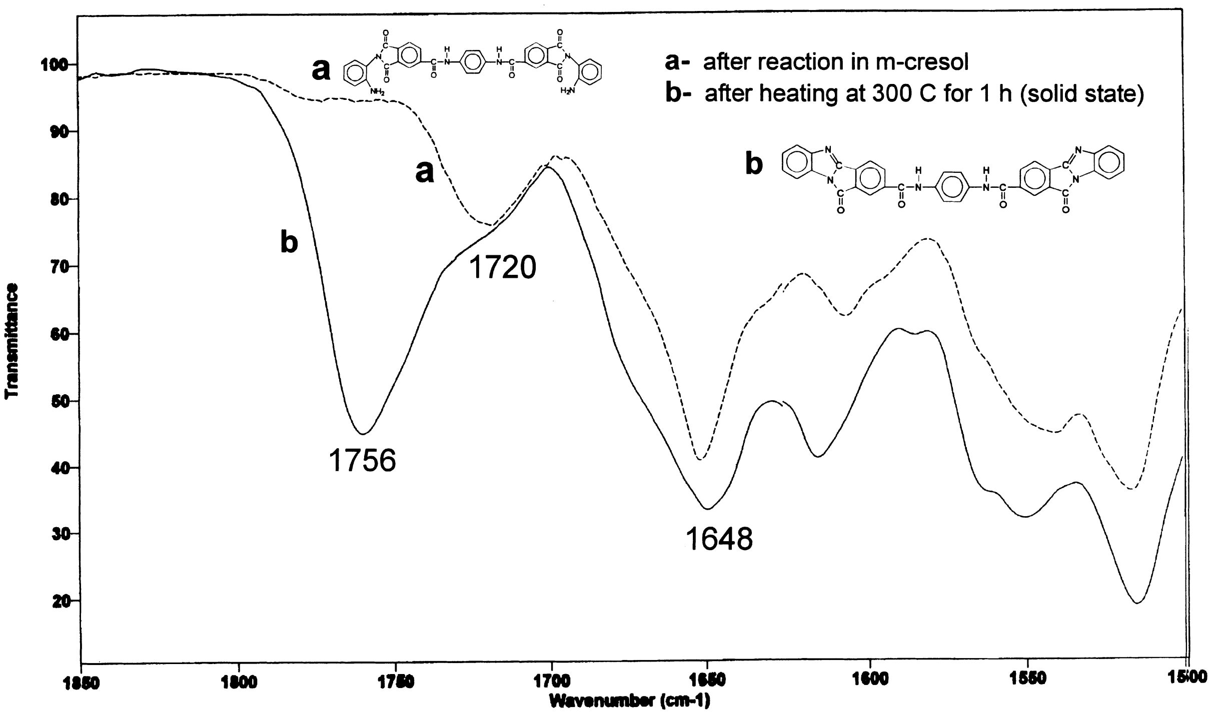


Fig. 2. FTIR spectrum of the model compound.

imidazopyrrolone structure formed after thermal cyclization. Characteristics of the model compounds are listed in Table 3.

3.2. Characterization of polymers

A series of polymers from the diamidedianhydrides and tetraamines, 3,3′-diaminobenzidine, 3,3′,4,4′-tetraaminodiphenylether, has been prepared using high and low temperature polycondensation.

High temperature polycondensation was carried out in *m*-cresol in the presence of benzoic acid used as a catalyst or in *p*-chlorophenol at 180°C for 10 h. When *m*-cresol was used as the reaction medium, polymers in most cases precipitated during synthesis, except the polymers obtained from diamidedianhydrides: No. 1, No. 3 and No. 4 and 3,3′-diaminobenzidine (Table 1). These polymers, obtained in *m*-cresol, gave brittle foils and their reduced viscosities (in *m*-cresol) are presented in Table 4 in parentheses.

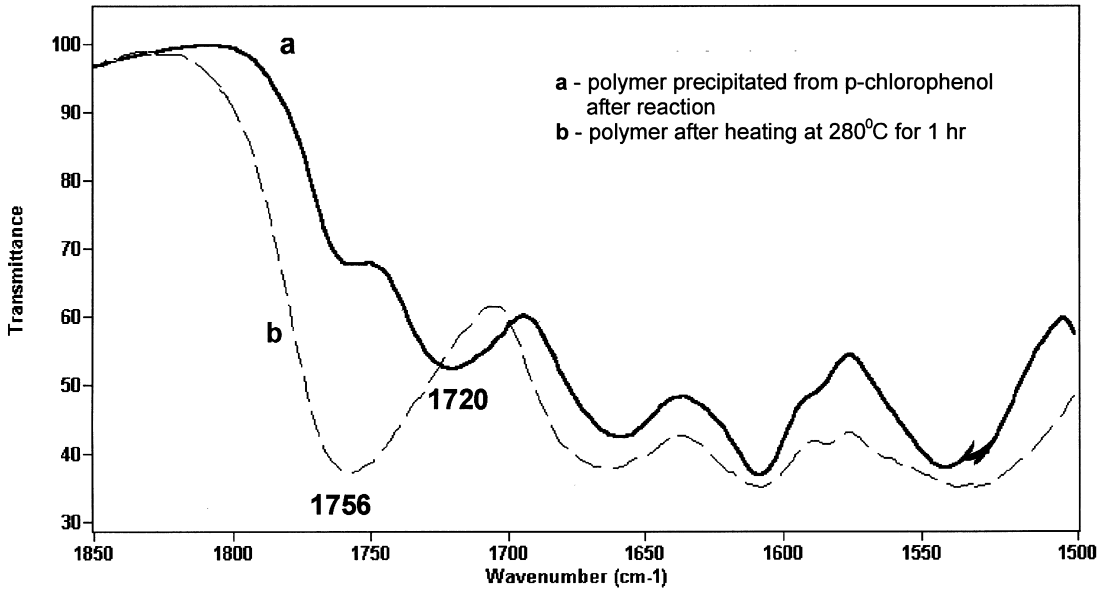
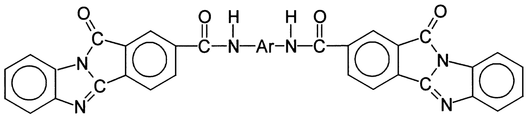
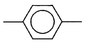
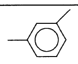
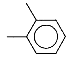
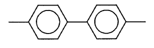
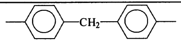
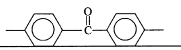
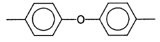
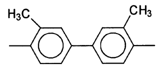
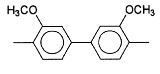


Fig. 3. FTIR spectrum of the polymer from 1,3-[phenylene-di(benzene-5-amide-1,2-dicarboxylic)] anhydride and 3,3′,4,4′-tetraaminodiphenylether.

Table 3
Structure and analysis of model compounds (after full cyclization at elevated temperature)



No.	Ar	M. p. ^{0}C	Carbon %		Hydrogen %		Nitrogen %		Yield %
			Found	Calcd	Found	Calcd	Found	Calcd	
1		-*	72.32	72.00	3.34	3.36	14.32	14.00	78
2		-*	69.44	72.00	3.27	3.36	13.63	14.00	30
3		368	72.10	72.00	3.29	3.36	13.81	14.00	13
4		-*	73.11	74.55	3.58	3.79	11.98	12.42	32
5		330	72.86	74.77	3.76	3.79	11.51	12.17	53
6		329	71.81	73.29	3.43	3.43	11.66	11.93	19
7		359	71.71	72.83	3.66	3.49	11.99	12.13	21
8		-*	76.02	74.99	4.13	4.01	12.64	11.93	53
9		350	71.24	71.64	3.99	4.09	11.37	11.36	34

* doesn't melt to 400^{0}C

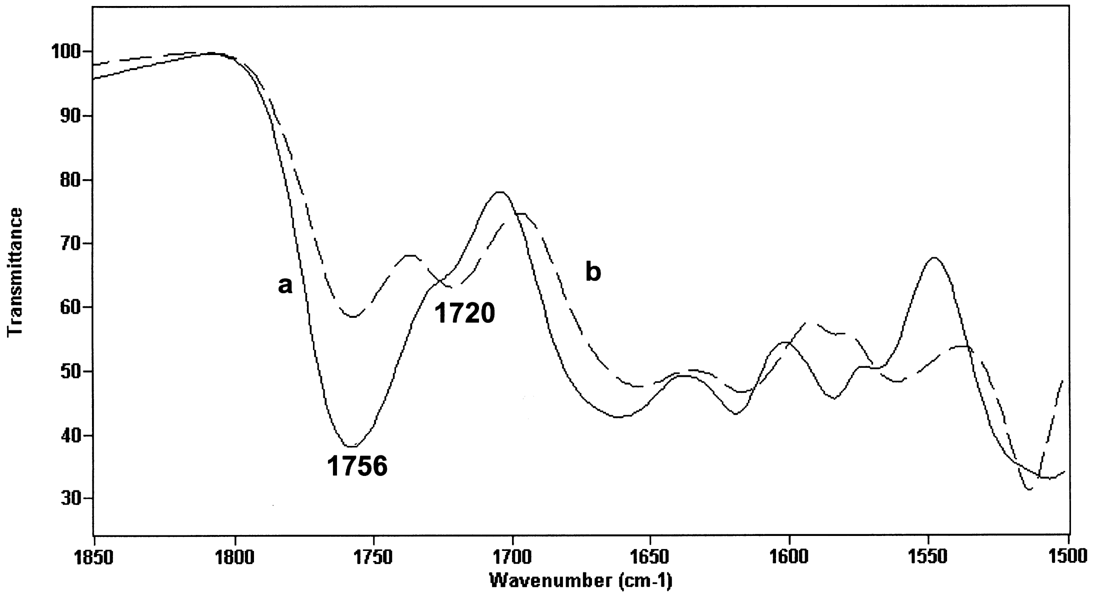


Fig. 4. FTIR spectrum of the polymer from different diamidedianhydrides: (a) 4,4′-[biphenylo-2,2′-dimethylo-di(benzene-5-amide-1,2-dicarboxylic)] anhydride; (b) 1,4-[phenylene-di(benzene-5-amide-1,2-dicarboxylic)] anhydride. Tetraamine, 3,3′,4,4′-tetraaminodiphenylether; after heating at 280°C in inert gas for 1 h.

For further investigation, *p*-chlorophenol was used as a solvent. It was found that the polymers obtained in *p*-chlorophenol had better foil formation ability. Some properties of the polymers obtained in *p*-chlorophenol are shown in Table 5.

Reduced viscosity of the polymers was investigated directly after the polycondensation reaction (before additional thermal cyclization). Polymers precipitated from the reaction mixture after polycondensation had the aminoimide structure or both the aminoimide and imidazopyrrolone structure, described as a mixture. To cause the second ring closure, i.e. the imidazopyrrolone structure formation, the samples after precipitation were heated at 280°C for 1 h in inert gas atmosphere. In these conditions, in some polymers, a small amount of aminoimide structure is still present, detected as the presence of absorption band at 1720 cm^{-1}. These polymers are also described as a mixture. (The quantitative investigations of both structures amount are in progress.)

Fig. 3 shows a spectrum of the polymer from 1,3-[phenylene-di(benzene-5-amide-1,2-dicarboxylic)] anhydride (No. 2 in Table 1) and 3,3′,4,4′-tetraaminodiphenylether before and after heating at 280°C in inert gas.

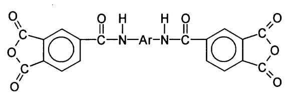
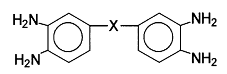
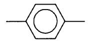
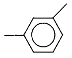
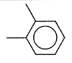
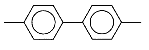
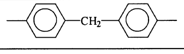
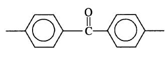
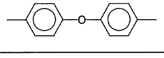
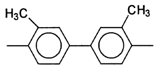
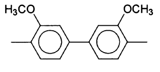
The absorption band at 1720 cm^{-1} characteristic of –C=O in the imide group is seen clearly in the polymer before heating which confirms the aminoimide structure. During heating of the polymer, the absorption band at 1756 cm^{-1} increased and the absorption band at 1720 cm^{-1} disappeared, which confirmed the ring closure.

This process was observed for the polymers obtained from all the diamidedianhydrides and both tetraamines used. The rate of the second ring closure depended on structure of diamidedianhydride. Fig. 4 presented FTIR spectrum of polymer obtained from 4,4-[biphenylo-2,2′-dimethylo-di(benzene-5-amide-1,2-dicarboxylic)] anhydride (No. 8 in Table 1) and 1,4-[phenylene-di(benzene-5-amide-1,2-dicarboxylic)] anhydride (No. 1 in Table 1) and 3,3′,4,4′-tetraaminodiphenylether after heating at 280°C in inert gas atmosphere.

The presence of absorption band at 1720 cm^{-1} in the FTIR spectrum of the polymer obtained from the diamidedianhydride without substitutes, confirms that even the heating at 280°C did not cause the complete ring closure to form an imidazopyrrolone structure. Some of the polymers gave flexible foils, as shown in Table 4.

Foils were obtained from the solution of the polymers in *p*-chlorophenol (after a polycondensation reaction without

Table 4
Some properties of the polymers obtained in *p*-chlorophenol (in *m*-cresol) from the various diamidedianhydrides and the tertaamines

					
No.	**Ar**	**X=nil**		**X= -O-**	
		η_{red}* $dl \cdot g^{-1}$	**Foil****	η_{red}* $dl \cdot g^{-1}$	**Foil****
1		insol. (0.92)	- (brittle)	0.32	brittle
2		0.63	flexible	0.86	flexible
3		insol. (0.29)	- (brittle)	0.20	brittle
4		insol. (0.20)	- (brittle)	0.46	brittle
5		0.82	brittle	0.37	brittle
6		0.83	flexible	1.12	flexible
7		7.60	flexible	0.61	brittle
8		4.22	flexible	0.9	brittle
9		6.30	flexible	0.9	flexible

*measured in p-chlorphenol, conc.=0.5 g/100 ml, temp. 50^{0}C
**after heating at 200^{0}C in vacuum for 8 hr.

the polymers precipitating) cast on a glass plate and dried at 200°C in vacuum for 8 h. The foils had an imidazopyrrolone structure with a little amount of aminoimide moieties, detected by IR spectroscopy. Also, some polymers obtained by low temperature polycondensation gave flexible foils. But generally the foils obtained from the polymers prepared by low temperature polycondensation exhibited a higher amount of aminoimide structure, confirmed by the presence of absorption band at 1720 cm^{-1}, than those obtained from the polymers being prepared by high temperature polycondensation. In fact, formation of the imidazopyrrolone structure from polyamide amino acid, formed during low temperature polycondensation, needs two steps of the dehydration which should take place during heating the foils, i.e. mostly in a solid state. In this case, these reactions may be more difficult because of various conformations of the polymers chains in comparison with the polymers prepared by high temperature polycondensation having aminoimide structures.

Low temperature polycondensation carried out in DMA at room temperature caused the formation at first of the polymer having an amide amino acid structure, and their reduced viscosities are presented in Table 6. The reduced viscosities of the polymers obtained in *p*-chlorophenol are higher than the corresponding polymers obtained in DMA. However, it is necessary to bear in mind that reduced viscosity is connected not only with a molecular weight but also with a polymer chain structure and, in our case, the polymers obtained by high and low temperature polycondensation have different chain structures. Foils from polyamide amino acids were obtained from the solution in DMA and *p*-chlorophenol and were dried at 200°C in vacuum for 8 h. According to FTIR data, the foil had the same structure independent of the solvent used.

The thermal stability of the polymers obtained in *p*-chlorophenol was evaluated by thermogravimetric (TG) analysis under argon. Thermal behaviour data of the polymers are listed in Table 7.

The polymers showed little weight loss below 300°C. The temperature of 10% weight loss depends on the diamide-dianhydride structure, but the tetraamine structure seems to influence this only slightly. The residue at 1000°C for the polymers is in the range 17–44%. This property seems to be worthy of notice in consideration of possibility of applications of these polymers. Polypyrrolone material that exhibits excellent thermal and chemical stability has been studied to determine its potential for novel applications in membrane-based separations at elevated temperatures [7], [8]. Insulating polypyrrolone film can be converted into an electrical conductor by pyrolysis at high temperature. In the pyrolysis process, which consists of carbonization ($T < 800°C$) and graphitization ($T > 800°C$), oxygen and hydrogen are removed completely

Table 5
Structure of polymers obtained in *p*-chlorophenol from the various diaminedianhydrides and the teraamines after reaction (before additional heating) and after heating at 280°C for 1 h in inert gas

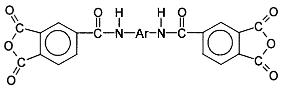
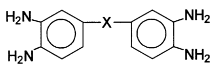
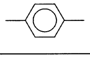
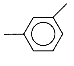
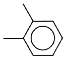
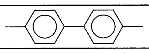
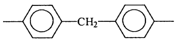
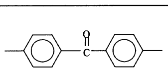
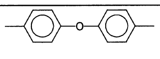
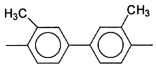
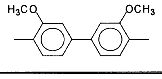
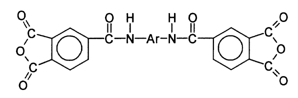
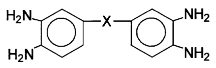
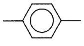
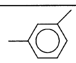
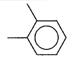
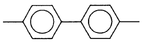
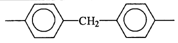
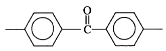
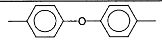
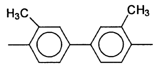
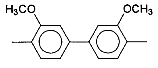
No.					
	Ar	X=nil		X= -O-	
		before heating	after heating	before heating	after heating
1		aminoimide	mixture	mixture	mixture
2		aminoimide	mixture	mixture	imidazopyrrolone
3		mixture	imidazopyrrolone	mixture	mixture
4		aminoimide	mixture	aminoimide	mixture
5		aminoimide	mixture	aminoimide	mixture
6		aminoimide	mixture	mixture	imidazopyrrolone
7		aminoimide	imidazopyrrolone	mixture	imidazopyrrolone
8		aminoimide	imidazopyrrolone	aminoimide	imidazopyrrolone
9		aminoimide	imidazopyrrolone	aminoimide	imidazopyrrolone

Table 6
Some properties of the polymers obtained in DMA at room temperature from the various diamidedianhydrides and the teraamines

					
No.	Ar	X=nil		X= -O-	
		η_{red}* dl·g^{-1}	Foil**	η_{red}* dl·g^{-1}	Foil**
1		0.63	flexible	0.26	brittle
2		0.40	flexible	0.25	brittle
3		0.21	brittle	0.57	flexible
4		0.21	brittle	0.22	brittle
5		0.25	brittle	0.25	brittle
6		0.26	brittle	0.32	brittle
7		0.31	flexible	0.26	brittle
8		0.65	flexible	0.47	flexible
9		0.49	flexible	0.59	flexible

*reduced viscosity of polyamideamino acid measured in DMA, conc.=0.5 g/100 ml, temp. 25^{0}C

**after heating at 200^{0}C in vacuum for 8 hr.

and an increase in the mobility of charge carriers may increase the conductivity with pyrolytic temperature. A graphite-like structure with heterocyclic rings containing nitrogen atoms is proposed for a polypyrrolone film pyrolyzed at 1200°C [9], [10].

4. Conclusion

Poly(amideimidazopyrrolones) were synthesized from diamidedianhydrides and aromatic tetraamines using high and low temperature polycondensation. The structure of the monomers, mainly diamidedianhydrides, and the polycondensation method influenced on reduced viscosity of the polymers and also the formation of the imidazopyrrolone structure.

Results of our investigations have suggested that the closure of the imidazopyrrolone ring in most of the polymers synthesized proceeds and we observed the presence of characteristic bands for this structure after heating at high temperature in vacuum or in inert gas atmosphere. Nevertheless, in some cases, the residue of aminoimide structure was still detected by IR measurement, being higher in the polymers obtained by low temperature polycondensation.

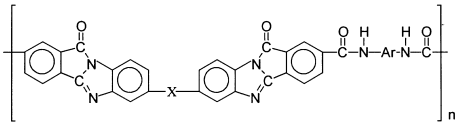
Some of the polymers obtained gave flexible foils. Better ability for flexible foil formation was exhibited by the polymers obtained by high temperature polycondensation and those being the condensation products of the diamidedianhydrides with 3,3′-diaminobenzidine.

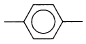
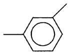
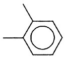
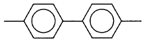
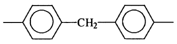
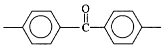
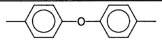
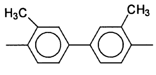
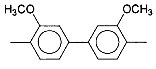
The residue at 1000°C for the polymers is rather high, which can creature additional possibilities for applications.

Acknowledgements

This work was carried out under financial support of the Scientific Research Committee (grant No. 3 T09A 123 10)

Table 7
Thermal properties of the polymers obtained in *p*-chlorophenol (after heating at 280°C in inert gas for 1 h)



No.	Ar	X=nil		X= -O-	
		TG in argon			
		Temp of 10% weight loss ^{0}[C]	Residue at 1000^{0}C [%]	Temp of 10% weight loss ^{0}[C]	Residue at 1000^{0}C [%]
1		480	32	480	32
2		440	35	490	38
3		300	40	390	44
4		530	35	450	38
5		470	38	430	35
6		500	32	480	29
7		550	25	500	30
8		540	36	640	17
9		580	30	430	38

References

[1] Landel RF, Rembaum A. Chemistry in space research. New York: Am Publ Co, 1972.
[2] Loncrini DF. J Polym Sci: Part A-1 1966;4:1531.
[3] Sato M, Kondo H, Yokoyama M. J Polym Sci, Polym Chem Ed 1982;20:335.
[4] Sęk D. Schab-Balcerzak E, Grabiec E. Polymer in press.
[5] Stille JK, Williamson JR, Arnold FE. J Polym Sci, Part A 1965;3:1013.
[6] Dawans F, Marvel CS. J Polym Sci, Part A 1965;3:3549.
[7] Gao XS, Tan ZS, Lu FC. J Membrane Sci 1994;88 (1):37.
[8] Colstello LM, Walker DRB, Koros WJ. J Membrane Sci 1994;90 (1) 2:117.
[9] Piao MJ, Wan MX, Lu FC. Synthetic Metals 1995;75 (3):191.
[10] Piao MJ, Wan MX, Lu FC. Synthetic Metals 1997;89 (3):209.