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New semiladder polymers: III. Synthesis and properties of new poly(etherimidazopyrrolone)s

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Abstract

A series of polymers from dietherdianhydrides of arylene-di(benzene-5-ether-1,2-dicarboxylic) anhydride type and tetraamines: 3,3′-diaminobenzidine and 3,3′,4,4′-tetraaminodiphenyl ether were synthesized using high and low temperature polycondensation. The polymers had a semiladder structure. The influence of the monomer structure on the polymer properties has been investigated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Thermostable polymers; Semiladder polymers; Polybenzoilenobenzimidazoles

1. Introduction

Ladder polymers are characterized by many valuable, important properties. Such polymers have found a wide range of applications as high-performance materials, owing to their excellent thermal and dielectrical properties [1,2]. Polypyrrolone was first synthesized in 1965 [3] and, recently, increasing interest in this type of polymer has been observed. This interest has arisen in view of their application as membranes for the separation of gas mixtures [4,5] and conducting materials [6,7].

The major limitation for the versatile applications of the ladder polymers is their poor solubility in organic solvents [8].

The introduction of single-chain segments with some flexibilizing groups such as amide, ether or ester between ladder segments should improve the solubility of the polymers. However, this modification may influence the thermal stability of such semiladder polymers.

In our previous works we have described the synthesis and properties of poly(esterimidazopyrrolone)s [9] and poly(amideimidazopyrrolone)s [10]. 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(etherimidazopyrrolone)s from dietherdianhydrides and tetraamines: 3,3′-diaminobenzidine and 3,3′,4,4′-tetraaminodiphenyl ether. Some of the dietherdianhydrides were used as monomers for poly(etherimide)s synthesis [11,12], but we have found information about the application of the three dietherdianhydrides, i.e. having hydroquinone, resorcinol and biphenyl cores, to the synthesis of poly(etherimidazopyrrolone)s [4,13].

2. Experimental

2.1. Materials

Phenylhydroquinone (Aldrich), 4,4′-biphenyldiol (Merck), catechol (Aldrich), resorcinol (Aldrich), 4,4′-dihydroxybenzophenone (Aldrich), hydroquinone (Aldrich), bis(4-hydroxyphenyl) methane (Aldrich), 4-nitrophthalonitrile (Aldrich) were used as laboratory reagents without further purification. Acetic anhydride, glacial acetic acid, acetonitrile, dimethylsulfoxide, potassium hydroxide and anhydrous potassium carbonate were laboratory grade reagents.

2.1.1. Purification of amines

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

3,3′-Diaminobenzidine (m.p. 179–180°C) and 3,3′,4,4′-tetraaminodiphenyl ether [14] (m.p. 150–151°C) were recrystallized from boiling water in the presence of charcoal.

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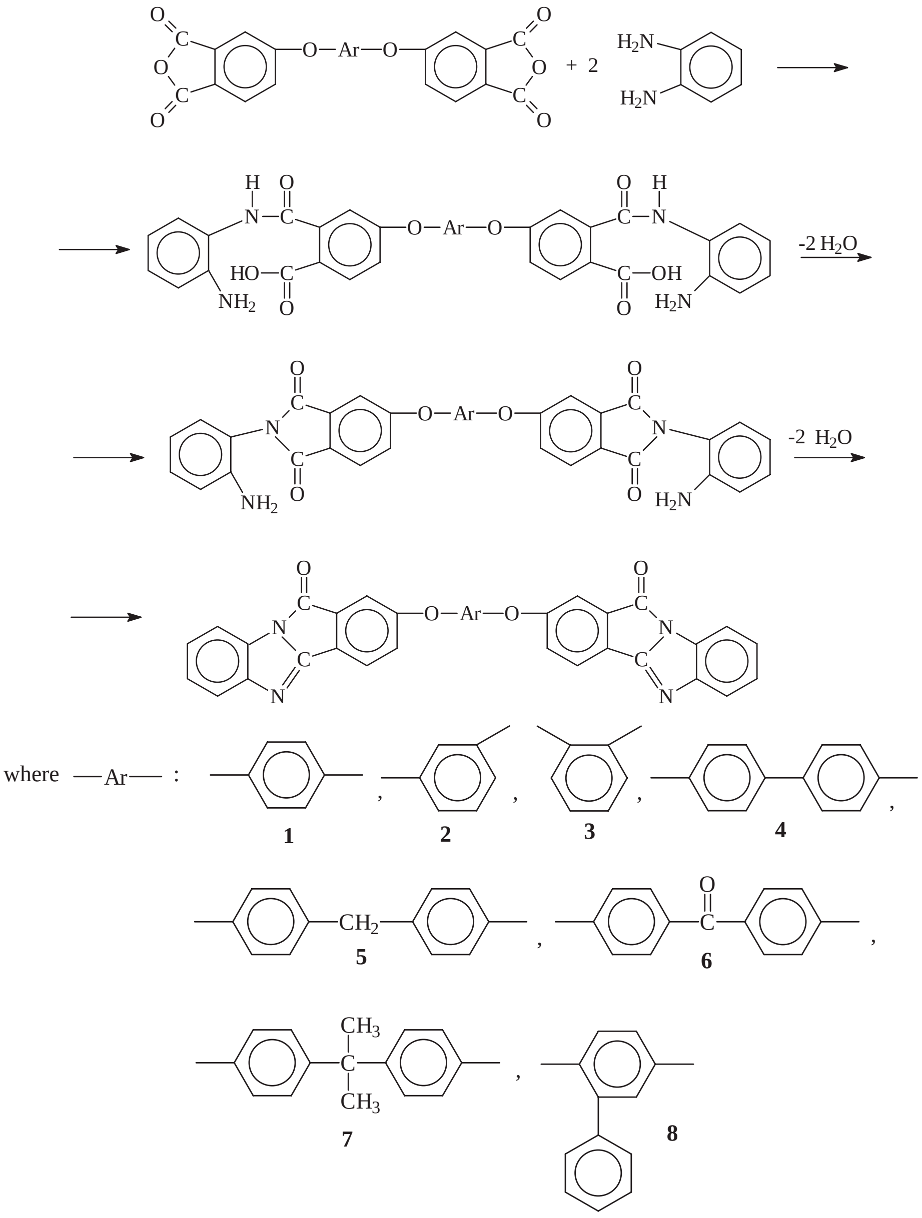


Fig. 1. Scheme of condensation of dietherdianhydrides with 1,2-phenylenediamine.

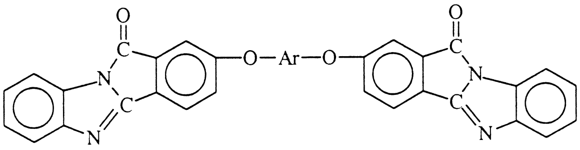
2.1.2. Purification of solvent

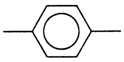
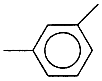
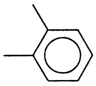
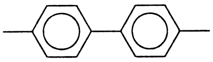
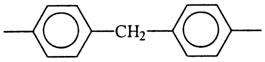
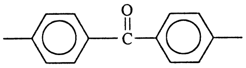
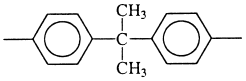
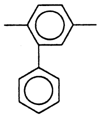
Dimethylacetamide (DMA) was distilled in the usual manner.

2.1.3. Measurements

For elemental analysis a 240C Perkin–Elmer analyzer was used. Melting points (detected as peak on a curve) and glass transition temperatures were determined on a DSC DuPont 1090B apparatus at a heating rate of 20 K/min using sealed aluminium pen (sample weight about 5 mg) at air atmosphere. Thermogravimetric (TG) analysis was performed on Paulik–Erdey apparatus at a heating rate of 10 K/min in argon. Viscosity was measured in *p*-chlorophenol at 50°C or in DMA at 25°C using an Ubbelohde viscometer. Molecular masses of the dietherdianhydrides 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. Measurements of the IR spectra were done using KBr discs (for powder samples) or films. Thermomechanical properties were determined on DMTA (Polymer Laboratories), over the heating range 30–300°C and frequency 1 Hz. Measurements were carried out in air atmosphere using samples having the dimensions of $2 \times 4 \times 0.01$ mm. Mechanical properties were investigated at room temperature, rate of tension 20 mm/min in air, thickness of foils about 0.05 mm, measuring error 2–5%.

Table 1
Structure and analysis of model compounds



Ar	M.p. (°C)	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Yield (%)
		Found	Calcd	Found	Calcd	Found	Calcd	
	290	75.80	74.72	3.19	3.32	10.14	10.25	33
	240	74.48	74.72	3.23	3.32	10.34	10.25	7
	302	73.75	74.72	3.10	3.32	10.10	10.25	14
	323	76.27	77.16	3.68	3.56	9.16	9.00	15
	186	75.95	77.35	3.75	3.80	8.65	8.80	23
	–[a]	75.20	75.68	3.86	3.40	8.40	8.60	50
	294	77.45	77.70	4.13	4.25	8.23	8.43	6
	–[a]	76.74	77.16	3.74	3.56	8.98	9.00	5

[a] Compound does not melt up to 400°C.

2.2. Synthesis of dietherdianhydrides

All dietherdianhydrides were synthesized according to the method described in literature [11]. The dianhydrides were purified by crystallisation from mixture of acetic acid and acetic anhydride (1:3 v/v) and dried in vacuum oven at 150°C for 24 h.

The structure of the dianhydrides was confirmed by: mass spectroscopy, FTIR spectra (characteristic bands at 1868 cm^{-1}, 1846 cm^{-1}, 1783 cm^{-1} for =C=O in anhydride, at 1200 cm^{-1} for ether group), elemental analysis, melting points (DSC). Data for the dianhydrides (number as in Fig. 1):

1. m.p. 273°C (lit. [12,15] 265–266°C), elem. anal. found (calcd): C—65.58% (65.68%); H—2.49% (2.52%), $m/e = 402$, yield 72%.
2. m.p. 168°C (lit. [13] 163–164°C, lit. [15] 284–286°C), elem. anal. found (calcd): C—65.75% (65.68%); H—2.41% (2.52%); $m/e = 402$, yield 71%.

3. m.p. 273°C (lit. [11] 265–266°C), elem. anal. found (calcd): C—65.53% (65.68%); H—2.50% (2.52%); *m/e* = 402, yield 72%.
4. m.p. 293°C (lit. [15] 285–286°C, lit. [13] 286–288°C), elem. anal. found (calcd): C—70.14% (70.30%); H—3.00% (2.95%); *m/e* = 478, yield 73%.
5. m.p. 178°C, elem. anal. found (calcd): C—69.85% (70.73%); H—3.20% (3.28%); *m/e* = 492, yield 91%.
6. m.p. 215°C (lit. [15] 215–216°C, elem. anal. found (calcd): C—68.46% (68.78%); H—2.76% (2.79%); *m/e* = 506, yield 44%.
7. m.p. 189°C (lit. [15] 192°C), elem. anal. found (calcd): C—71.40% (71.54%); H—3.92% (3.87%); *m/e* = 520, yield 71%.
8. m.p. 229°C, elem. anal. found (calcd): C—69.65% (70.30%); H—2.85% (2.95%); *m/e* = 478, yield 75%.

2.3. Synthesis of model compounds

The dietherdianhydride (1 mmol) and 1,2-phenylenediamine (2 mmol) in *p*-chlorophenol (10 ml) were put into a pot equipped with a stirrer, condenser and argon inlet and heated at 180°C for 5 h. Models were precipitated with ethanol (150 ml), filtered, washed with ethanol and dried at 80°C. Models from dietherdianhydrides No 6–8 (Fig. 1) were additionally heated at 330°C to receive full cyclization.

2.4. Polymer synthesis

For synthesis of the polymers high and low temperature polycondensation were used.

2.4.1. High temperature polycondensation

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

2.4.2. Low temperature polycondensation

Tetraamine (1 mmol) was dissolved in dry DMA (10 ml) and the stoichiometric amount of a given dietherdianhydride (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. Foils for DMTA and mechanical measurements were prepared by pouring the reaction mixture on to a glass plate (without polymer precipitation), slowly heating in a vacuum to 200°C (about 5 h), then heating at 200°C in a vacuum for 8 h, and then heating at 280°C in a vacuum for 2 h.

3. Results and discussion

3.1. Characterization of the model compounds

Condensation of dietherdianhydrides 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 evolves water to form aminoimide. In the next step of reaction the second ring closure takes place and 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 for –C=N– [16].

According to FTIR measurements during reaction of the dietherdianhydrides with 1,2-phenylenediamine in the conditions used, the formation of imidazopyrrolone structure was observed. The only model compounds from dietheranhydrides 6–8 i.e. having in the centre of the molecule benzophenone, bisphenol A and phenylohydroquinone structures, exhibited in FTIR spectra the presence of weak absorption bands at 1720 cm^{-1} characteristic for carbonyl group in imide ring and needed additional heating to 330°C in solid state to receive full cyclization. The model compounds characteristics are presented in Table 1.

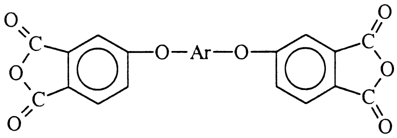
The yields of the model compounds are rather low but reaction conditions were not optimised because the models were used only for comparison of their structures with the proper polymers.

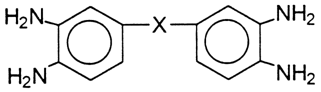
3.2. Characterization of the polymers

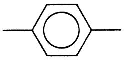
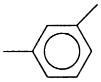
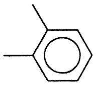
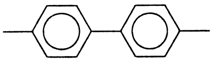
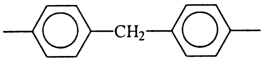
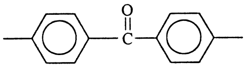
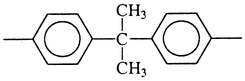
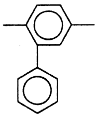
A series of polymers from the dietherdianhydrides and tetraamines: 3,3′-diaminobenzidine, and 3,3′,4,4′-tetraaminodiphenyl ether were prepared using high and low temperature polycondensation routes.

High temperature polycondensation was carried out in *p*-chlorophenol at 180°C for 10 h. The structures of the polymers were detected after reaction by FTIR spectroscopy. When 3,3′,4,4′-tetraaminodiphenyl ether was used, polymers precipitated from the reaction mixture had the both aminoimide and imidazopyrrolone structures described as a mixture. When 3,3′-diaminobenzidine was used, polymers in most cases had the same structure, except the polymers obtained from dietherdianhydrides 3 and 8 (Fig. 1), which exhibit aminoimide structure. To cause the second ring closure, i.e. the imidazopyrrolone structure formation, the polymers after precipitation were heated at 280°C for 1 h in an inert gas atmosphere. After thermal cyclization all polymers from tetraamine with ether linkage had an imidazopyrrolone structure. Only three of the polymers arising from 3,3′-diaminobenzidine had such a structure: i.e. polymers

Table 2
Some properties of the polymers obtained in *p*-chlorophenol from the various dietherdianhydrides and the tetraamines





Ar	X = nil		X = –O–	
	η_{red}[a] dl g^{-1}	Foil[b]	η_{red}[a] dl g^{-1}	Foil[b]
	4.65	Flexible	0.34	Brittle
	1.00	Flexible	0.23	Brittle
	0.34	Brittle	0.23	Brittle
	5.10	Flexible	0.53	Flexible
	1.00	Flexible	0.17	Brittle
	1.00	Brittle	0.45	Brittle
	4.38	Brittle	1.53	Flexible
	3.38	Brittle	0.17	Brittle

[a] Measured in *p*-chlorophenol, conc. = 0.5 g/100 mL, temp. 50°C.

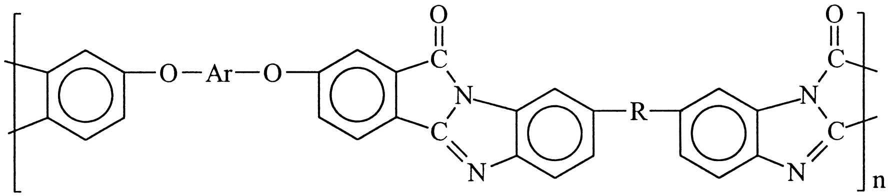
[b] Foils obtained in *p*-chlorophenol after heating at 200°C in vacuum for 8 h.

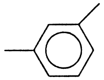
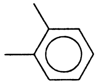
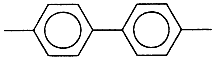
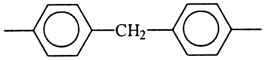
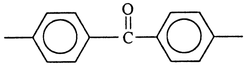
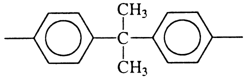
obtained from dietherdianhydrides 1, 6 and 8 (Fig. 1). The other polymers were a mixture of aminoimide and imidazopyrrolone structures. The rate of the second ring closure depended on structure of dietherdianhydride and tetraamine. The presence of absorption band at 1720 cm^{-1} in the FTIR spectrum of the polymers obtained from some dietherdianhydrides and 3,3′-diaminobenzidine, confirms that even the heating at 280°C did not cause the complete ring closure to form an imidazopyrrolone structure.

Some properties of the polymers obtained in *p*-chlorophenol are shown in Table 2. The reduced viscosity of the polymers was investigated directly after polycondensation reaction (before additional thermal cyclization).

It was found that some polymers obtained in *p*-chlorophenol had foil formation ability. Foils were obtained from the solution of the polymers in *p*-chlorophenol (after polycondensation reaction without the polymers precipitation) cast on glass plate and dried at 200°C in vacuum for 8 h. The

Table 3
Mechanical and thermomechanical properties of foils from the polyetherimidazopyrrolones (heated at 200°C for 8 h and at 280°C for 2 h)

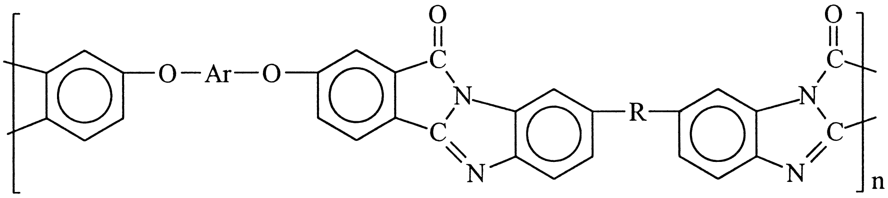


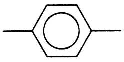
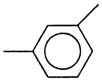
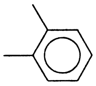
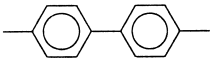
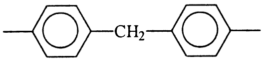
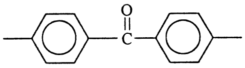
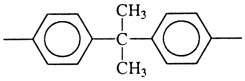
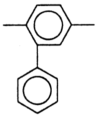
Ar	R	η_{red}[a] (dl g^{-1})	Glass transition temperature[b] (°C)	Tensile strength (MPa)	Elongation at break (%)	Tangent modulus (MPa)	Modulus E′ at 50°C (MPa)	Modulus E′ at 200°C (MPa)	Modulus E′ at 250°C (MPa)
	–	1.20	251	–	–	–	583	346	52
	–O–	2.46	309	83	4.5	2354	717	259	4
	–	0.27	328	43	3.0	1727	–	–	–
	–O–	0.60	318	62	5.0	1609	1153	917	780
	–	0.22	309	147	8.0	3522	760	538	465
	–O–	0.38	309	39	4.5	1491	–	–	–
	–	1.07	325	39	5.0	1432	–	–	–
	–O–	1.83	–	–	–	–	449	375	385
	–	0.23	–	–	–	–	701	484	440
	–	0.20	325	69	6.0	1364	2256	1731	1689

[a] Reduced viscosity of polyetheramide-amino-acid in DMA, conc. 0.5 g/100 ml, temperature 25°C (before thermal treatment).

[b] Detected on foils by DSC method.

Table 4
Thermal properties of the foils



Ar	X = nil		X = –O–	
	TG in argon Temp of 10% weight loss (°C)	Residue at 1000°C (%)	Temp of 10% weight loss (°C)	Residue at 1000°C (%)
	550	71	480	71
	550	74	490	56
	560	55	480	67
	630	75	620	82
	560	62	490	66
	520	68	520	68
	510	60	490	61
	520	55	490	72

foils had an imidazopyrrolone structure with a small amount of aminoimide moieties, detected by IR spectroscopy. However, because of the toxicity of *p*-chlorophenol the foils were not prepared in a higher scale sufficient for mechanical and thermomechanical measurements.

A low temperature polycondensation carried out in DMA at room temperature initially caused the formation polymers having an amide-amino-acid structure, and their reduced viscosities are presented in Table 3. The reduced viscosities of the polymers obtained at high temperature in *p*-chlorophenol are higher than the corresponding polymers obtained in DMA. However, it is necessary to keep 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.

Most of the polymers obtained by low temperature polycondensation gave flexible foils after heating at 200°C in vacuum for 8 h. Generally, however, the foils obtained from the polymers prepared by low temperature polycondensation exhibited higher amounts of the aminoimide structure as confirmed by the presence of absorption band at 1720 cm^{-1}, than those obtained from the polymers prepared by high temperature polycondensation. In fact, formation of the imidazopyrrolone structure from polyamide-amino-acid, needs two dehydration steps which should take place during heating the foils mostly in a solid state. In this case, these reactions may be more difficult because of various conformations of the polymers chains being possible in comparison with the polymers prepared by high temperature polycondensation having aminoimide structures.

To complete the cyclization, the foils prepared from the polymer obtained in low temperature polycondensation were additionally heated at 280°C in vacuum for 2 h.

After thermal treatment the absorption band at 1720 cm^{-1} in FTIR spectra of the foils was either absent or only slightly visible; such prepared foils were used for further investigations.

Mechanical and thermomechanical properties of some foils obtained in DMA and their glass transition temperatures are listed in Table 3.

Foils from the polyetherimidazopyrrolones had glass transition temperatures above 300°C. The highest tensile strength and elongation at break exhibits polymer obtained from dietherdianhydride having biphenyl core and 3,3′-diaminobenzidine.

Taking into consideration changes of the modulus E', it can be seen that at 200°C the values are lower in the range of 17–31% in comparison to the ones at 50°C. However, even at the temperature of 250°C the foils preserve a rather high value of the modulus, confirming their high heat stability.

Thermal stability of the foils was evaluated by TG analysis under argon. The results are presented in Table 4.

The foils made of the polymers synthezised by the low temperature polycondensation route showed little weight loss below 400°C. It is believed that the thermal stability of the polymers depends on the tetraamine structure. Polymers arising from 3,3′-diaminobenzidine exhibited higher temperatures of 10% weight loss and higher residue at 1000°C. The residue at 1000°C for the polymers ranges between 71 and 56%. This property seems to be worthy of note, considering the possible applications of these polymers. The polypyrrolone material that exhibits excellent thermal and chemical stability has been studied to determine its potential for novel applications in membrane-based separation processes at elevated temperatures [17]. 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) processes, oxygen and hydrogen are removed and an increase the mobility of charge carriers may increase conductivity. A graphite-like structure with heterocyclic rings containing nitrogen atoms is proposed for polypyrrolone film pyrolyzed at 1200°C [6,7].

4. Conclusion

Poly(etherimidazopyrrolone)s from dietherdianhydrides and aromatic tetraamines were synthesized using high and low temperature polycondensation routes.

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 a vacuum. Nevertheless, in some cases the residue of an aminoimide structure was still detected by IR measurement [18].

Poly(etherimidazopyrrolone)s exhibited high thermal stability. The residue at 1000°C for the polymers is rather high, which can create additional possibilities in their applications. Some of the polymers obtained gave flexible foils, which kept good mechanical properties up until 200°C.

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