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New semiladder polymers: 1. Synthesis and properties of new poly(esterimidazopyrrolone)s

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A series of polymers formed from diesterdianhydrides of arylene-di(benzene-5-estro-1,2-dicarboxylic) anhydride type and tetraamines, 3,3′diaminobenzidine and 3,3′,4,4′tetraaminodiphenyl ether, has been synthesized using one-step high temperature polycondensation in m-cresol at 180°C. The relation between polymer reduced viscosity and reaction time was studied and structures of the polymers were detected by *FT*i.r. spectroscopy. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: semiladder polymers; poly(esterimidazopyrrolone)s)

INTRODUCTION

Ladder polymers are characterized by many valuable and important properties. Such polymers have found a wide range of applications as high performance materials, owing to their excellent thermal and dielectrical properties. However, in most cases they are insoluble, or dissolve only in aggressive solvents.

In order to improve their solubility, one should introduce single-chain segments with groups such as amide, ether or ester between ladder segments. Such semiladder polymers, which may be considered as having 'hard' and 'soft' segments in the main chain, seem to be a promising class of polymers because they should exhibit better solubility and processability than ladder polymers, even though reduced thermal stability can be expected.

In our work we have synthesized a series of new semiladder poly(esterimidazopyrrolone)s from diesterdianhydrides and tetraamines: 3,3′diaminobenzidine and 3,3′,4,4′tetraaminodiphenyl ether. Some of the diesterdianhydrides have been used as monomers for poly(esterimide)s synthesis[1,2], but we have found no information on their application to the synthesis of poly(esterimidazopyrrolone)s.

EXPERIMENTAL

Materials

Trimellitic andydride acid chloride (Aldrich) was used without further purification. Bisphenol A (Aldrich), phenylhydroquinone (Aldrich), 4,4′-biphenyldiol (Merck), catechol (Aldrich), resorcinol (Aldrich), 4,4′-dihydroxybenzophenone (Aldrich) and hydroquinone (Aldrich) were used as laboratory reagents without further purification.

Purification of amines. 1,2-Diaminobenzene was recrystallized several times from chloroform in the presence of decolourizing 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′-Tetraaminodiphenyl ether was used as received, m.p. 150–151°C.

Pyridine was dried and distilled.

Purification of solvents. m-Cresol was distilled in the usual manner. Acetone was dried and distilled in the usual manner.

Dianhydrides

4,4′[diphenylopropane-di(benzene-5-estro-1,2-dicarboxylic)]anhydride, 4,4′[biphenylo-di(benzene-5-estro-1,2-dicarboxylic)] anhydride and 1,4[phenylene-di(benzene-5-estro-1,2-dicarboxylic)]anhydride were synthesized according to the method described in literature[3].
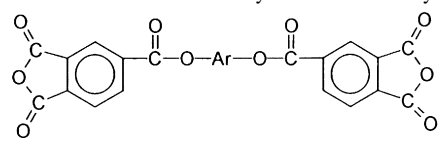
The synthesis of the new diesterdianhydrides (not described in the literature) was carried out as follows. In a 100 ml flask equipped with a condenser, stirrer and dropping funnel, 2.2 mmol of trimellitic anhydride acid chloride and 22 ml of dry acetone were placed under an argon atmosphere. After the mixture was heated under reflux, a solution of 1 mmol of a proper aromatic dihydroxy compound (i.e. resorcinol, catechol, phenylhydroquinone or benzophenone) 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. After cooling to room temperature, pyridine hydrochloride precipitated. This was removed by filtration and the product was precipitated with dry hexane. The product was washed several times with dry hexane and dried in a vacuum oven at 50°C for 24 h. The crude product was crystallized from a mixture of acetic andydride and acetic acid (3:1 v/v) and dried in a vacuum oven at 200°C or 180°C (depending on the dianhydride melting point) for 24 h.
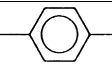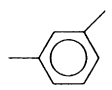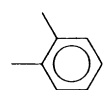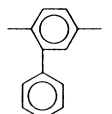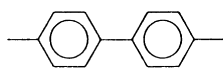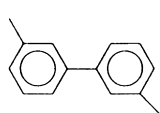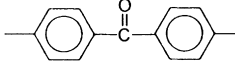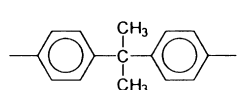
The structure and characteristics of the esterdianhydrides are listed in *Table 1*. The structure of these dianhydrides was confirmed by i.r. spectra (characteristic bands at 1868 cm^{-1}, 1846 cm^{-1}, 1783 cm^{-1} for =C=O in anhydride, at 1741 cm^{-1} for –O–CO– in ester).

Synthesis of model compounds

1 mmol of a given dianhydride and 2 mmol of 1,2-diaminobenzene in 10 ml of solvent (m-cresol, pyridine,

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Table 1 Structure and analysis of diesterdianhydrides

No.	Ar	M.p. (°C)	Carbon (%) Found	Calculated	Hydrogen (%) Found	Calculated	MW (MS)	Yield[a] (%)
1		280(274[b])	62.83(62.84[b])	62.89	2.19(2.03[b])	2.20	—	82 (69)
2		215	61.99	62.89	2.11	2.2	458	96 (54)
3		185	62.79	62.89	2.13	2.2	459	94 (86)
4		204.6	67.14	67.47	2.5	2.64	534	86 (41)
5		320(298–301[b])	66.91(66.89[b])	67.42	2.61(2.66[b])	2.64	534	62 (31)
6		255	67.80	67.42	3.06	2.64	534	40 (26)
7		252	65.9	66.2	2.52	2.51	562	71 (34)
8		189(192[b])	68.73(67.96[b])	68.75	3.63(4.10[b])	3.50	—	95 (28)

[a]Crude (after crystallization)
([b]Date described in literature[1,2])

DMA or p-chlorophenol were used, depending on the dianhydride solubility) were put into a pot equipped with a stirrer, condenser and argon inlet and heated at 180°C (or at 100°C when pyridine was used or at 160°C when DMA was used) for 5 h. When the reaction was carried out in m-cresol, benzoic acid was used as catalyst, amounting to 2 mmol. Models of imidazopyrrolone were precipitated with 150 ml of ethanol, filtered, washed with methanol, and dried at 80°C. When water was added to the solution after separation of the imidazopyrrolone models, precursors of the imidazopyrrolone having an amineimide structure were also separated.

Polymer synthesis

The stoichiometric amount of a given dianhydride (6 mmol) and a tetraamine (6 mmol) in m-cresol (60 ml) were stirred at 180°C under nitrogen in the presence of benzoic acid (12 mmol) for 72 h. The reaction mixture was poured into ethanol and the resulting precipitate was filtered, extracted with boiling methanol and dried at 70°C.

Measurements

For elemental analysis a 240C Perkin–Elmer analyser was used. Melting points were determined on a DuPont 1090B d.s.c. 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 using an Ubbelohde viscometer. Molecular masses 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. To determine the quantitative relations of the bands characteristic for stretching vibrations of the C=O group in different surroundings, a curve fitting program was used in the region of 1850–1650 cm^{-1}. An interactive procedure and Gauss–Lorentz type curves were chosen to compute individual peaks.

RESULTS AND DISCUSSION

Characterization of model compounds

Condensation of diesterdianhydrides with 1,2-diaminobenzene leads to the formation of model compounds. The structure and melting points of the models synthesized are shown in *Table 2*.

Table 2 Structure and melting points of the model compounds

No.	Structure	Melting point (°C)	Colour	Yield (%) (in reaction medium)
1		311	yellow	26 (DMA)
2		330	yellow	30 (m-cresol)
3		202	yellow	36 (p-chlorophenol)
4		290	green	10 (m-cresol)
5		> 350	grey	12 (pyridine)
6		290	yellow	21 (pyridine)
7		312	yellow	18 (m-cresol)
8		185	yellow	11 (m-cresol)

The structure of the imidazopyrrolone compounds was confirmed by *FT*i.r. spectroscopy. The absorption bands at 1760 cm^{-1}, characteristic for carbonyl –C(=O)–N= in fused rings, and at 1618 cm^{-1}, characteristic for –C=N–, confirmed the imidazopyrrolone structure[3]. The absorption at 1741 cm^{-1} characteristic for the ester carbonyl group was also seen.

The amineimide precursors were also investigated by *FT*i.r. spectroscopy. The absorption at 1634 cm^{-1} characteristic for the presence of the amine group as well as at 1782 cm^{-1} and 1720 cm^{-1} characteristic for imide groups confirmed the precursor's structure. *Figure 1* shows the spectra of the model derived from 1,4[phenylene-di(benzene-5-estro-1,2 dicarboxylic)] anhydride (No. 1 in *Table 2*) in the form of amineimide and imidazopyrrolone. In the spectrum of the amineimide the absorption at 1782 cm^{-1} and 1720 cm^{-1} characteristic for carbonyl imide, and at 1634 cm^{-1} due to the –NH$_2$ group, can be seen. In the spectrum of the imidazopyrrolone the absorption band at 1634 cm^{-1} disappears, and the additional bands at 1760 cm^{-1} and at 1618 cm^{-1}, characteristic for carbonyl –C(=O)–N= in fused rings and the =C=N– group respectively, confirm the structure.

Characterization of polymers

A series of polymers from dianhydrides and tetraamines has been prepared by high temperature polycondensation.

Polycondensation was carried out in m-cresol in the presence of benzoic acid as the catalyst at 180°C for 72 h. A scheme of this reaction is shown in *Figure 2*.

The samples were collected every few hours and the influence of the reaction time on reduced viscosity of the polymer was investigated (detection of molecular weight was difficult because the samples were soluble only in m-cresol). The results are shown in *Figure 3a* and *b*.

For the polymers investigated, we have observed that the reduced viscosity increases with the reaction time to a maximum, followed by some decrease. The time after which the reduced viscosity reaches maximum depends on the structure of the anhydrides The same dependence was observed in the case of polymers derived from tetraamine having ether linkages between aromatic rings. The relationship between the monomer structure and the reaction time at which the reduced viscosity of poly(esterimidazopyrrolone)s reaches maximum is shown in *Table 3*.

Generally, the reduced viscosity of the polymers derived from tetraamine with ether linkage between benzene rings is
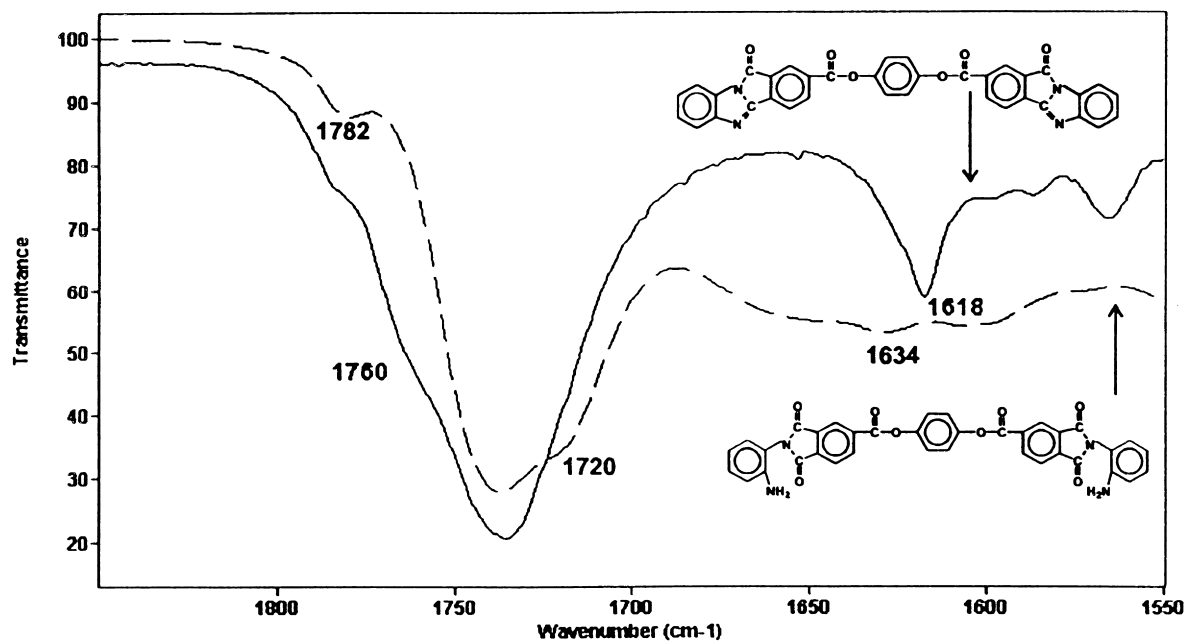
Figure 1 *FT*i.r. spectrum of the model derived from 1,4[phenylene-di(benzene-5-estro-1,2-dicarboxylic)] anhydride and 1,2 diaminobenzidine
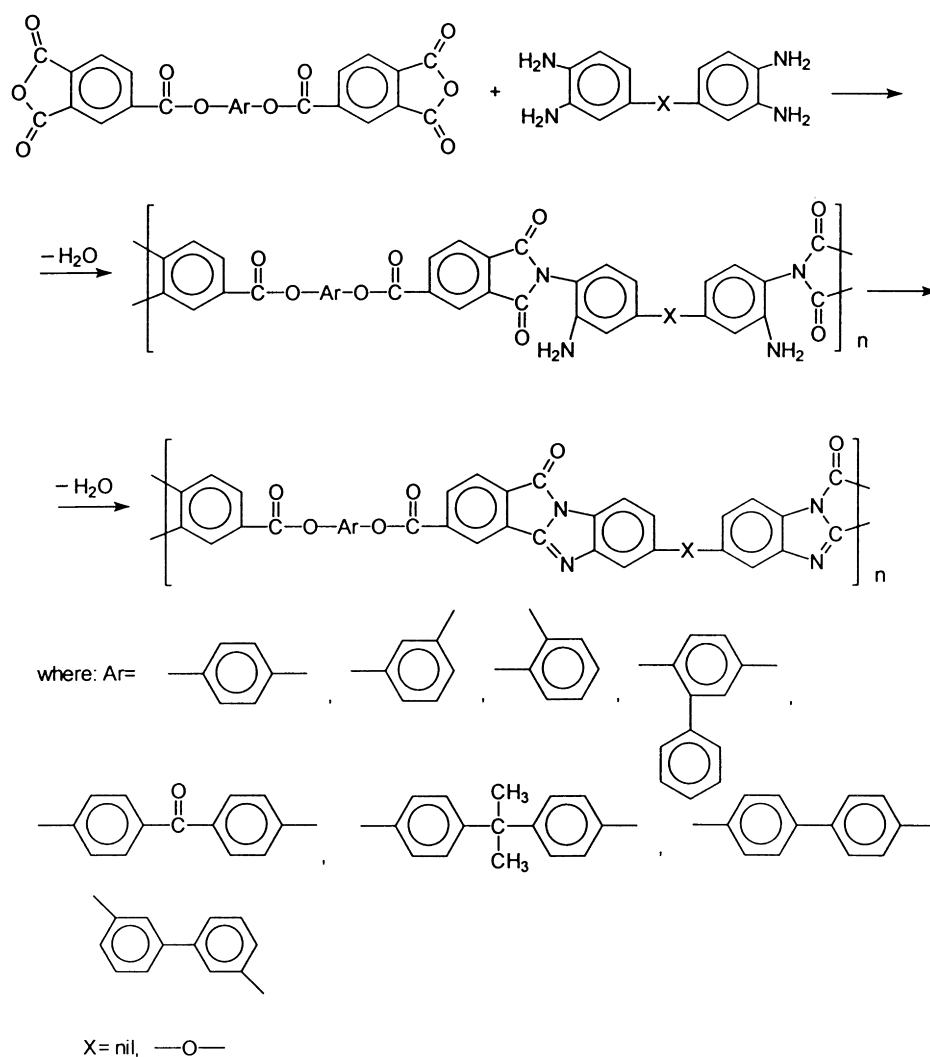

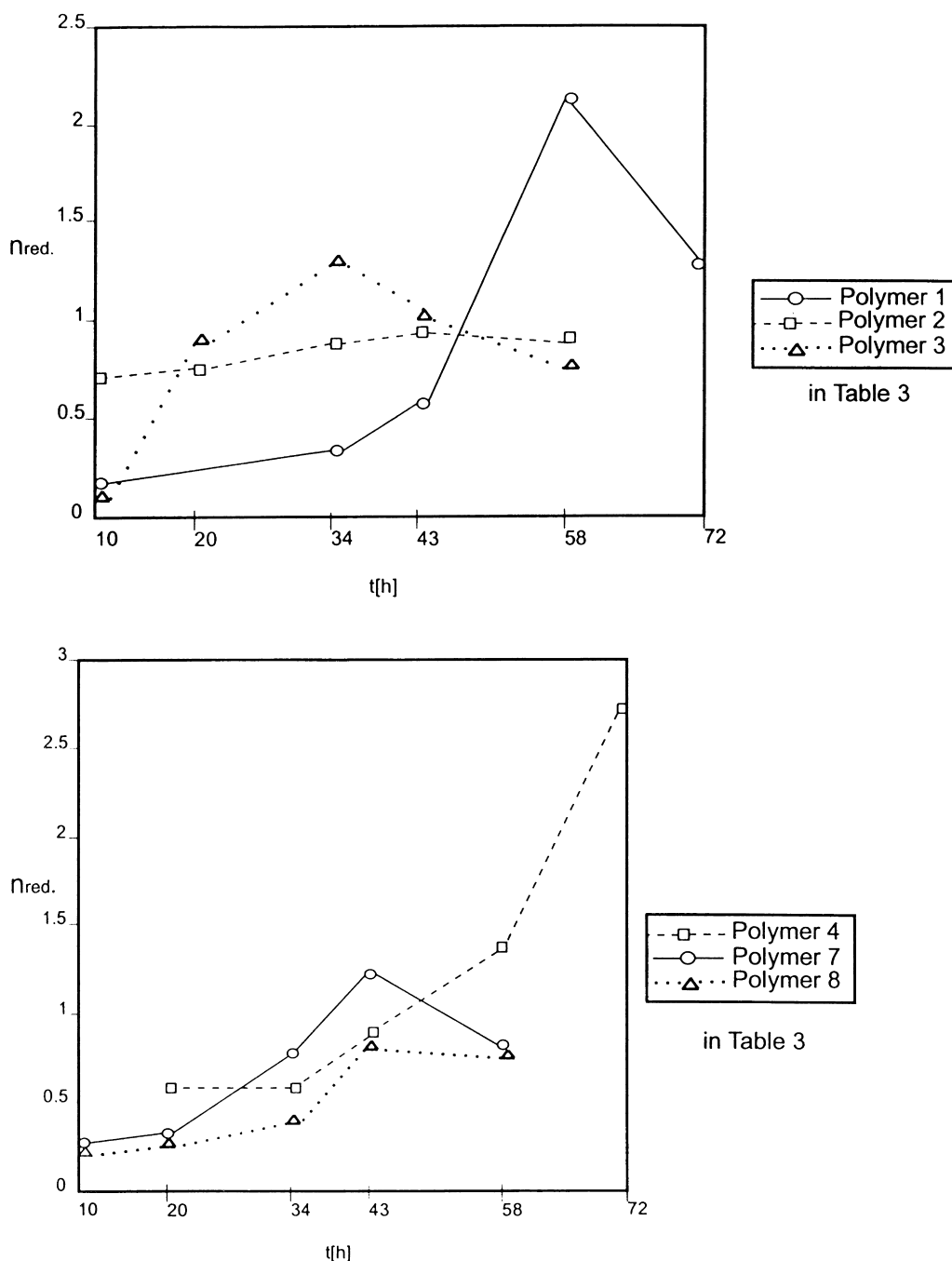
Figure 2 Scheme of polycondensation

Figure 3 Relation between reduced viscosity of the polymers and the reaction time

higher than that of the polymers made from the tetraamine with directly connected rings. Also, the polymers made from the tetraamine with ether linkage reached maximum viscosity after a shorter heating time.
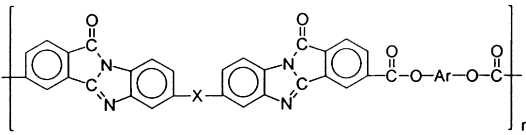
It is known that the viscosity of a polymer solution depends not only on the polymer molecular weight but also on the polymer chain structure. Because of this, along with measurements of the reduced viscosity, the *FT*i.r. spectra of the polymers were evaluated.
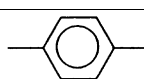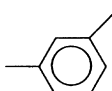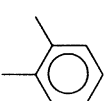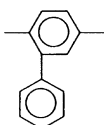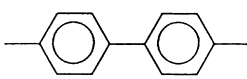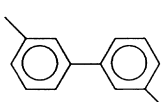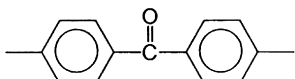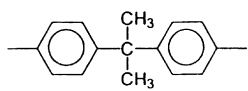
It was observed that the increase in polymer viscosity is accompanied by an increase in intensity of the absorption band of carbonyl $-C(=O)-N=$ in the imidazopyrrolone ring structure in the polymer. When the viscosity decreases the absorption intensity of the band due to the presence of the imidazopyrrolone structure decreases. The absorption bands at $1762\ cm^{-1}$ characteristic for the carbonyl group in imidazopyrrolone rings, at $1720\ cm^{-1}$ arising from the

imide ring and at $1741\ cm^{-1}$ due to carbonyl in the ester group are partially overlapped. In order to follow their changes, a curve-fitting calculation program was used.

Figure 4 shows the result of the curve-fitting calculations of the areas of carbonyl group in the polymer derived from 4,4′[phenylobenzophenone-di(benzene-5-estro-1,2 dicarboxylic)] anhydride and 3,3′diaminobenzidine (No. 7 in *Table 3*) after the time of reaction when the reduced viscosity reaches a maximum and when it is decreasing.

Table 4 shows the intensity ratio of the imidazo-pyrrolone carbonyl group band to the ester carbonyl group band as reference, for the polymer made from 4,4′[phenylobenzophenone-di(benzene-5-estro-1,2-dicar-boxylic)] anhydride and 3,3′diaminobenzidine (No. 7 in *Table 3*) as an example. The calculation data confirm that the increase in the reduced viscosity of the polymer is also connected with the increasing amount of the imidazopyrrolone structure.

Table 3 Relationship between monomer structure and reaction time in which the reduced viscosity of the polymer reached a maximum

No.	Ar	X	t_{max} (h)	$\eta_{red}{}^{a}$ (dl g^{-1})
1		—	58	2.09
1a		–O–	34	2.28
2		—	34	0.82
2a		–O–	20	1.1
3		—	34	1.33
3a		–O–	20	2.4
4		—	72	2.7
4a		–O–	72	5.8
5		—	—[b]	—[b]
5a		–O–	—[b]	—[b]
6		—	—[b]	—[b]
6a		–O–	—[b]	—[b]
7		—	43	1.24
7a		–O–	20	2.0
8		—	72	0.62
8a		–O–	72	4.86

[a]At the maximum in *Figure 3*, η_{red} measured in m-cresol, conc. = 0.5 g/100 ml, temp. = 25°C
[b]Insoluble in m-cresol
X = nil (⊖) or oxygen (–O–)

*FT*i.r. spectra seem to confirm that the observed decrease in the reduced viscosity of the polymers after a longer duration of the polycondensation reaction is accompanied by partial hydrolysis of the imidazopyrrolone. As we have observed decreasing polymer viscosity in all cases, it seems to be the rule in this type of polymer, and the time of deflection depends on the dianhydride structure. The hydrolysis occurs probably because of the presence of water in the reaction mixture. Although the polycondensation reaction is carried out in an open system which enables azeotrope of m-cresol and water to evaporate, probably some water is still present in the reaction mixture, causing hydrolysis after a longer time of heating. To confirm this, the polymer derived from 4,4′[phenylobenzophenone-di(benzene-5-estro-1,2 dicarboxylic)] anhydride and 3,3′diaminobenzidine was precipitated (after 43 h of

heating) from the reaction mixture with ethanol and dried. Then it was dissolved again in a mixture of m-cresol and water (5/0.25 v/v) and heated for an additional 4 h at 180°C. In the spectrum of the polymer after additional heating in m-cresol with water the absorption band at 1760 cm^{-1}, characteristic for the carbonyl group in imidazopyrrolone rings, was hardly seen.

Even though the presence of bands characteristic for imidazopyrrolone structure can be seen in the polymers after a certain time of reaction in m-cresol solution, it seems that the temperature of 180°C may be not sufficient for the cyclization ratio to occur with 100% yield[4]. To confirm this, the polymer films after evaporation of m-cresol were heated under vacuum at 200°C for 24 h. In all cases a small increase in intensity of absorption bands at 1760 cm^{-1} and 1618 cm^{-1} (characteristic for carbonyl –C(=O)–N= in
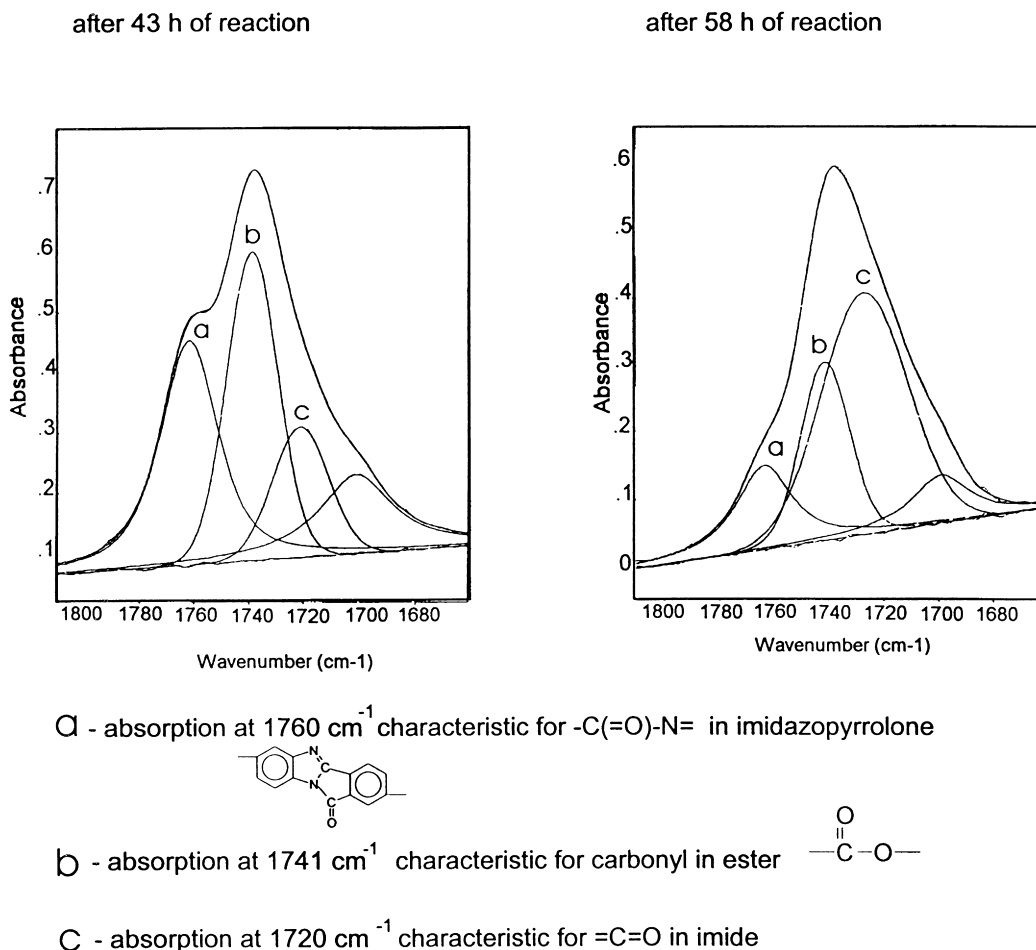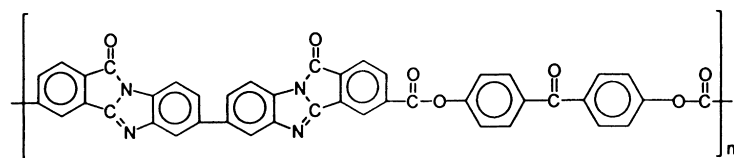
after 43 h of reaction

after 58 h of reaction

a - absorption at 1760 cm^{-1} characteristic for -C(=O)-N= in imidazopyrrolone

b - absorption at 1741 cm^{-1} characteristic for carbonyl in ester

c - absorption at 1720 cm^{-1} characteristic for =C=O in imide

Figure 4 Curve-fitting calculation of the areas of the =C=O group of imidazopyrrolone (1760 cm^{-1}), ester (1740 cm^{-1}) and imide (1720 cm^{-1}) for the polymer derived from 4,4′[phenylobenzophenone-di(benzene-5-estro-1,2-dicarboxylic)] anhydride and 3,3′diaminobenzidine

Table 4 Intensity ratios of absorption bands at 1762 cm^{-1}, characteristic for carbonyl –C(=O)–N= in fused imidazopyrrolone rings, *versus* 1740 cm^{-1}, characteristic for the ester carbonyl group, for the polymer shown below:

Reaction time	η_{red}[a] (dl g^{-1})	$\frac{A_{1760}}{A_{1740}}$
20	0.34	0.956
43	1.24	0.966
58	0.61	0.887

[a]Measured in m-cresol, conc. = 0.5 g/100 ml, temp. = 25°C

fused rings and the =C=N– group) was observed, which confirms the higher cyclization ratio.

Thus, in order to obtain polymers having high reduced viscosity and high cyclization ratio it is necessary to carry out the polycondensation reaction in solution till the time of the deflection point and then heat the film under vacuum at a higher temperature.
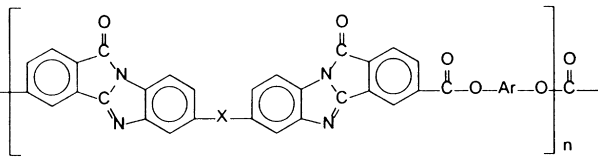
Most of the poly(esterimidazopyrrolone)s obtained can form films having a glittering surface with good adhesion to aluminium and copper plate. Free foils are rather brittle.
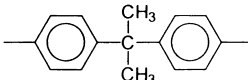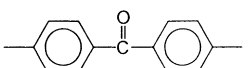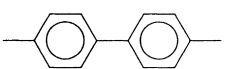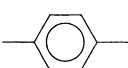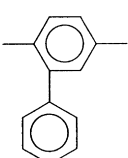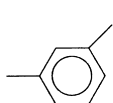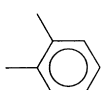
The thermal stability of the polymers (obtained at optimal reaction times) was evaluated by thermogravimetric (TG) analysis under argon. Data for thermal behaviour of the polymers are listed in *Table 5*. The polymers showed a small weight loss below 300°C. The temperature of 10% weight loss depends on the dianhydride structure but the structure of diamines seems to influence it only slightly. The residue at 1000°C for the polymers is in the range of 40–50%.

CONCLUSION

Poly(esterimidazopyrrolone)s derived from diesterdianhydrides and aromatic tetraamines were synthesized using one-step high temperature polycondensation. The structure of the monomers influenced the reduced viscosity of the

Table 5 Thermal properties of the poly(ester-imidazopyrrolone)s presented in *Table 3*

Ar	X = nil TG in argon		X = −O−	
	Temp. of 10% weight loss (°C)	Residue at 1000°C (%)	Temp. of 10% weight loss (°C)	Residue at 1000°C (%)
(isopropylidene diphenyl)	330	51	300	51
(carbonyl diphenyl)	320	42	320	42
(biphenyl)	340	45	340	45
(phenyl)	280	48	280	48
(phenyl with pendant phenyl)	290	42	210	47
(methyl phenyl)	330	41	330	46
(dimethyl phenyl)	380	45	390	42

polymers and also the ability of the imidazopyrrolone structure to form.

The results of our investigations suggest that closure of the imidazopyrrolone ring occurs in most of the polymers studied, and we observed the presence of characteristic bands for this structure after 10 h of the reaction. Extension of the reaction time causes an increase in the polymer reduced viscosity and an increase of the amount of imidazopyrrolone structure, but after a certain time, which depends on the monomer structure, the viscosity starts to lower and the hydrolysis of imidazopyrrolone occurs.

For each pair of the monomers, i.e. diesterdianhydride and tetraamine, there is an optimal reaction time at which the polymer reduced viscosity reaches a maximum value. The reaction time at which the maximum value of the reduced viscosity was reached was, in most cases, shorter for the polymers made from 3,3′,4,′4 tetraaminodiphenyl ether than for the polymers made from 3,3′diaminobenzidine and the proper diesterdianhydrides. Also, the reduced viscosities of the polymers made from the tetraamine with ether linkage and the proper diesterdianhydrides exhibited higher values.

The poly(esterimidazopyrrolone)s obtained form glittering films having good adhesion to aluminium and copper plate.

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