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FT-i.r. study of thermal cyclization processes in synthesis of polyesterimidazopyrrolones

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Abstract

An FT-i.r. method was used to investigate the thermal cyclization process in synthesis of polyesterimidazopyrrolones from diesterdianhydrides and 3,3′-diaminobenzidine. It was proved that the structure of diphenols in the diesterdianhydrides influences the cyclization which goes via an amino-imide to the imidazopyrrolone structure. The presence of an electron-donating group in the diphenol causes the beginning of cyclization at a lower temperature than in the case when in the diesterdianhydride there is a diphenol with electron-withdrawing group. The cyclization process was investigated by dynamic and isothermal heating. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Thermal cyclization; Polyesterimidazopyrrolones; FT-i.r. spectra

1. Introduction

The aim of our investigation was the determination of the progress of thermal cyclization processes which occur during synthesis of polyesterimidazopyrrolones.

The polyesterimidazopyrrolones studied were obtained in the reaction of various diesterdianhydrides with 3,3′-diaminobenzidine. In the first step of the reaction between anhydride group and *o*-diamine the amide–amino acid is formed which can cyclize via an amino–imide to imidazopyrrolone structure. The reaction route and the structure of the polymers studied is presented in Fig. 1.

The influence of the Ar group on the thermal cyclization process was investigated using two methods: dynamic heating in the range from 20 to 245°C and isothermal heating for definite times at 200, 245 and 260°C.

2. Experimental

2.1. Materials

Prepolymers with amide–amino acid structures used for these investigations were obtained as follows: 3,3′-diaminobenzidine (1 mmol) was dissolved in 10 ml dry *N*,*N*-dimethylacetamide (DMA) and the stoichiometric amount of the given diesterdianhydride (1 mmol) was added slowly over a period of 30 min. The mixture was stirred for 1 h at room temperature and the polymers were precipitated with ethanol.

The samples investigated were in the form of films obtained by casting solutions of the polymers in DMA onto potassium bromide windows and evaporating at 50°C for 5 h under vacuum.

2.2. Measurements:

Infrared spectra were acquired on a Bio-Rad FTS-40A Fourier transform infrared spectrometer in the range of 4000–700 cm^{-1} at a resolution of 2 cm^{-1} for an accumulated 64 scans. Spectra recorded at elevated temperatures were obtained using Carl Zeiss Jena high temperature control equipment in the temperature range from 20 to 245°C. The samples were heated under nitrogen at the rate of 20°C/min and kept at elevated temperatures for 10 min before a spectrum was recorded. Additional heating at 260 and 300°C was carried out in a muffle furnace under nitrogen for 1 h at each temperature. Spectra were recorded after cooling to 20°C.

For the isothermal method, samples were heated under vacuum at 200°C for 1, 3, 5, 8, 11, 17 h, then at 245°C for 3 h, and at 260°C for 1 h; FT-i.r. spectra were always recorded after cooling to 20°C.

In order to determine the quantitative relations among the bands which reflected the cyclization process, a WIN-IR curve-fitting program was used in the region of 1850–1550 cm^{-1}. The initial parameters, i.e. number of peaks, centres, heights and widths of particular peaks, were

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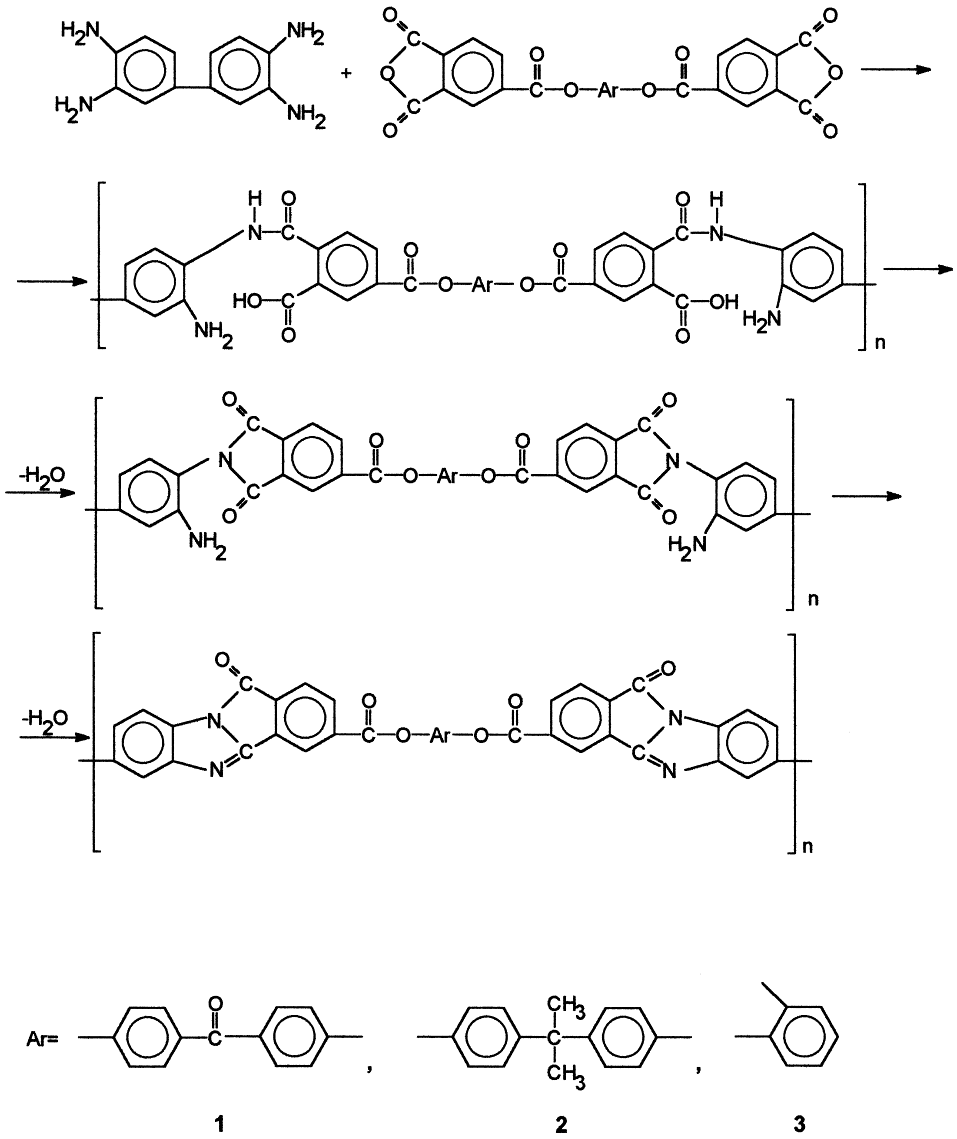

Fig. 1. Scheme of the reaction route and the structure of polymers.

obtained from the second derivative spectra. An interactive procedure and Gaussian–Lorentzian fitting of curves were chosen to correct these parameters and compute particular peaks.

3. Results and discussion

In order to determine the changes which appear during heating, the following regions were carefully studied: 3600–2500 cm^{-1} (the region characteristic for N–H stretching vibrations of NH_2 amine, NH amide and O–H acid groups); 1800–1700 cm^{-1} (the region corresponding to C=O imide, ester, acid groups and C=O groups in fused pyrrole cycle); 1700–1630 cm^{-1} (the region characteristic for the amide I bands (free and bonded C=O amide groups)); 1630–1600 cm^{-1} (the region due to deformation vibrations of NH_2 amine groups, stretching vibrations of C=N groups in fused cycle and stretching vibrations of aromatic ring); and 1550–1500 cm^{-1} (the region characteristic for the amide II bands (free and bonded NH_2 amide groups)) [1–4].

3.1. Absorption band in the region 3600–2500 cm^{-1}

The band at ~ 3450 cm^{-1} observed in the spectra for the all polymers investigated (Fig. 2a) can be ascribed as combination bands of the overtone of C=O ester groups, stretching vibrations of NH_2 amine groups (asymmetrical) and stretching vibrations of NH free amide groups.

The bands at ~ 3350 and 3230 cm^{-1} are due to stretching vibrations of NH_2 amine groups (symmetrical) and NH-bonded amide groups.

The band at ~ 3030 cm^{-1} can be ascribed as the overtone

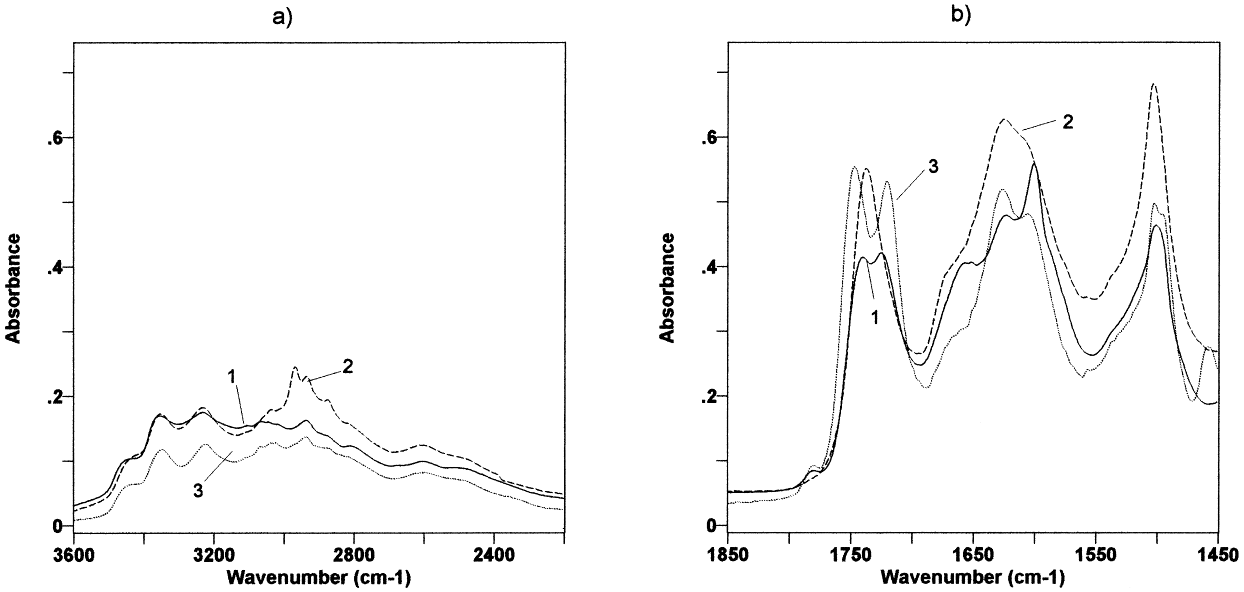

Fig. 2. FTIR spectra of polymers 1, 2 and 3 at 20°C in the region of 3600–2200 cm^{-1} (a) and 1850–1450 cm^{-1} (b).

of C=O amide groups. Several bands in the region of 3000–2500 cm^{-1} correspond to OH-bonded acid group vibrations, whereas the bands in the region of 3100–3000 cm^{-1} correspond to C–H stretching vibrations in aromatic ring. The bands observed in the spectrum of polymer 2 at 2968, 2936 and 2876 cm^{-1} are also due to CH_3 group stretching vibrations.

With regard to the complex character of the overlapping bands in the region of 3600–2500 cm^{-1} (indefinite assignment of bands and unknown influence of hydrogen bonds) curve-fitting calculations and thus quantitative investigations are not possible to make in that region.

3.2. Absorption bands in the region 1800–1700 cm^{-1}

For the all polymers investigated, a high intensity band at ~ 1740 cm^{-1} due to the stretching vibration of C=O ester groups is observed in this region. In spite of the fact that polymers were synthesized using conditions favourable to polyamide–amino acids formation, in their FT-i.r. spectra bands characteristic for imide groups at ~ 1780 and 1721 cm^{-1} are also detected (Fig. 2b). This may be due to heating the foils at 50°C during their preparation.

As seen from curve fitting calculations (Tables 1–3) the areas of bands ascribed to imide groups are different for particular compounds and suggest that the highest amount of imide was formed in the case of polymer 3, whereas only slight amount in polymer 2. It can be explain by the influence of connecting group. Benzophenone and bisphenol A groups exhibiting electron-withdrawing and electron-donating character, respectively, in opposite to the inert catechol group, changes the charge distribution in the ester groups and simultaneously in aromatic ring. This may cause some differences in reactivity of acid and amide groups.

Curve fitting calculations indicate also that the band arising from C=O acid groups is observed at 1709, 1715 and 1713 cm^{-1} for polymers 1, 2 and 3, respectively.

3.3. Absorption bands in the region 1700–1600 cm^{-1}

This region is characteristic for the amide I band. Fig. 2b proves that polyesteramide–amino acids investigated exhibit broad bands with some shoulders in that region.

Curve fitting calculations (Tables 1–3) conclude the presence of a lower area band arising from free C=O amide band at 1679, 1675 and 1675 cm^{-1} and higher area band and 1659, 1653 and 1665 cm^{-1} due to bonded C=O amide group for polymers 1, 2 and 3, respectively.

In the case of polymer 1 the band at 1659 cm^{-1} consists also of C=O ketone groups vibrations.

The bands at 1625, 1628 and 1627 cm^{-1} for polymers 1, 2 and 3, respectively, can be ascribed as characteristic for NH_2 amine groups. With regard of the fact that the band arising from aromatic ring stretching vibrations at ~ 1600 cm^{-1} strongly overlaps the bands due to NH_2 and C=N group vibrations, the values of areas calculated for these bands can be erroneous and should be treated as additional information.

3.4. Absorption bands in the region 1550–1500 cm^{-1}

Bands observed in this region are characteristic for amide II band. As seen in Fig. 2b for all polymers investigated broad bands due to free and bonded NH amide groups overlapped with the bands at ~1500 cm^{-1} arising from aromatic ring are observed.

Table 1
The results of curve fitting in the region of 1850–1550 cm^{-1} for polymer 1 (dynamic heating)

Temp. (°C)	C=O imide asym.		C=O in pyrrole structure		C=O imide sym		C=O acid		C=O free amide		C=O bonded amide + C=O ketone		NH_2		C=N in pyrrole ring	
	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area
20	1782	0.230			1724	4.340	1709	4.015	1679	1.826	1659	9.879	1625	7.120		
50	1782	0.224			1724	4.457	1709	3.384	1678	2.004	1658	9.507	1625	7.278		
80	1782	0.240			1724	4.747	1709	3.903	1678	1.417	1658	8.752	1625	7.310		
100	1781	0.683			1724	6.532	1703	4.127	1677	1.493	1656	7.904	1625	6.955		
120	1781	0.679			1723	7.512	1703	4.218	1677	1.627	1657	6.479	1625	7.441		
140	1781	0.708			1723	10.881	1700	2.305	1677	1.294	1658	5.466	1625	7.761		
160	1781	1.016			1723	10.347	1699	1.671	1680	1.148	1658	5.236	1625	7.812		
180	1781	0.827			1723	11.969					1656	5.488	1623	7.692		
200	1781	0.791			1722	11.605					1656	5.362	1623	5.368		
220	1781	0.725			1722	11.578					1656	5.820	1623	5.021		
245	1780	0.685	1756	0.172	1722	8.772					1658	5.919	1623	3.456	1617	0.515
20 (after cooling)	1780	0.642	1756	0.239	1723	8.899					1658	5.569	1623	3.462	1620	0.596
260	1780	0.613	1756	3.603	1725	7.056					1659	3.276	1624	3.109	1621	1.032
300	1784	0.566	1755	5.433	1724	3.848					1659	3.239	1624	2.847	1622	1.418

Table 2
The results of curve fitting in the region of 1850–1550 cm^{-1} for polymer 2 (dynamic heating)

Temp. (°C)	C=O imide asym.		C=O in pyrrole structure		C=O imide sym.		C=O acid		C=O free amide		C=O bonded amide		NH_2		C=N in pyrrole ring	
	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area
20					1720	0.847	1715	8.548	1675	1.783	1653	9.360	1628	12.190		
50					1720	0.891	1715	8.628	1675	1.548	1652	11.206	1628	12.518		
80					1722	0.924	1715	8.121	1675	2.277	1653	10.346	1628	12.909		
100					1722	1.293	1715	7.370	1675	2.343	1652	6.608	1628	12.347		
120	1782	0.038			1722	2.563	1715	6.556	1676	1.686	1652	5.918	1628	12.022		
140	1780	0.795			1722	15.862							1626	12.148		
160	1780	1.021			1722	15.292							1627	12.005		
180	1780	0.922	1754	0.488	1721	15.944							1625	10.303		
200	1780	1.092	1754	0.708	1721	15.464							1623	9.044		
220	1779	1.263	1754	0.624	1721	13.746							1623	8.275		
245	1779	0.866	1755	1.627	1721	12.410							1623	7.336		
20 (after cooling)	1780	0.753	1760	2.074	1722	12.154							1623	6.200		
260			1760	10.252											1620	7.267

Table 3
The results of curve fitting in the region of 1850–1550 cm^{-1} for polymer 3 (dynamic heating)

Temp. (°C)	C=O imide asym.		C=O in pyrrole structure		C=O imide sym.		C=O acid		C=O free amide		C=O bonded amide		NH_2		C=N in pyrrole ring	
	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area
20	1781	0.283			1721	8.427	1713	5.784	1675	1.851	1665	5.043	1627	6.885		
50	1781	0.318			1721	8.039	1713	5.404	1678	3.012	1665	2.333	1629	6.621		
80	1780	0.374			1721	8.028	1710	4.933	1678	3.482	1665	2.312	1629	6.834		
100	1780	0.470			1721	7.974	1713	3.645	1678	4.373	1665	2.020	1628	6.012		
120	1780	0.705			1721	10.075	1709	1.052	1670	2.929			1627	6.613		
140	1780	0.867			1721	10.457							1627	6.408		
160	1780	0.515	1754	2.047	1722	8.937							1627	4.777		
180	1780	0.435	1754	5.033	1727	7.416							1628	2.215	1617	0.400
200	1780	0.403	1754	9.068	1728	4.331									1617	2.378
220	1780	0.417	1754	10.213	1721	2.999									1616	1.963
245	1780	0.411	1754	12.018	1721	2.656									1615	2.349
20 (after cooling)	1780	0.285	1754	12.900	1721	2.265									1619	2.502
260			1755	13.495											1620	4.903

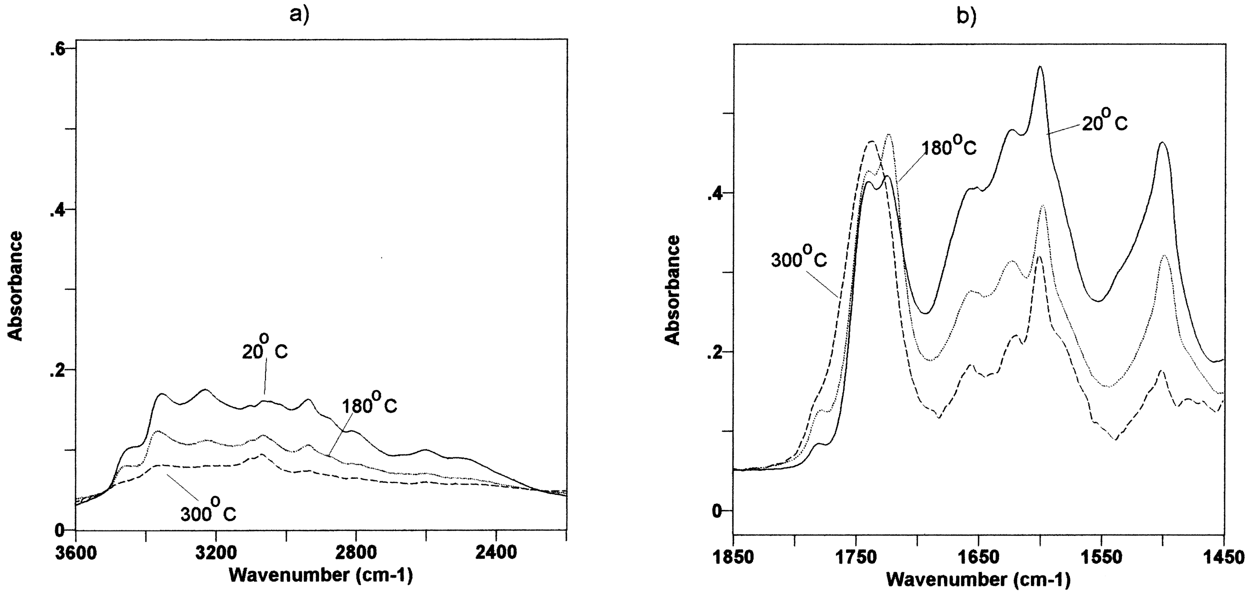

Fig. 3. FTIR spectra of polymer 1 at 20 (—), 180 (· · ·) and 300°C (- - -) in the region of 3600–2200 cm^{-1} (a) and 1850–1450 cm^{-1} (b).

4. Thermal investigations

4.1. Dynamic heating

In order to determine the progress of thermal cyclization process running during dynamic heating, samples were heated and FT-i.r. spectra at 20, 50, 80, 100, 120, 140, 160, 180, 200, 220 and 245°C, and after cooling were recorded.

At the first stage of the dehydration reaction the formation of a polyester–amino–imide took place, which is reflected in the FT-i.r. spectra by decreasing in the intensities of the bands characteristic for acid and amide groups and a simultaneous increasing in the intensities of bands corresponding to imide groups.

The second stage of cyclization process causes formation of a polyesterimidazo–pyrrolone structure. This is associated with a decrease in the intensities of bands arising from imide groups and NH_2 amine groups. The process should proceed with the simultaneous appearance of new bands due to C=O and C=N group vibrations in the fused cycle at about 1755 and 1620 cm^{-1}, respectively.

4.1.1. Polymer 1

From FT-i.r. spectra (Fig. 3a,b) and curve-fitting

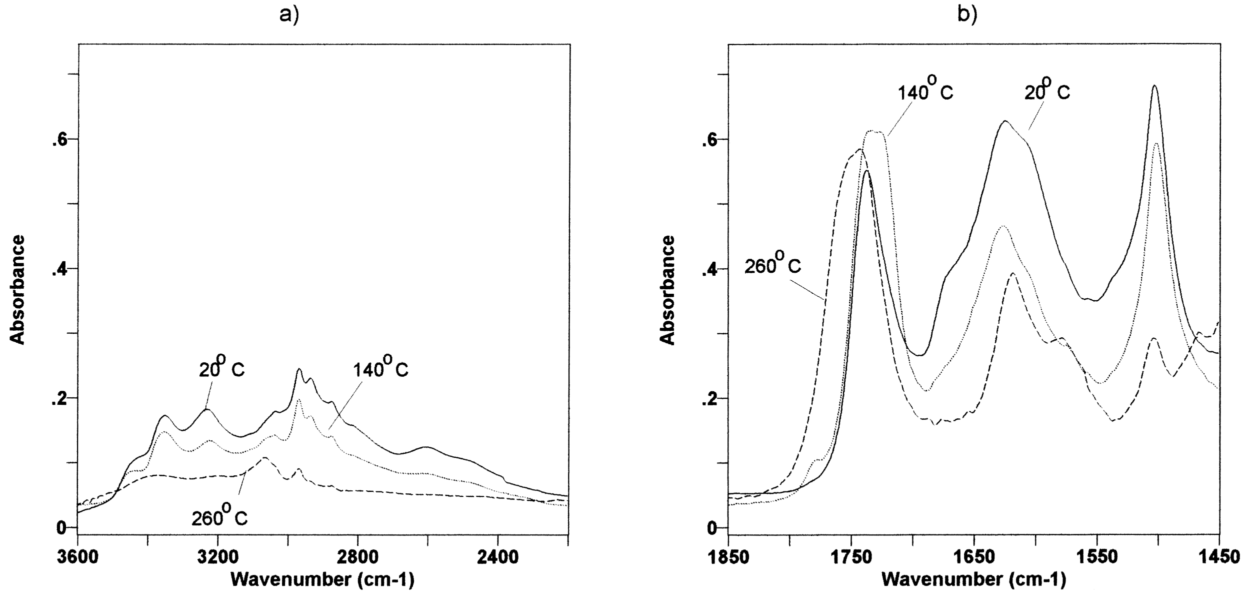

Fig. 4. FTIR spectra of polymer 2 at 20 (—), 140 (· · ·) and 260°C (- - -) in the region of 3600–2200 cm^{-1} (a) and 1850–1450 cm^{-1} (b).

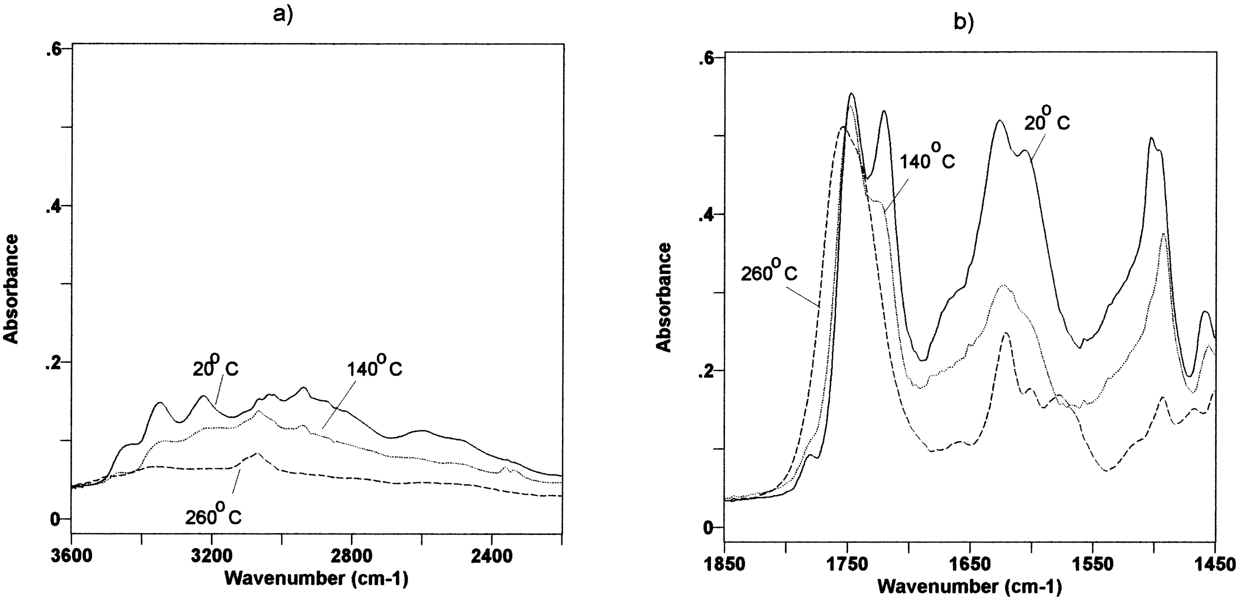

Fig. 5. FTIR spectra of polymer 3 at 20 (—), 140 (· · ·) and 260°C (- - -) in the region of 3600–2200 cm^{-1} (a) and 1850–1450 cm^{-1} (b).

calculations (Table 1) indicates that some amount of imide formed during the foil preparation is present at 20°C. During heating to 180°C continuous increase in the bands areas due to C=O imide groups (1782 and 1724 cm^{-1}) is observed. Simultaneously, the areas of bands arising from C=O acid and C=O amide groups (1711, 1679 and 1659 cm^{-1}) are systematically decreasing. At 180°C only bands characteristic for imide are observed. It is confirmed by the region of 3000–2400 cm^{-1}. FT-i.r. spectrum (Fig. 3a) indicates that at 180°C bands arising from OH acid and NH amide groups disappear. Further heating to 220°C does not give any marked changes. The bands corresponding to C=O and C=N groups in fused cycle at 1756 and 1617 cm^{-1}, respectively, appear at 245°C. Simultaneously, the decrease in areas of bands characteristic for imide groups and NH_2 amine groups follows systematically. After cooling to 20°C, only slight shifts and changes in areas in relation to the spectrum recorded at 245°C are observed.

Further heating was led under nitrogen in a muffle furnace at 260 and then at 300°C. FT-i.r. spectra were recorded after cooling the samples to 20°C. Curve fitting calculations obtained from the spectrum acquired after cooling from 260°C exhibit certain increase in areas of bands due to C=O and C=N groups in fused cycle. The next changes are noticed after heating the samples at 300°C, but even at this case low area bands arising from imide groups are still observed. Longer heating at 300°C (for 2 h) caused the beginning of the polymer degradation.

Thus it confirms that the polyester–amino–imide with benzophenone connecting group undergoes thermal cyclization at 300°C. However, heating longer then 1 h at this temperature causes a beginning of degradation.

4.1.2. Polymer 2

In comparison to the other polymers only slight amount of imide groups formed during drying of the film is present in the polymer 2 (Table 2). Changes caused by temperature increase to 120°C follow slowly. At 120°C still relatively high areas of bands ascribed to C=O acid and C=O amide groups are observed. Curve fitting calculations and FT-i.r. spectra (Fig. 4a,b) indicate that at 140°C only the bands corresponding to imide and amine groups are observed. During heating from 180 to 245°C only slight decreases in areas of bands due to imide groups (1780 and 1721 cm^{-1}) and NH_2 amine groups (1623 cm^{-1}) are observed. Simultaneously low area band at 1754 cm^{-1} appears. The spectrum obtained after cooling to 20°C is similar to that acquired at 245°C. Remarkable changes in the spectrum follow at 260°C. FT-i.r. spectrum and curve fitting calculations exhibit that at this temperature only the bands arising from C=O (1760 cm^{-1}) and C=N (1620 cm^{-1}) groups in the fused cycle are present.

It may be concluded that in polyesteramide–amino acid with a bisphenol A connecting group, imidization process starts at 140°C, whereas the cyclization to the imidazopyrrolone structure takes place at 260°C.

4.1.3. Polymer 3

As described above, polymer 3 contains the highest amount of imide groups formed during drying of the film in comparison to the other polymers. As indicates from FT-i.r. spectra (Fig. 5a,b) and curve fitting calculations (Table 3) changes in areas of bands follow continuously during heating to 140°C. The areas of bands characteristic for C=O acid (1713 cm^{-1}) and C=O amide groups (1675,

Table 4
The results of curve fitting in the region of 1850–1550 cm^{-1} for polymer 1 (isothermal heating)

Time (h)	C=O imide asym.		C=O in pyrrole structure		C=O imide sym.		C=O acid		C=O free amide		C=O bonded amide + C=O ketone		NH_2		C=N in pyrrole ring	
	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area
200°C																
0	1781	0.292			1723	5.023	1710	3.417	1676	2.143	1657	7.307	1623	5.814		
1	1784	0.585	1758	1.069	1723	11.683					1659	4.719	1623	3.854		
3	1783	1.267	1758	2.863	1723	11.442					1659	4.495	1622	3.415		
5	1783	1.064	1757	2.733	1723	10.653					1669	4.082	1622	2.987		
8	1783	0.959	1758	3.108	1724	11.033					1659	3.440	1624	3.152	1622	0.904
11	1784	0.735	1759	3.165	1724	10.497					1659	2.764	1624	1.830	1622	1.668
17	1785	0.486	1758	3.270	1725	10.469					1658	2.252	1624	1.030	1621	2.313
245°C																
3	1784	0.498	1758	4.808	1725	8.055					1658	2.392	1625	0.643	1620	2.538
260°C																
1	1784	0.198	1759	8.399	1724	2.101					1658	2.384			1622	4.298

Table 5
The results of curve fitting in the region of 1850–1550 cm^{-1} for polymer 2 (isothermal heating)

Time (h)	C=O imide asym.		C=O in pyrrole structure		C=O imide sym.		C=O acid		C=O free amide		C=O bonded amide		NH_2		C=N in pyrrole ring	
	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area
200°C																
0					1722	1.427	1708	8.344	1672	1.828	1655	7.591	1628	13.545		
1	1782	0.772	1758	1.831	1722	14.272							1627	7.873		
3	1783	0.839	1758	2.798	1722	13.554							1627	6.714		
5	1783	0.904	1758	2.810	1722	12.845							1627	5.790		
8	1783	0.908	1760	3.286	1722	12.573							1625	5.747		
11	1784	0.755	1760	4.935	1722	11.969							1625	5.226		
17	1784	0.296	1763	5.869	1722	5.476									1621	4.818
245°C																
3			1760	6.625	1722	4.389									1621	4.400
260°C																
1			1760	8.302	1723	0.840									1621	4.472

Table 6
The results of curve fitting in the region of 1850–1550 cm^{-1} for polymer 3 (isothermal heating)

Time (h)	C=O imide asym.		C=O in pyrrole structure		C=O imide sym.		C=O acid		C=O free amide		C=O bonded amide		NH_2		C=N in pyrrole ring	
	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area	ν (cm^{-1})	Area
200°C																
0	1782	0.789			1723	10.071	1712	4.912	1674	1.259	1657	4.019	1627	10.312		
1	1782	0.580	1754	2.058	1722	13.561							1624	8.067		
3	1782	0.708	1758	3.158	1723	12.263							1625	5.415		
5	1783	0.673	1756	3.236	1723	12.265							1625	5.398		
8	1783	0.638	1757	3.277	1723	12.008							1625	5.285		
11	1783	0.645	1757	3.429	1723	11.578							1624	4.643		
17	1783	0.745	1756	3.538	1724	10.086							1625	3.369		
245°C																
3	1783	0.849	1756	6.505	1725	4.633							1625	2.650	1620	0.778
260°C																
1	1783	0.301	1758	8.155	1725	1.677									1620	4.259

1665 cm^{-1}) are decreasing, whereas the areas of bands due to imide groups (1781, 1721 cm^{-1}) are increasing. At 140°C only bands ascribed to imide groups are detected. Also FT-i.r. spectrum obtained at 140°C in the region of 3500–2500 cm^{-1} does not exhibit the bands corresponding to OH acid and NH amide groups (Fig. 5a). In the case of polymer 3 the bands arising from C=O (1754 cm^{-1}) and C=N (1617 cm^{-1}) groups in fused cycle appear already at 160 and at 245°C only slight areas of the bands characteristic for imide are present. FT-i.r. spectrum obtained after heating to 260°C and curve fitting calculations indicate that at 260°C only bands corresponding to C=O and C=N groups in fused cycle are observed. The bands due to imide groups (1780, 1721 cm^{-1}) and NH_2 amine groups (3500–3100 and 1627 cm^{-1}) disappear.

The above results prove that polyester–amino-imide with catechol connecting group is formed at 140°C and cyclization to imidazopyrrolone structure proceeds continuously from 160 to 260°C.

4.2. Isothermal heating

In the case of isothermal heating the samples were heated under vacuum at 200°C at first for 1 h, and after cooling to 20°C FT-i.r. spectrum was recorded. Heating in these conditions were repeated for the definite times and every time spectra were recorded after cooling to 20°C. In the Tables 4–6 the total times of heating at 200°C are given.

As seen from the Tables 4–6 for the all polymers, already after heating at 200°C for 1 h low area bands corresponding to imidazopyrrolone structure appears. However, further heating even for 17 h causes only small increase in areas of the bands due to polyimidazopyrrolone structure with simultaneous decrease in the areas of bands ascribed to C=O imide and NH_2 amine groups. More changes can be observed after the following heating at 245°C for 3 h and then at 260°C for 1 h.

Comparing the results of curve-fitting calculations obtained for polymer 1 during the dynamic and isothermal heating (Tables 1 and 4) can be noticed that on the contrary to isothermal heating the bands due to polyimidazopyrrolone structure are not detected to 220°C during dynamic heating. Consequently, bigger areas of bands characteristic for C=O and C=N groups in imidazopyrrolone can be seen after heating at 260°C in the case of isothermal heating.

In the case of polymer 2 during isothermal heating (Table 5) a slight amounts of imide groups are detected even after heating at 260°C on the contrary to dynamic heating when after heating to 260°C (Table 2) the total cyclization is observed.

Similar differences can be seen for polymer 3 but during dynamic heating considerably more polyimidazopyrrolone groups at 200, 245 and 260°C are formed than in the case of isothermal heating (Tables 3 and 6).

The observed changes between dynamic and isothermal heating can be explained by different conditions of the heating processes: in the case of dynamic heating cyclization runs from 20 to 245°C under nitrogen without cooling for recording the spectra while during isothermal heating cyclization proceeds under vacuum and samples were cooled before recording the spectra. On the other hand during dynamic heating the polymers were kept at the elevated temperature during 10 min.

5. Conclusions

It was demonstrated that the progress of thermal imidization and cyclization to imidazopyrrolone rings depends on the structures of diphenols in ester-connecting groups in diesteranhydrides used for polycondensation with 3,3′-diaminobenzidine.

In the case of polymers with a catechol group in the middle of diesteranhydride imidization takes place continuously with temperature increase up to 140°C. Cyclization process to imidazopyrrolone structure begins already from 160°C, and at 245°C almost complete cyclization is observed. During isothermal heating a smaller degree of cyclization is observed.

The presence of a bisphenol A group having an electron-donating character causes imidization to proceed mostly at 120°C, and likewise, as above, polymer ends at 140°C. On the contrary, the cyclization to imidazopyrrolone takes place mainly at 260°C. More imidazopyrrolone groups were formed during isothermal heating at 200 and 245°C.

The benzophenone group exhibiting electron-withdrawing character causes the increase in imidization temperature to 160°C. The cyclization to imidazopyrrolone structure is not completed even at 300°C. Better cyclization is observed in the case of isothermal heating.

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