FTIR study of thermal cyclization processes in the synthesis of polyetherimidazopyrrolones

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Abstract

An FTIR method was used to investigate the thermal cyclization process in synthesis of polyetherimidazopyrrolones from dietherdianhydrides and 3,3′-diaminobenzidine. It was concluded that the highest degree of cyclization to imidazopyrrolone structure is observed in the case of polymer with bisphenol A group having electron-donating character after dynamic heating, though for the all polyether-imides investigated even at 320°C cyclization are not complete. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Thermal cyclization; Polyetherimidazopyrrolones; FTIR spectra

1. Introduction

In our previous article [1] the results of thermal cyclization processes occurring in synthesis of polyesterimidazopyrrolones were presented. It was proved that the structure of diphenols in the diesterdianhydrides influences the cyclization which goes via an amino-imide to 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.

This article describes the results of similar investigations that led to polyetherimidazopyrrolones.

Likewise as previously, the polyetherimidazopyrrolones studied were obtained in the reaction of 3,3′-diaminobenzidine with dietherdianhydrides exhibiting the same connecting groups as in the case of polyesterimidazopyrrolones. In the first step of the reaction between anhydride group and *o*-diamine the amide-aminoacid 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.

In order to determine the influence of the Ar group on the thermal cyclization process the infrared spectroscopy was used and the changes in spectra which proceed during dynamic heating in the range from 20 to 245°C and

isothermal heating for definite times at 200, 260 and at 300°C were investigated.

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 dietherdianhydride (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 FTIR spectrometer in the range of 4000–700 cm^{-1} at a resolution of 2 cm^{-1} and 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^{-1} and kept at elevated temperatures for 10 min before a spectrum was
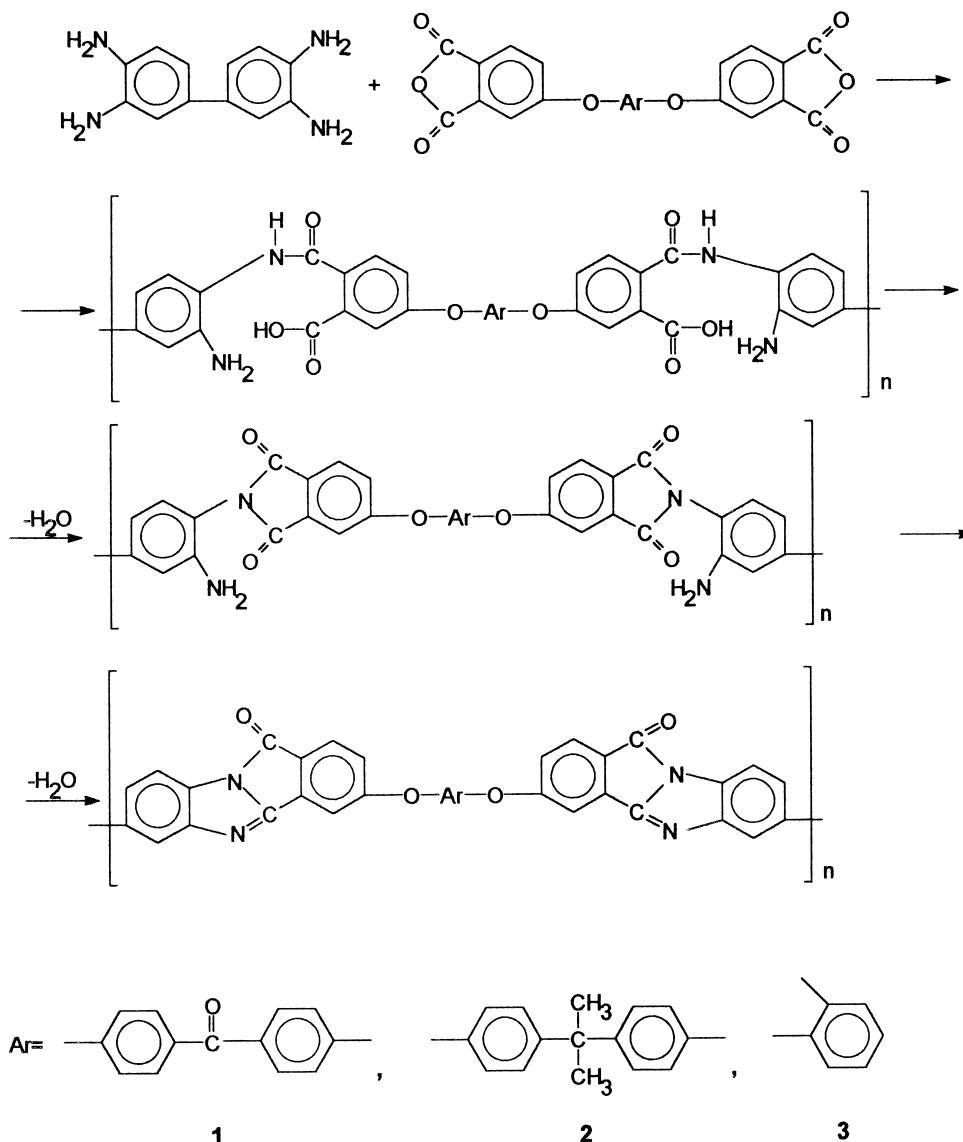

Fig. 1. Scheme of the reaction route and the structure of polymers.

recorded. Additional heating at 260, 300 and 320°C was carried out in a BÜCHI TO-51 furnace under vacuum for 1 h at each temperature and 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 260, 300 and at 320°C for 1 h, FTIR 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. the number of peaks, the center, the height and the width of particular peaks, were 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. The accuracy of band area measurements is about 1%. But in the case of the small areas the error may be higher. Therefore, we take into consideration in our discussion only the band areas which change up to one decimal place.

3. Results and discussion

Progress of the thermal cyclization process was studied using infrared spectra in the following regions: 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
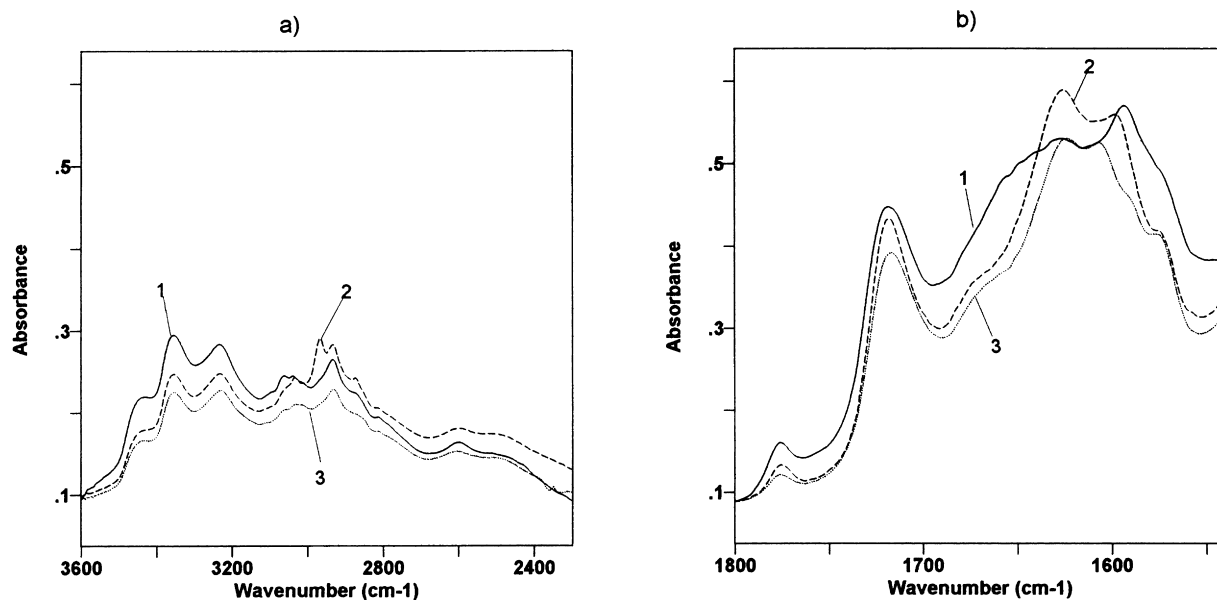
a)

b)

Fig. 2. FTIR spectra of polymer 1, 2, 3 at 20°C in the region 3600–2300 cm^{-1} (a) and 1800–1540 cm^{-1} (b).

imide, 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) and 1630–1600 cm^{-1}—the region due to deformation vibrations of NH$_2$ amine groups and stretching vibrations of C=N groups in fused cycle and vibrations of aromatic ring [1–5].

Absorption band in the region 3600–2500 cm^{-1}: For all the polymers investigated the bands characteristic for the free and bonded NH amide groups are detected at 3400 cm^{-1} and 3356 cm^{-1}, respectively [Fig. 2(a)]. These bands are overlapped by those arising from asymmetrical and symmetrical stretching vibrations of NH$_2$ amine groups, respectively.

The band at 3065 cm^{-1} can be ascribed as the overtone of C=O amide groups. The bands corresponding to OH-bonded acid group vibrations appear in the spectrum as several shoulders in the region of 3000–2400 cm^{-1}. In the case of polymer 2 additional band observed at 2968 cm^{-1} ascribed to CH$_3$ group stretching vibrations is detected.

The areas of overlapping bands in that region were not calculated with regard to very complicated character of the recorded spectra, e.g. unknown influence of hydrogen bonds.

Absorption bands in the region 1800–1700 cm^{-1}: As seen from the spectra [Fig. 2(b)] and curve-fitting calculations (Tables 1–3) the band arising from C=O acid groups is observed at 1712, 1714 and 1713 cm^{-1} for polymers 1, 2 and 3, respectively. Likewise as for the previously reported polyesterimidazopyrrolones [1] apart from these bands, the bands at ∼1777 and ∼1724 cm^{-1} characteristic for asymmetrical and symmetrical C=O imide group vibrations, respectively, are also detected. It can be explained by the

fact that during the preparation of polyamide-aminoacid foils were heated at 50°C for 5 h and some amount of acid and amide groups have reacted.

The results of curve-fitting calculations exhibit that 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 1 whereas considerably less amount in polymers 2 and 3.

Absorption bands in the region 1700–1600 cm^{-1}: The spectra [Fig. 2(b)] indicate that polyetheramide-aminoacids investigated exhibit broad band with some shoulders in that region corresponding to bonded and free C=O amide groups (the amide I band).

Curve-fitting calculations (Tables 1–3) reveal the presence of a band assigned to free C=O amide band at 1677, 1671 and 1675 cm^{-1} for polymers 1, 2 and 3, respectively, a higher area band at 1650 cm^{-1} for polymers 1 and 2 and at 1654 cm^{-1} for polymer 3 due to bonded C=O amide group.

In comparison to the polymer 2 the areas of bands ascribed to bonded C=O amide groups are relatively high for other polymers.

Area of the band at 1650 cm^{-1} in the case of polymer 1 are higher in relation to the other polymers with regard to the presence of C=O ketone groups having the same group frequency.

The band characteristic of NH$_2$ amine groups can be observed at 1625, 1629 and 1623 cm^{-1} for the polymer 1, 2 and 3, respectively. Nevertheless the band arising from aromatic ring stretching vibrations at ∼1600 cm^{-1} strongly overlaps the bands due to NH$_2$ and C=N groups vibrations, therefore the values of areas calculated for these bands can

Table 1
The results of curve fitting in the region 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	1777	0.937			1724	3.070	1712	5.584	1677	5.069	1650	12.235	1625	10.911		
50	1777	0.772			1724	2.817	1713	6.693	1677	5.814	1655	12.173	1626	10.446		
80	1777	0.859			1724	3.410	1713	6.984	1680	5.257	1654	10.889	1624	9.707		
100	1776	0.838			1724	2.913	1713	7.888	1680	6.034	1653	9.433	1625	9.176		
120	1776	1.230			1724	3.030	1713	8.984	1679	6.591	1654	9.428	1625	9.876		
140	1776	1.942	1755	0.119	1724	5.080	1713	4.667	1685	5.835	1654	8.677	1624	9.670		
160	1776	2.435	1758	0.672	1720	15.443					1653	8.273	1622	10.900		
180	1776	2.670	1758	1.486	1720	16.931					1655	8.405	1623	10.928		
200	1776	2.646	1758	2.198	1721	16.921					1656	8.978	1622	10.831		
220	1777	2.595	1758	3.258	1721	16.326					1656	8.251	1621	10.953		
245	1778	2.365	1758	4.736	1722	15.217					1656	7.961	1620	10.722		
20 after cooling	1780	2.692	1758	5.644	1724	14.206					1657	5.076	1623	7.234		
260	1782	2.430	1760	7.857	1727	11.774					1658	5.328	1628	5.498	1619	1.980
300	1776	1.347	1760	8.018	1727	11.523					1659	5.042	1631	2.592	1620	1.393
320	1777	1.252	1760	8.052	1730	11.619					1659	5.141	1631	2.601	1620	1.372

Table 2
The results of curve fitting in the region 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	1776	0.392			1722	1.953	1714	6.921	1671	0.601	1650	7.542	1629	13.012		
50	1776	0.423			1722	1.883	1715	6.838	1671	1.742	1650	7.397	1629	13.462		
80	1777	0.420			1722	2.358	1714	6.795	1679	2.241	1656	6.899	1627	13.795		
100	1776	0.427			1721	2.717	1714	6.364	1677	4.255	1653	3.506	1627	13.252		
120	1776	0.589			1721	4.318	1714	5.515	1676	4.570	1651	1.882	1627	14.628		
140	1776	0.929			1722	4.685	1715	4.711	1675	4.271	1652	1.327	1625	9.975		
160	1776	1.752			1721	6.305	1715	2.624	1675	2.871	1652	1.039	1624	10.353		
180	1775	2.177	1757	0.611	1720	15.205							1625	10.091		
200	1775	2.598	1757	0.775	1720	16.800							1625	10.073		
220	1775	1.574	1757	0.962	1720	16.079							1625	10.022		
245	1775	1.341	1758	1.825	1720	14.814							1623	9.891		
20 after cooling	1773	1.456	1759	2.285	1722	14.906							1623	9.610		
260	1781	0.753	1760	5.654	1726	10.886							1628	2.664	1620	1.656
300	1782	0.643	1760	6.424	1729	8.649							1629	2.062	1619	3.042
320	1781	0.678	1760	6.325	1730	8.023							1628	2.176	1618	2.983

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	1777	0.289			1722	1.629	1713	6.228	1675	2.398	1654	8.720	1623	13.366		
50	1777	0.278			1722	1.577	1714	6.518	1676	2.211	1654	8.565	1623	13.313		
80	1777	0.279			1721	1.749	1713	6.700	1678	1.757	1655	8.273	1623	13.975		
100	1776	0.291			1721	1.740	1713	6.722	1678	1.726	1655	7.787	1623	13.940		
120	1776	0.434			1721	2.671	1714	5.070	1679	2.294	1655	4.539	1623	11.970		
140	1776	1.108			1721	4.226	1711	8.667	1671	5.175	1653	1.217	1623	13.362		
160	1776	1.302	1757	0.373	1721	14.988							1622	13.401		
180	1775	1.347	1757	0.589	1719	14.923							1620	13.266		
200	1775	1.412	1756	0.970	1719	15.014							1619	12.773		
220	1775	1.383	1757	2.045	1719	14.581							1618	12.427		
245	1776	0.975	1759	3.039	1720	12.622							1617	9.993		
20 after cooling	1779	1.104	1760	4.379	1722	11.715							1625	8.011		
260	1780	0.667	1760	5.992	1725	10.921							1626	4.467	1617	2.544
300	1782	0.596	1760	8.383	1729	8.383							1633	1.547	1620	3.721
320	1782	0.568	1761	5.942	1730	8.556							1634	1.279	1620	4.076

be erroneous and should be treated as additional information.

4. Thermal investigations

4.1. Dynamic heating

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

At the first stage of the dehydration reaction the formation of polyether-amino-imide took place, which is reflected in the FTIR spectra by the decrease in the intensities of the bands characteristic for acid and amide groups and a simultaneous increase in the intensities of the bands corresponding to the imide groups.

The second stage of cyclization process causes the formation of a polyetherimidazopyrrolone structure. This is associated with a decrease in the intensities of bands arising from imide groups and NH$_2$ amine groups in FTIR spectrum. 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.

Polymer 1: As mentioned earlier, some amount of imide formed during the foil preparation is present at 20°C. FTIR spectra [Fig. 3(a) and (b)] and curve-fitting calculations (Table 1) indicate that during heating to 120°C no marked changes in areas of the bands ascribed to imide and also acid groups can be detected. Some small changes appearing in areas of the amide I bands follow as an effect of breaking hydrogen bonds formed in amide groups. Increase in areas of bands due to C=O imide groups (1777 and 1724 cm^{-1}) is observed at 140°C but distinguished changes can be seen at 160°C. Simultaneously the areas of bands arising from C=O acid and C=O amide groups (1711, 1679 and 1659 cm^{-1}) are systematically decreasing and at 160°C they are not observed.

This is confirmed from the features in the region 3000–2400 cm^{-1}. FTIR spectrum [Fig. 3(a)] indicates that at 160°C bands arising from OH acid and NH amide groups disappear.

However the bands assigned to C=O groups in fused cycle at 1756 cm^{-1} can be observed previously at 140°C but the further increase in area of this band until 245°C is very small. Little decrease in areas of bands characteristic for imide groups starts from 200°C. Simultaneously till 245°C the changes in areas of band arising from NH$_2$ groups are only slightly visible. After cooling to 20°C, small shifts and changes in areas in relation to the spectrum recorded at 245°C are observed.

Further heating was led in the furnace under vacuum at 260, 300 and then at 320°C. FTIR spectra were recorded after cooling the samples to 20°C.
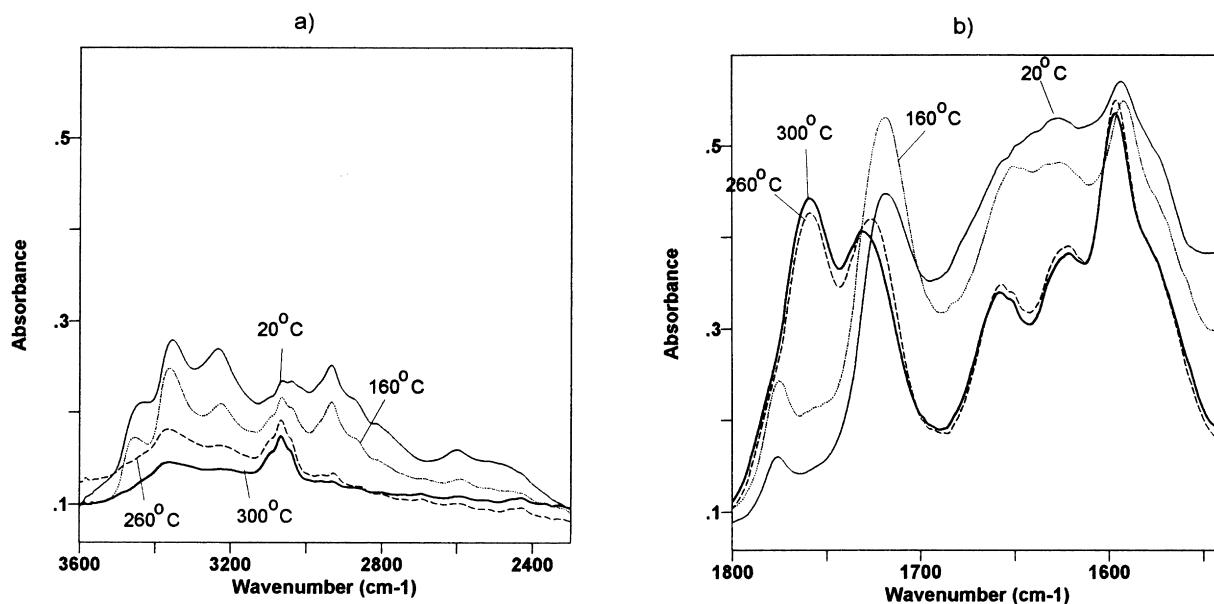
Fig. 3. FTIR spectra of polymer 1 at 20 (—), 160 (······), 260 (---) and 300°C (—) in the region 3600–2300 cm^{-1} (a) and 1800–1540 cm^{-1} (b).

As seen from curve-fitting calculations obtained from the spectrum acquired after cooling from 260°C a relatively high increase in area of the band due to C=O in fused cycle takes place at this temperature. Simultaneously, the band due to C=N groups is detected. The changes noticed after heating the samples at 300°C are rather small and even in this case bands arising from imide groups are still observed. Further heating at 320°C does not make any marked changes.

These results confirm that the polyether-amino-imide with benzophenone connecting group forms at 160°C and undergoes thermal cyclization mainly at 260°C. However, relatively big amount of imide and amine groups remains unreacted, even after heating at 320°C.

Polymer 2: In polymer 2 lesser amount of imide groups formed during drying of the film is present (Table 2) in comparison to polymer 1. Continuous but rather low changes caused by temperature increase follow slowly until 160°C. At 160°C the bands ascribed to C=O acid and C=O amide groups are still observed. Curve-fitting calculations and FTIR spectra [Fig. 4(a) and (b)] indicate that the highest increase in areas of bands corresponding to C=O imide groups (1776 and 1722 cm^{-1}) is observed at 180°C. However, at this temperature small band at 1757 cm^{-1} due to C=O groups in the fused cycle is also present. During further heating from 180 to 245°C only slight decreases in areas of bands due to C=O imide groups and NH$_2$ amine groups (1629 cm^{-1}) are observed with simultaneous small increase in area of the band at 1757 cm^{-1}. The spectrum obtained after cooling to 20°C is similar to that acquired at 245°C. More remarkable changes in the spectrum follow at 260°C but further heating

at 300°C does not give any marked changes. FTIR spectrum and curve-fitting calculations exhibit that even at 320°C, bands arising from imide groups are still detected.

Thus it proves that in polyetheramide-aminoacid with a bisphenol A connecting group, imidization process runs mainly at 180°C whereas the cyclization to the imidazopyrrolone structure takes place at 260°C.

Polymer 3: Polymer 3 contains the smallest amount of imide groups formed during drying of the film in comparison to the other polymers. FTIR spectra [Fig. 5(a) and (b)] and curve-fitting calculations (Table 3) exhibit that during heating to 140°C the changes in areas of bands follow slowly. Remarkable increase in areas of bands due to imide groups (1777, 1722 cm^{-1}) occurs at 160°C and at this temperature the bands ascribed to C=O acid and amide groups are not detected. Also FTIR spectrum obtained at 160°C in the region of 3500–2500 cm^{-1} does not exhibit the bands assigned to OH acid and NH amide groups [Fig. 5(a)]. The small area band at 1757 cm^{-1} arising from C=O groups in the fused cycle appears at 180°C but more visible increase in area of this band begins from 245°C and follows continuously to 300°C. The bands corresponding to C=N groups in pyrrolone cycle (1617 cm^{-1}) are detected at 260°C.

It may be concluded that polyether-amino-imide with a catechol connecting group is formed at 160°C and the cyclization to imidazopyrrolone structure proceeds continuously from 180°C.

For all the polymers investigated, a shift of the band ascribed to C=O imide group symmetrical vibrations is observed from 1722 to 1730 cm^{-1}. This can be probably caused by changes in the ordering of polymers after heating.

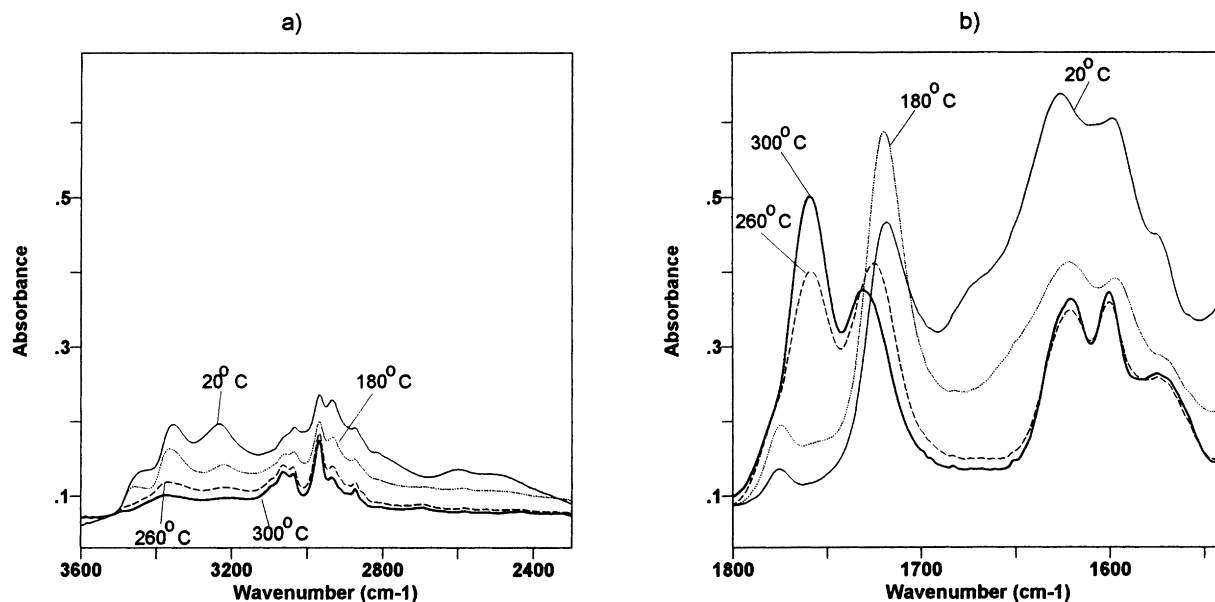Fig. 4. FTIR spectra of polymer 2 at 20 (—), 180 (······), 260 (---) and 300°C (—) in the region 3600–2300 cm^{-1} (a) and 1800–1540 cm^{-1} (b).

4.2. Isothermal heating

During isothermal heating the samples were heated under vacuum at 200°C at first for 1 h and after cooling to 20°C FTIR spectrum was recorded. After this samples were heated at 200°C for definite time periods and then heated at 260 and 300°C. The total time for heating at 200°C and the results of curve-fitting calculations obtained for the spectra acquired during isothermal heating are shown in the Tables 4–6. Each time the spectra were recorded after cooling to 20°C.

Table 7 exhibits the ratio of the areas of bands due to C=O groups in the pyrrolone structure to the areas of bands ascribed to C=O imide group symmetrical vibrations.

For polymer 1, as for the other polymers investigated already, after heating at 200°C for 1 h low area bands corresponding to imidazopyrrolone structure can be detected (Tables 4–6). Further heating at 200°C even for 17 h, at 260°C and then at 300°C for 1 h causes a continuous increase in areas of the bands corresponding to polyimidazopyrrolone structure and consequently a simultaneous decrease in areas of bands ascribed to C=O imide and NH$_2$ amine groups. Comparing the results of curve-fitting calculations obtained for polymer 1 during the dynamic and isothermal heating (Tables 1, 4 and 7) can be noticed that
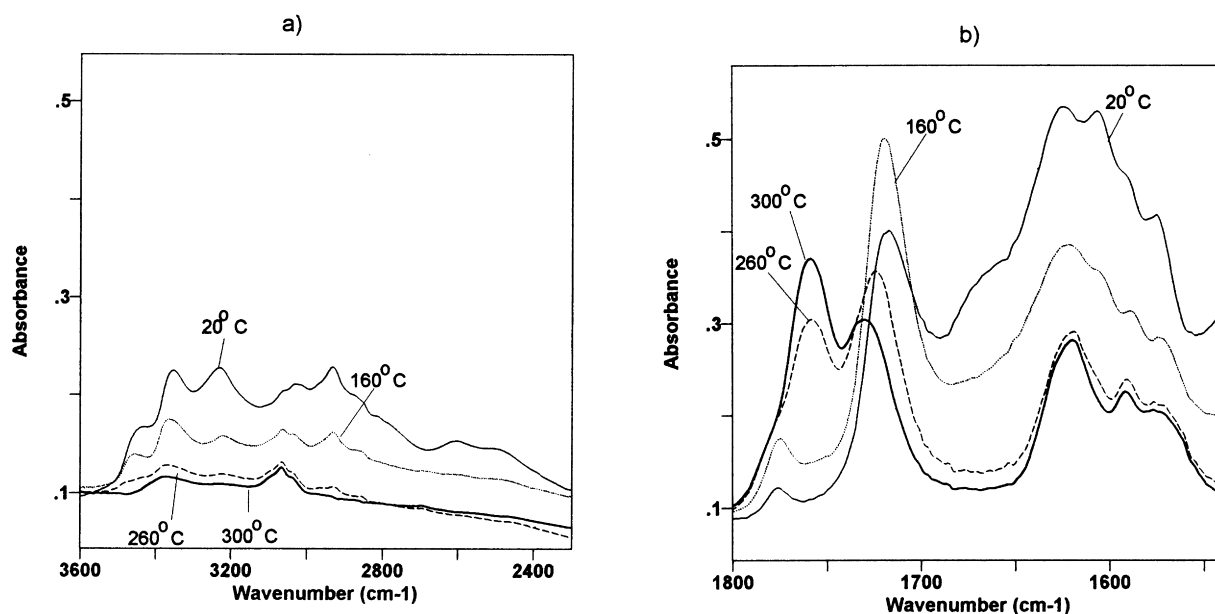

Fig. 5. FTIR spectra of polymer 3 at 20 (—), 160 (······), 260 (---) and 300°C (—) in the region 3600–2300 cm^{-1} (a) and 1800–1540 cm^{-1} (b).

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		NH₂		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	1777	0.576			1723	4.427	1713	5.269	1677	5.818	1653	12.230	1626	9.896		
1	1778	2.491	1759	1.586	1722	13.111					1656	8.170	1626	9.295		
3	1778	2.163	1759	2.388	1722	12.334					1657	7.417	1625	7.809		
5	1779	2.181	1760	3.430	1723	10.699					1658	6.909	1625	6.295		
8	1779	1.203	1760	3.793	1723	10.332					1657	6.562	1625	6.186		
11	1780	1.115	1760	4.110	1724	9.321					1658	5.510	1625	5.786		
17	1780	1.259	1760	4.162	1725	9.189					1658	4.085	1625	5.118		
260°C																
1	1781	1.860	1760	5.080	1728	8.541					1658	4.018	1628	2.144	1620	1.239
300°C																
1	1782	1.504	1760	6.833	1731	8.966					1659	4.236	1631	1.267	1620	4.465

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		NH₂		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	1776	0.410			1722	2.595	1713	6.245	1671	0.650	1650	7.334	1630	12.010		
1	1776	1.730	1758	1.063	1721	17.557							1624	12.242		
3	1778	1.534	1759	2.518	1722	15.804							1626	8.423		
5	1778	1.330	1760	3.065	1723	14.969							1627	5.881		
8	1779	1.308	1760	3.297	1723	14.823							1627	5.677	1618	0.475
11	1779	1.110	1760	3.763	1723	14.074							1627	4.150	1618	0.691
17	1779	1.045	1760	4.212	1724	12.942							1628	3.191	1619	0.984
260°C																
1	1781	0.699	1760	6.386	1728	8.799							1628	2.253	1618	2.257
300°C																
1	1782	0.804	1760	6.907	1730	8.602							1629	2.412	1619	2.486

Table 6
The results of curve fitting in the region 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		NH₂		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	1777	0.357			1722	1.822	1714	7.424	1673	5.280	1653	6.441	1624	13.488		
1	1777	1.458	1759	1.579	1721	14.931							1623	10.844		
3	1778	1.185	1759	2.368	1722	13.287							1622	8.214		
5	1779	1.063	1759	2.334	1722	12.188							1623	7.478		
8	1779	0.836	1760	2.514	1722	11.360							1623	6.358		
11	1780	0.845	1760	2.710	1723	11.015							1623	6.326		
17	1780	0.790	1760	2.733	1724	10.341							1622	5.210		
260°C																
1	1781	0.677	1760	4.185	1728	7.700							1628	4.239	1618	1.552
300°C																
1	1782	0.586	1760	4.888	1730	7.114							1629	1.720	1618	2.998

despite the fact that after dynamic heating at 200°C the ratio of band corresponding to C=O group in the fused cycle to that characteristic for C=O imide group symmetrical vibrations is almost the same as after isothermal heating at 200°C for 1 h, slightly better cyclization to imidazopyrrolone structure after heating at 260°C is observed during dynamic heating.

As seen in the Tables 5 and 7 polymer 2, contrary to the other polymers, exhibits better cyclization to imidazopyrrolone structure during isothermal heating at 200, 260 and 300°C then during dynamic heating. The band ascribed to C=N groups in pyrrole ring is recorded even after heating at 200°C for 8 h.

Curve-fitting calculations obtained for the polymer 3 (Table 6) reveal that during isothermal heating at 200°C a relatively small increase in areas of the band assigned to C=O in pyrrolone ring is observed. A higher increase is recorded after heating at 260°C (Table 7). After heating at 300°C a slightly higher degree of cyclization to imidazopyrrolone structure is observed in the case of dynamic heating.

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. However, during dynamic heating the polymers were kept at the elevated temperature for 10 min.

5. Conclusions

The observations may indicate that the progress of thermal imidization and cyclization to imidazopyrrolone rings depend on the structures of dietheranhydrides used for polycondensation with 3,3′-diaminobenzidine.

The presence of a catechol group in the middle of dietheranhydride causes the imidization process to take place at 160°C during dynamic heating, whereas the cyclization to imidazopyrrolone structure proceeds continuously from 180°C. Relatively small increase in imidazopyrrolone ring is noticed during isothermal heating at 200°C even for 17 h. Almost the same degree of cyclization is observed after both dynamic and isothermal heating at 300°C.

The electron-donating character of a bisphenol A group causes that during dynamic heating imidization proceeds mostly at 180°C and the cyclization to imidazopyrrolone structure takes place mainly at 260°C. Better cyclization at 200, 260 and 300°C is observed during isothermal heating.

In the case of polymer with the a benzophenone connecting group exhibiting electron-withdrawing character imide structure forms at 160°C and undergoes the cyclization to imidazopyrrolone structure at 260°C. Better cyclization

Table 7
The ratios of the area of bands corresponding to imidazopyrrolone and imide structure

Temp. (°C)	A_P/A_{im}[a]					
	Polymer 1		Polymer 2		Polymer 3	
	Dynamic heating	Isothermal heating	Dynamic heating	Isothermal heating	Dynamic heating	Isothermal heating
200	0.129	0.121/1 h	0.046	0.061/1 h	0.039	0.106/1 h
200	—	0.453/17 h	—	0.325/17 h	—	0.264/17 h
260	0.667	0.595	0.519	0.726	0.401	0.544
300	0.696	0.762	0.743	0.803	0.715	0.687

[a] A_P/A_{im} is the ratio of the area of band due to C=O group in imidazopyrrolone structure to the area of band corresponding to C=O imide group symmetrical vibrations.

after heating at 300°C is observed during isothermal heating.

Although the degrees of cyclization to imidazopyrrolone structure obtained for all the polymers investigated, after heating at 300°C differ a little, a slightly higher degree is observed in the case of polymer with electron-donating bisphenol A group after isothermal heating. However for the all polymers investigated the cyclization was not complete, even at 320°C.

Acknowledgements

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