

# FTi.r. study of hydrogen bonds in aliphatic polyesteramides

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FTi.r. spectroscopy was used to investigate hydrogen bonds in aliphatic block/segmented polyesteramides. It was proved that amide–amide and amide–ester hydrogen bonds are formed in these polymers. The investigations at elevated temperature in the range of 20–245°C show that amide–ester hydrogen bonds are more thermostable than amide–amide bonds. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Recently we have published the results of investigations concerning hydrogen bonds forming in aliphatic–aromatic polyesteramides, their models being liquid crystalline compounds<sup>1</sup>. It was demonstrated that in that case amide–amide and amide–ester hydrogen bonds were formed, but the amounts of the various types of them depend on the structure of the compounds, i.e. on the position of the amide and ester groups.

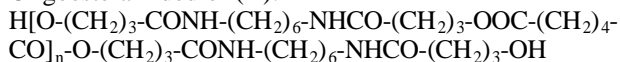
To continue the study, hydrogen bonds appearing in the aliphatic–aliphatic polyesteramides were investigated. The polyesteramides investigated belong to the block/segmented polymers that exhibit dynamic mechanical properties over a large range of working temperature. They were synthesized by a polycondensation reaction of oligoesteramidediol (A) as a hard segment and oligoesterdiol (B) as a soft segment. The synthesis method, thermal and mechanical properties were reported previously<sup>2,3</sup>.

## EXPERIMENTAL

### Materials

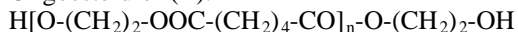
The structural formulae of the oligomers are as follows:

Oligoesteramidediol (A):



$M_n = 1400$ , m.p. = 196°C

Oligoesterdiol (B):



$M_n = 3000$ , m.p. = 40°C

Polyesteramides:

The contents of the oligoamidoester segment are as follows:

polyesteramide 1—0.8 mol/unit (m.p. = 212°C),

polyesteramide 2—0.6 mol/unit (m.p. = 208°C).

### Measurements

Infrared spectra were acquired on a BIO-RAD FTS 40A Fourier transform infrared spectrometer in the region of 4000–700  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$  and a number of

scans of 220. Spectra recorded at elevated temperatures were obtained using Carl Zeiss Jena IR high-temperature control equipment in the temperature range from 20 to 245°C.

In order to determine the quantitative relations between two types of hydrogen bonds, a WIN-IR curve fitting program was used in the following regions corresponding to hydrogen bonding: 3500–3100, 1800–1690, 1690–1600 and 1590–1500  $\text{cm}^{-1}$ . The initial parameters were obtained from the second derivative spectra. The interactive procedure and Gauss–Lorentz type curves were chosen to correct these parameters and compute particular peaks.

The specimens were in the form of films obtained by casting solutions of samples in *N,N'*-dimethylformamide onto potassium bromide windows and evaporating firstly at room temperature and afterwards to remove the residual solvent at 50°C for 5 hours under vacuum.

## RESULTS AND DISCUSSION

For the purpose of studying hydrogen bonds appearing in the polyesteramides described above, the infrared spectra of oligoesteramidediol, oligoesterdiol and the two polyesteramides were recorded.

From the obtained spectra, the areas of bands in the following regions characteristic of: stretching vibrations of NH groups (3500–3100  $\text{cm}^{-1}$ ), stretching vibrations of C=O ester groups (1800–1690  $\text{cm}^{-1}$ ) and the amide I bands (1690–1600  $\text{cm}^{-1}$ ) were calculated. The results are compared in Tables 1–3.

### Oligoesteramidediol (A)

In the case of oligoesteramidediol (A), in the region characteristic of stretching vibrations of N–H groups a broad band exhibiting shoulders is observed (Figure 1a). From curve fitting calculations, a strong band at 3305  $\text{cm}^{-1}$  and a lower area band at 3385  $\text{cm}^{-1}$  (both attributed to the bonded NH groups) appear (Table 1). The band at 3305  $\text{cm}^{-1}$  can be interpreted as characteristic of amide–amide hydrogen bonds whereas the band at 3385  $\text{cm}^{-1}$  is of amide–ester type<sup>1</sup>. Simultaneously at 3442  $\text{cm}^{-1}$  a broad band with relatively high area is observed. This band arises from the

**Table 1** The results of curve fitting calculations in the region of 3500–3100 cm<sup>-1</sup> for oligoesteramide (A) and aliphatic–aliphatic polyesteramides (1,2)

Sample	Band of free NH groups			Band of bonded NH groups amide–ester			Band of bonded NH groups amide–amide		
	Wavenumber [cm <sup>-1</sup> ]	A <sub>f</sub>	A <sub>f</sub> /A <sub>t</sub>	Wavenumber [cm <sup>-1</sup> ]	A <sub>ba-e</sub>	A <sub>ba-e</sub> /A <sub>t</sub>	Wavenumber [cm <sup>-1</sup> ]	A <sub>ba-a</sub>	A <sub>ba-a</sub> /A <sub>t</sub>
A	3442	7.547	0.210	3385	5.326	0.148	3305	23.005	0.641
1	3455	0.123	0.008	3386	1.326	0.084	3303	14.326	0.908
2	3455	0.298	0.029	3386	1.022	0.099	3304	8.952	0.871

A<sub>f</sub>—area of band attributed to free NH groups, A<sub>ba-e</sub>—area of band attributed to amide–ester bonded NH groups, A<sub>ba-a</sub>—area of band attributed to amide–amide bonded NH groups

$$A_t = A_f + A_{ba-e} + A_{ba-a}$$

**Table 2** The results of curve fitting calculations in the region of 1800–1690 cm<sup>-1</sup> for oligoesteramide (A) and aliphatic–aliphatic polyesteramides (1,2)

Sample	Band of disordered free C=O ester groups			Band of ordered free C=O ester groups			Band of disordered bonded C=O ester groups			Band of ordered bonded C=O ester groups		
	Wave-number [cm <sup>-1</sup> ]	A <sub>df</sub>	A <sub>df</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>of</sub>	A <sub>of</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>db</sub>	A <sub>db</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>ob</sub>	A <sub>ob</sub> /A <sub>t</sub>
A	1738	3.690	0.527	1734	1.200	0.171	1714	1.328	0.190	1698	0.781	0.112
1	1744	6.628	0.322	1731	12.417	0.604	1711	1.361	0.066	1694	0.116	0.006
2	1746	3.664	0.204	1735	11.568	0.644	1714	2.177	0.121	1700	0.562	0.031

A<sub>df</sub>—area of band attributed to free C=O ester groups in disordered form, A<sub>of</sub>—area of band attributed to free C=O ester groups in ordered form, A<sub>db</sub>—area of band attributed to bonded C=O ester groups in disordered form, A<sub>ob</sub>—area of band attributed to bonded C=O ester groups in ordered form

$$A_t = A_{df} + A_{of} + A_{db} + A_{ob}$$

**Table 3** The results of curve fitting calculations in the region of 1690–1600 cm<sup>-1</sup> for oligoesteramide (A) and aliphatic–aliphatic polyesteramides (1,2)

Sample	Band of disordered free C=O amide groups			Band of ordered free C=O amide groups			Band of disordered bonded C=O amide groups			Band of ordered bonded C=O amide groups		
	Wave-number [cm <sup>-1</sup> ]	A <sub>df</sub>	A <sub>df</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>of</sub>	A <sub>of</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>db</sub>	A <sub>db</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>ob</sub>	A <sub>ob</sub> /A <sub>t</sub>
A	1676	2.374	0.189	1663	1.208	0.096	1649	4.613	0.366	1636	4.400	0.349
1	1671	0.942	0.083	1654	1.243	0.109	1638	3.252	0.285	1632	5.603	0.491
2	1671	0.846	0.105	1652	1.093	0.136	1638	1.125	0.140	1633	4.975	0.619

A<sub>df</sub>—area of band attributed to free C=O amide groups in disordered form, A<sub>of</sub>—area of band attributed to free C=O amide groups in ordered form, A<sub>db</sub>—area of band attributed to bonded C=O amide groups in disordered form, A<sub>ob</sub>—area of band attributed to bonded C=O amide groups in ordered form

$$A_t = A_{df} + A_{of} + A_{db} + A_{ob}$$

free N-H group stretching vibrations and also from stretching vibrations of the end O-H groups.

In the region characteristic of C=O ester group stretching vibrations, four bands at 1738, 1734, 1714 and 1698 cm<sup>-1</sup> are observed (*Figure 1b*, *Table 2*). The total area of these bands is lower in relation to that observed in polyesteramides. It is a result of the relatively lower content of ester groups in oligoesteramidediol.

The bands at 1738 and 1734 cm<sup>-1</sup> can be ascribed to vibrations of free C=O ester groups in disordered and ordered form, respectively, whereas the bands at 1714 and 1698 cm<sup>-1</sup> can be ascribed to bonded C=O ester group vibrations in disordered and ordered form, respectively.

Such discrimination of the bands attributed to C=O ester groups for ordered and disordered domains is known in the literature reporting investigations of polyesters and polyester blends<sup>4,5</sup>.

As indicated from curve fitting calculations, the area of bands corresponding to disordered form is higher than that corresponding to ordered form. The presence of the band corresponding to ordered form proves that oligoesteramidediol is the compound exhibiting a certain degree of orientation.

The amide I band corresponds mainly to C=O amide stretching vibrations. Consequently, similarly to the band characteristic of C=O ester groups, the amide I band is

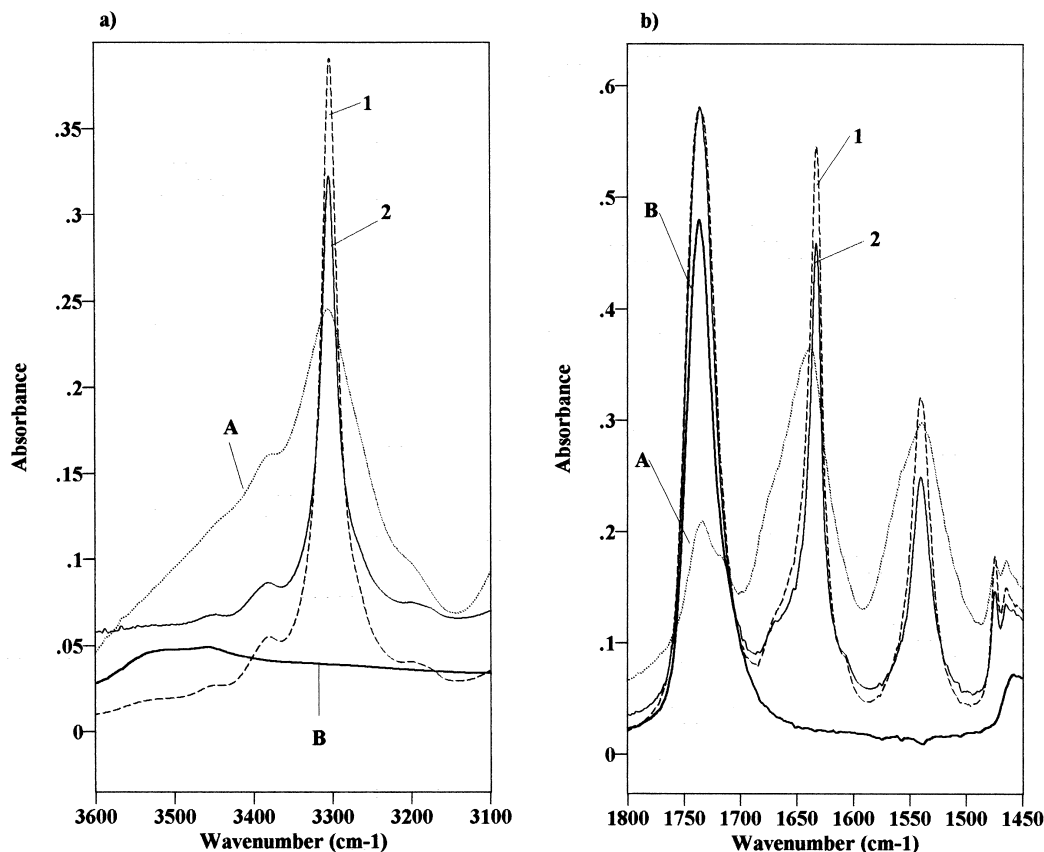
sensitive to ordered and disordered domains<sup>6–8</sup> through the dipole–dipole interactions between C=O and NH groups. For oligoesteramidediol, this band appears in the spectrum as a broad band exhibiting shoulders (*Figure 1b*). Curve fitting calculations show that four bands: at 1676 and 1663 cm<sup>-1</sup> due to free C=O amide groups in disordered and ordered form, respectively, and at 1649 and 1636 cm<sup>-1</sup> characteristic of bonded C=O amide groups for disordered and ordered form, respectively, are present (*Table 3*).

The amide II band is a combination band of NH deformation and C–N stretching vibrations. For oligoesteramidediol in that region a broad but symmetrical band centred at 1540 cm<sup>-1</sup> is observed (*Figure 1b*).

In conclusion, in oligoesteramidediol, amide–amide and amide–ester hydrogen bonds are present. In spite of a low content of ester groups in oligoesteramidediol, relatively more amide–ester hydrogen bonds are formed.

#### Oligoesterdiol (B)

As is seen from the FTi.r. spectrum of oligoesterdiol (B) (*Figure 1b*) and from curve fitting calculations in the region characteristic of stretching vibrations of C=O ester groups, a high area band at 1738 cm<sup>-1</sup> (area 14.22) and a considerably weaker band at 1713 cm<sup>-1</sup> (area 3.70) ascribed to free and bonded ester groups, respectively, are present. In this case C=O ester groups form hydrogen bonds with the



**Figure 1** FTIR spectra of oligoesteramidediol (· · ·), oligoesterdiol (—), polyesteramide 1 (- - -) and polyesteramide 2 (- · -) in the regions of 3600–3100  $\text{cm}^{-1}$  (a) and 1800–1450  $\text{cm}^{-1}$  (b)

end OH groups. The presence of bonded OH groups is confirmed in the region of 3600–3100  $\text{cm}^{-1}$  (Figure 1a), in which a broad but low intensity band at about 3500  $\text{cm}^{-1}$  is observed.

#### Polyesteramides (1,2)

In comparison with the FTIR spectrum of oligoesteramidediol, the spectra of polyesteramides exhibit notably sharper bands in all regions investigated (Figure 1). In the case of polyesteramide 1 the content of the hard segment (oligoesteramidediol) and simultaneously the content of amide groups is higher than in the case of polyesteramide 2.

In the region characteristic of NH group stretching vibrations, the spectra of polyesteramides 1 and 2 show relatively strong and sharp bands at 3303  $\text{cm}^{-1}$  and 3304  $\text{cm}^{-1}$  respectively, arising from bonded NH groups in the case of amide–amide hydrogen bonds. For both polyesteramides, curve fitting calculations indicate also the presence of a band at 3386  $\text{cm}^{-1}$  characteristic of vibrations of associated NH groups in the case of amide–ester hydrogen bonds (Figure 1a, Table 1). The ratio of area of this band to that of the band ascribed to amide–amide hydrogen bonds is slightly higher in the case of polyesteramide 2. In both cases a relatively weak band at 3455  $\text{cm}^{-1}$  arising from vibrations of free NH groups is also observed.

In the region characteristic of stretching vibrations of C=O ester groups, four bands appear (Figure 1b, Table 2). The bands at 1744 and 1731  $\text{cm}^{-1}$  for polyesteramide 1 and at 1746 and 1735  $\text{cm}^{-1}$  for polyesteramide 2 correspond to vibrations of free ester groups for disordered and ordered form, respectively. On the contrary, the bands at 1711 and 1694  $\text{cm}^{-1}$  for polyesteramide 1 and at 1714 and 1700  $\text{cm}^{-1}$  for polyesteramide 2 arise from vibrations of bonded C=O

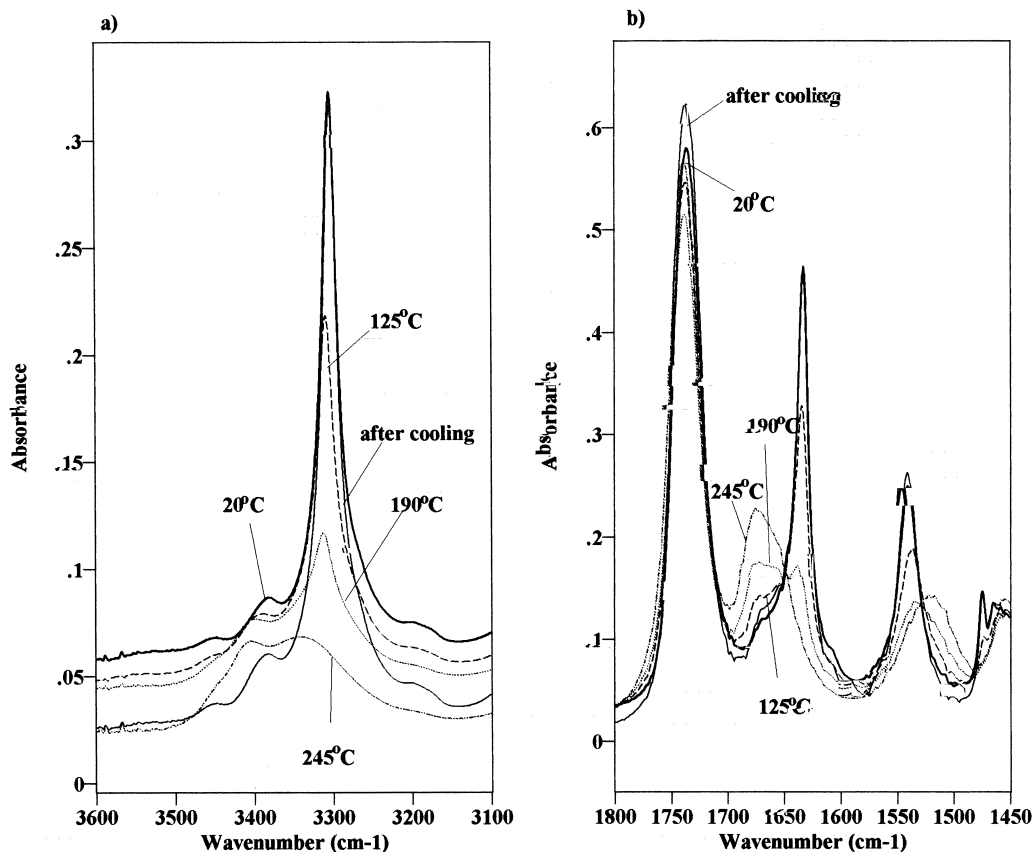
ester groups for disordered and ordered form, respectively. Comparing the results of curve fitting calculations for both polyesteramides, it can be proved that in polyesteramide 2 relatively more amide–ester hydrogen bonds were formed, which is confirmed by the results obtained in the region characteristic of stretching vibrations of N–H groups. On the contrary, a higher content of ordered form is shown in polyesteramide 2.

The above results were confirmed by the curve fitting calculations in the region of the amide I band (Table 3). Polyesteramide 2 exhibits higher areas of the bands corresponding to vibrations of free C=O amide groups in disordered (at 1671  $\text{cm}^{-1}$ ) and in ordered (at 1654  $\text{cm}^{-1}$ ) form in relation to the bands corresponding to vibrations of bonded C=O amide groups than polyesteramide 1. This confirms that in polyesteramide 2 more C=O amide groups are not engaged in hydrogen bonding.

For both polymers, a higher area of the bands ascribed to bonded C=O amide group vibrations in the case of ordered form (band at 1633  $\text{cm}^{-1}$ ) than that of disordered form (band at 1638  $\text{cm}^{-1}$ ) is observed.

In the region characteristic of the amide II band, symmetrical and relatively sharp bands centred at 1540  $\text{cm}^{-1}$  are observed for both polymers (Figure 1b).

In conclusion, it was demonstrated that more amide–amide hydrogen bonds appear in the case of oligoesteramidediol, which is thus the compound with a higher content of amide groups in relation to the polymers. The ratio of the area of the band characteristic of bonded ester groups to the area of the band arising from free ester groups is higher for oligoesteramidediol than for polyesteramides. In the case of polyesteramides, more amide–ester hydrogen bonds form in the polyesteramide with a lower content of



**Figure 2** FTIR spectra of polyesteramide 2 at 20 (—), 125 (---), 190 (···) and 245°C (- · - ·) and after cooling (—) in the regions of 3600–3100  $\text{cm}^{-1}$  (a) and 1800–1450  $\text{cm}^{-1}$  (b)

amide groups. Comparing the bands characteristic of ordered and disordered forms, it can be noticed that the order (orientation) in oligoesteramidediol is notably lower than in the polyesteramides investigated.

#### THERMAL INVESTIGATIONS

In order to achieve a better idea of the nature of hydrogen bonds in the polyesteramides described above, investigations in the temperature range from 20 to 245°C have been made. The samples were heated and spectra at 20, 50, 100, 125, 150, 170, 190, 210, 230, 245°C and after cooling were recorded.

#### Absorption bands in the region 3600–3100 $\text{cm}^{-1}$

During heating to 245°C the bands in that region shift notably in the direction of higher wavenumbers and simultaneously broaden in width. The intensities of the bands characteristic of amide–amide hydrogen bonds decrease considerably. On the contrary, the intensities of the bands corresponding to amide–ester hydrogen bonds change only slightly. However, an increase in the intensity of the band arising from free N-H amide groups is not observed. As was demonstrated for polyesteramides by Coleman *et al.*<sup>9</sup>, the hydrogen bonded N-H stretching frequency reflects the overall distribution of hydrogen bond strengths, and the absorptivity coefficient of this mode is a very strong function of the strength of the hydrogen bond. Thus area changes of this band with temperature increase are not only the result of hydrogen bonded N-H groups transforming to free groups. Figure 2a exhibits the spectra of polyesteramide 2 in that region at 20, 125, 190, 245°C and after cooling.

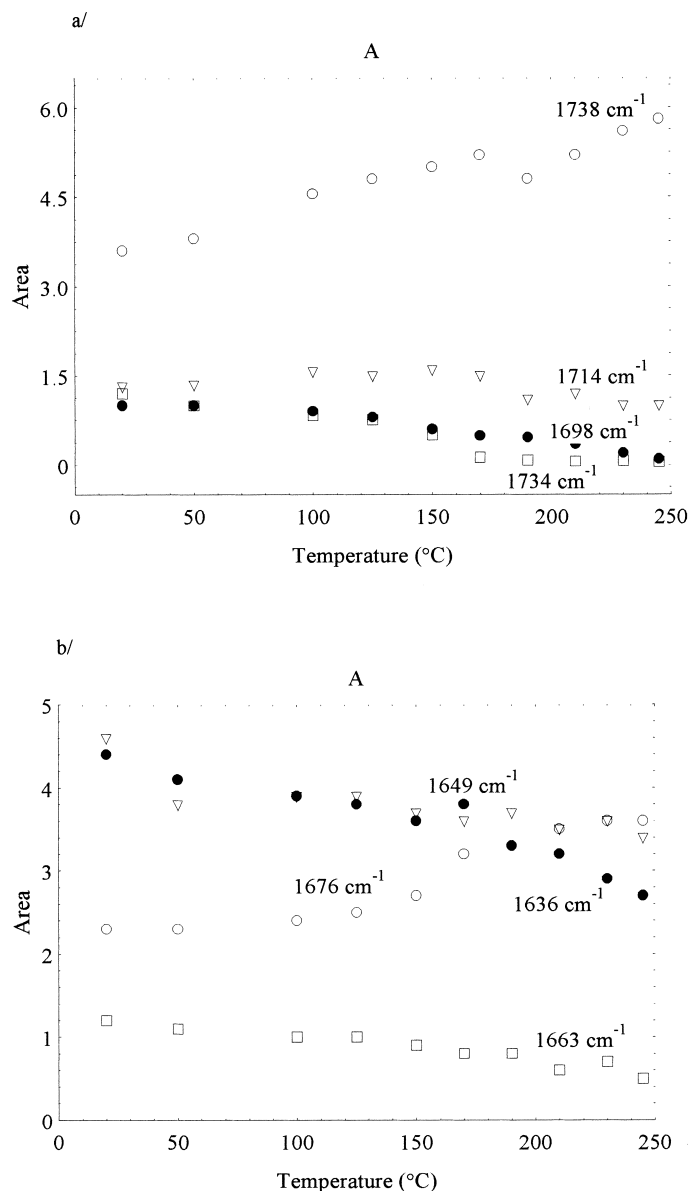
#### Absorption bands in the region 1850–1690 $\text{cm}^{-1}$

With increasing temperature in the region characteristic of stretching vibrations of C=O ester groups, a decrease in areas of the bands arising from free C=O ester groups in ordered forms is observed, whereas the areas of the bands corresponding to the groups in disordered forms increase. It is best visible for oligoesteramidediol, for which at 190°C the area of the band characteristic of ordered form (at 1734  $\text{cm}^{-1}$ ) is almost equal to zero (Figure 3a).

The area of the band arising from bonded C=O ester groups in ordered form (1698  $\text{cm}^{-1}$ ) starts to diminish from 50°C, whereas in the case of disordered form (1714  $\text{cm}^{-1}$ ) the area of that band at first increases and only from 170°C decreases. Changes in the spectra observed below 170°C correspond to decrease of order in that compound; however above that temperature they are connected with breaking of the hydrogen bonds.

Also for polyesteramides, an increase in intensities of bands characteristic of free C=O ester groups in disordered form is observed (Figures 4a and 5a) but at 245°C, and thus above their melting points, bands arising from ordered form are still visible. It supports the view that in the case of the polyesteramides investigated, even above the melting point a certain order is present. This can be caused by the block structure of the polymers.

In polyesteramides the changes in areas of bands corresponding to bonded C=O ester groups caused by the temperature increase are smaller than those in the case of oligoesteramidediol. For polyesteramide 1 (Figure 4a) a decrease in area of the band characteristic of disordered form (1694  $\text{cm}^{-1}$ ) begins from 50°C. The area of the band arising from ordered form (1711  $\text{cm}^{-1}$ ) slightly increases at first but from 210°C decreases. Thus from 210°C the



**Figure 3** Plot of the areas of bands attributed to stretching vibrations of C=O ester groups (a) and to the amide I band (b) versus temperature for oligoesteramidediol (A): ○○○—free C=O groups in disordered form, □□□—free C=O groups in ordered form, ▽▽▽—bonded C=O groups in disordered form, ●●●—bonded C=O groups in ordered form

breaking of amide–ester hydrogen bonds takes place. Below that temperature only the changes connected with the changes in polyesteramide order are noticed. Similar changes are observed for polyesteramide 2 (Figure 5a).

*Absorption bands in the region 1690–1600 cm<sup>-1</sup>.* The visible changes caused by temperature increase are observed best in the region characteristic of the amide I band (Figure 2b). For all compounds investigated the increase in the areas of bands arising from C=O amide groups in disordered form follows the increase in the temperature.

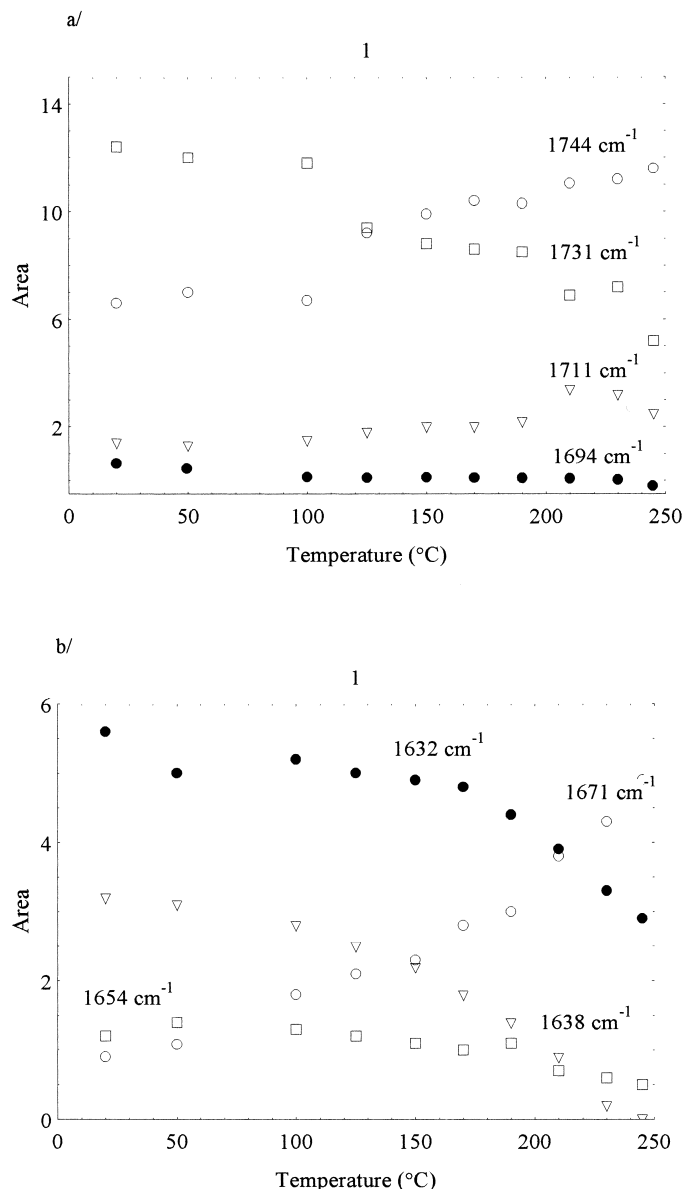
For oligoesteramidediol (Figure 3b) the areas of bands arising from bonded C=O amide groups decrease (1649 and 1636 cm<sup>-1</sup>), likewise the area of the band corresponding to free C=O amide groups in the ordered form (1663 cm<sup>-1</sup>). Simultaneously the area of the band characteristic of free C=O amide groups in disordered form (1676 cm<sup>-1</sup>) increases.

For polyesteramide 1 (Figure 4b) the area of the band

arising from free C=O amide groups in disordered form (1671 cm<sup>-1</sup>) increases significantly, at first as a result of decreasing the order and only above the temperature 170°C as a result of breaking of hydrogen bonds. Simultaneously a decrease in the area of the band corresponding to free amide groups in ordered form (1638 cm<sup>-1</sup>) is observed.

For polyesteramide 2 the area of the band characteristic of free amide groups in ordered form (1652 cm<sup>-1</sup>) decreases systematically from the temperature 170°C (Figure 5b). Simultaneously, a significant decrease in the area of the band corresponding to bonded C=O amide groups in ordered form (1633 cm<sup>-1</sup>) is observed and at 245°C it reaches a value near zero. The area of the band corresponding to those groups in disordered form (1638 cm<sup>-1</sup>) increases at first, but above the temperature 170°C a decrease is observed.

*Absorption bands in the region 1590–1500 cm<sup>-1</sup>.* In the region characteristic of the amide II bands, a decrease in the intensities of bands attributed to bonded NH groups can be



**Figure 4** Plot of the areas of bands attributed to stretching vibrations of C=O ester groups (a) and to the amide I band (b) versus temperature for polyesteramide 1: ○○○—free C=O groups in disordered form, □□□—free C=O groups in ordered form, ▽▽▽—bonded C=O groups in disordered form, ●●●—bonded C=O groups in ordered form

**Table 4** The results of curve fitting calculations in the region of 3500–3100  $\text{cm}^{-1}$  for oligoesteramide (A) and aliphatic–aliphatic polyesteramides (1,2) after cooling

Sample	Band of free NH groups			Band of bonded NH groups amide–ester			Band of bonded NH groups amide–amide		
	Wavenumber [ $\text{cm}^{-1}$ ]	$A_f$	$A_f/A_t$	Wavenumber [ $\text{cm}^{-1}$ ]	$A_{ba-e}$	$A_{ba-e}/A_t$	Wavenumber [ $\text{cm}^{-1}$ ]	$A_{ba-a}$	$A_{ba-a}/A_t$
A	3442	5.567	0.178	3385	5.987	0.191	3305	19.385	0.621
1	3455	0.163	0.011	3386	1.457	0.099	3303	13.024	0.889
2	3455	0.193	0.020	3386	1.099	0.115	3304	8.294	0.865

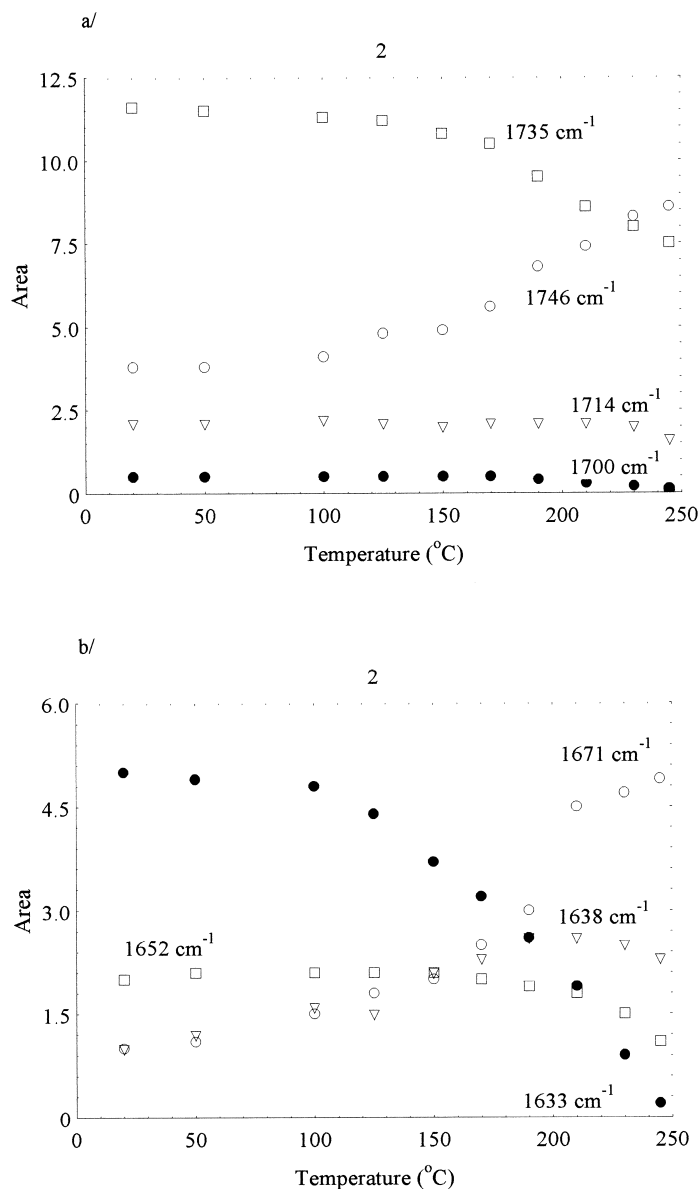
$A_f$ —area of band attributed to free NH groups,  $A_{ba-e}$ —area of band attributed to amide–ester bonded NH groups,  $A_{ba-a}$ —area of band attributed to amide–amide bonded NH groups

$$A_t = A_f + A_{ba-e} + A_{ba-a}$$

observed during heating for all compounds investigated (Figure 2b). Breaking of hydrogen bonds during heating is manifested by the broadening of the bands widths and their shifting in the direction of lower wavenumbers, i.e. in the direction of the band ascribed to free NH groups. A 245°C maximum of this band appears at 1517  $\text{cm}^{-1}$ . Similarly to the region characteristic of stretching vibrations of

NH groups, the region of the amide II bands is not sensitive to order. The amide II mode is a mixed vibration that is sensitive to conformation via mechanical coupling and hydrogen bonding and consequently to polymorphism where there is a significant difference in chain conformation<sup>9</sup>.

Thus, as indicated from the results described above, the breaking of amide–amide hydrogen bonds follows the



**Figure 5** Plot of the areas of bands attributed to stretching vibrations of C=O ester groups (a) and to the amide I band (b) versus temperature for polyesteramide 2: ○○○—free C=O groups in disordered form, □□□—free C=O groups in ordered form, ▽▽▽—bonded C=O groups in disordered form, ●●●—bonded C=O groups in ordered form

**Table 5** The results of curve fitting calculations in the region of 1800–1690 cm<sup>-1</sup> for oligoesteramide (A) and aliphatic–aliphatic polyesteramides (1,2) after cooling

Sample	Band of disordered free C=O ester groups			Band of ordered free C=O ester groups			Band of disordered bonded C=O ester groups			Band of ordered bonded C=O ester groups		
	Wave-number [cm <sup>-1</sup> ]	$A_{df}$	$A_{df}/A_t$	Wave-number [cm <sup>-1</sup> ]	$A_{of}$	$A_{of}/A_t$	Wave-number [cm <sup>-1</sup> ]	$A_{db}$	$A_{db}/A_t$	Wave-number [cm <sup>-1</sup> ]	$A_{ob}$	$A_{ob}/A_t$
A	1738	4.247	0.551	1734	1.001	0.130	1714	1.853	0.240	1698	0.612	0.079
1	1744	7.176	0.365	1731	10.889	0.554	1711	1.510	0.077	1694	0.091	0.005
2	1746	5.637	0.322	1735	9.817	0.560	1714	1.498	0.086	1700	0.562	0.032

$A_{df}$ —area of band attributed to free C=O ester groups in disordered form,  $A_{of}$ —area of band attributed to free C=O ester groups in ordered form,  $A_{db}$ —area of band attributed to bonded C=O ester groups in disordered form,  $A_{ob}$ —area of band attributed to bonded C=O ester groups in ordered form

$$A_t = A_{df} + A_{of} + A_{db} + A_{ob}$$

increase in the temperature. Simultaneously with that process, a decrease in order takes place in the compounds investigated. At 245°C, and thus after melting, certain amounts of amide–amide and amide–ester hydrogen bonds are still observed.

The spectra obtained after cooling the compounds to 20°C

are similar to those obtained before cooling. Thus, the amide–amide and amide–ester hydrogen bonds form again after heating to 245°C and cooling to 20°C. From calculations of the areas of the bands, it follows that after cooling the amounts of ordered form were increased in relation to the initial spectra (Tables 4–6).

**Table 6** The results of curve fitting calculations in the region of 1690–1600 cm<sup>-1</sup> for oligoesteramide (A) and aliphatic–aliphatic polyesteramides (1,2) after cooling

Sample	Band of disordered free C=O amide groups			Band of ordered free C=O amide groups			Band of disordered bonded C=O amide groups			Band of ordered bonded C=O amide groups		
	Wave-number [cm <sup>-1</sup> ]	A <sub>df</sub>	A <sub>df</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>of</sub>	A <sub>of</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>db</sub>	A <sub>db</sub> /A <sub>t</sub>	Wave-number [cm <sup>-1</sup> ]	A <sub>ob</sub>	A <sub>ob</sub> /A <sub>t</sub>
A	1676	2.920	0.220	1663	1.007	0.076	1649	5.321	0.401	1636	4.021	0.303
1	1671	1.590	0.147	1654	1.580	0.146	1638	2.391	0.220	1632	5.275	0.487
2	1671	0.710	0.094	1652	1.062	0.141	1638	1.929	0.256	1633	3.838	0.509

A<sub>df</sub>—area of band attributed to free C=O amide groups in disordered form, A<sub>of</sub>—area of band attributed to free C=O amide groups in ordered form, A<sub>db</sub>—area of band attributed to bonded C=O amide groups in disordered form, A<sub>ob</sub>—area of band attributed to bonded C=O amide groups in ordered form  
A<sub>t</sub> = A<sub>df</sub> + A<sub>of</sub> + A<sub>db</sub> + A<sub>ob</sub>

## CONCLUSION

In aliphatic–aliphatic block/segmented polyesteramides amide–amide and amide–ester hydrogen bonds are formed. The greatest amount of amide–ester hydrogen bonds forms in the case of oligoesteramidediol, in which the content of ester groups is considerably lower than for polyesteramides. A greater amount of amide–ester hydrogen bonds appears in the polymer with a lower content of amide groups.

Heating of these polymers causes the breaking of hydrogen bonds. The amide–ester hydrogen bonds appear stronger, because they have not broken until 210°C, whereas the amide–amide hydrogen bonds undergo breaking from 170°C.

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