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Hydrogen bonds in poly(ester amide)s and their model compounds

Bożena Kaczmarczyk and Danuta Sęk*
Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland
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The hydrogen bonds in poly(ester amide)s and their model compounds were investigated using infra-red spectroscopy in the temperature range from 20 to 240°C. It was found that in the polymers investigated both amide–amide and amide–ester hydrogen bonds were formed, while in the corresponding model compounds only amide–amide hydrogen bond formation was observed.

(Keywords: poly(ester amide)s; hydrogen bonds; model compounds)

INTRODUCTION

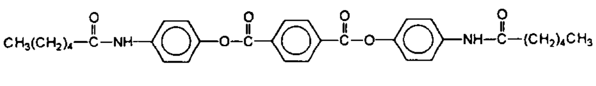
Hydrogen bonds in polymers have a real influence on their physical and chemical properties, such as melting temperature, reactivity, solubility, adhesion or thermal stability. They also have a strong influence on the mechanical properties of the polymers.

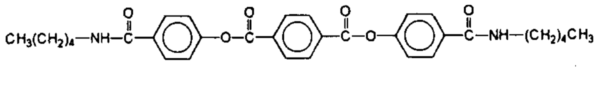
In the poly(ester amide)s there are two possibilities for hydrogen-bond formation, i.e. the amide–amide bond, as observed in polyamides[1–3], and also the amide–ester hydrogen bond, namely the bond between the hydrogen of the amide group and the carbonyl oxygen of the ester group[4–6]. These two possibilities are determined by the position of the ester and the amide groups along the polymer chains.

Infra-red spectroscopy is a useful method for the determination of hydrogen bonds, because the latter cause certain shifts of the bands corresponding to the groups which take part in that particular bond. The aim of our investigations was the determination of hydrogen bonds in aromatic-aliphatic poly(ester amide)s and their corresponding model compounds by using i.r. spectroscopy.

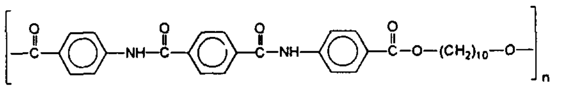
The structural formulae of the compounds investigated in this work are shown below:

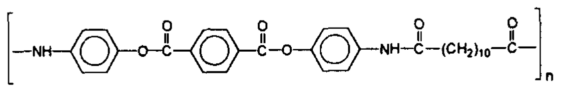
Model compounds

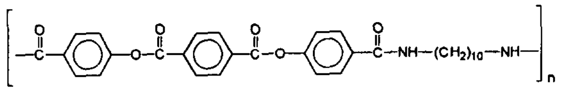
2M.


3M.


Polyesteramides

1.


2.


3.


As the polymers and model compounds examined have different positions of the amide and ester groups in the molecule, it was considered interesting to determine the influence of the structure on hydrogen-bond formation.

EXPERIMENTAL

Materials

The poly(ester amide)s and their corresponding model compounds were prepared as described in ref. 7. Some of the properties of the materials are presented in *Table 1*.

Measurements

Infra-red spectra were measured (KBr pellets (1.5%)) by using a Zeiss M-80 spectrophotometer fitted with temperature control equipment, in the temperature range from 20 to 240°C. The i.r. spectra were recorded in the region 4000–700 cm^{-1}. Particular attention was paid to the bands characteristic of hydrogen bonding, i.e. 3600–3000 cm^{-1} as the region of stretching vibrations of N–H groups and at ~ 1670, ~ 1540 and ~ 1260 cm^{-1}, for the amide I, II and III bands, respectively.

RESULTS AND DISCUSSION

The poly(ester amide)s and model compounds investigated in this work, some of the properties of which are

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* To whom correspondence should be addressed

Table 1 Some properties of the poly(ester amide)s and their model compounds

No.	Melting point[a] (°C)	η_{red}[b]
Polymers		
1	321	0.36[c]
2	270	0.44[c]
3	291	0.28[d]
Model compounds		
2M	295	
3M	321	

[a] Measured on a Du Pont 1090 B differential scanning calorimeter at a heating rate of 10°C min^{-1}

[b] Reduced viscosity, using a concentration of 0.5 g per 100 ml of solvent at 25°C

[c] In dichloroacetic acid

[d] In methanesulfonic acid

presented in *Table 1*, contain the same functional groups, but their positions along the polymer chain are different. Therefore, their i.r. spectra are similar and exhibit the same bands, which show only certain shifts and have a slightly different shape. I.r. spectra of the poly(ester amide)s and the model compounds are presented in *Figure 1*, with the most characteristic bands being given in *Table 2*.

Absorption bands in the region 3600–3000 cm^{-1}

In general, the spectra of the model compounds are sharper than the spectra of the polymers. Some obvious differences can be seen in the case of the bands in the 3600–3000 cm^{-1} region, which corresponds to the stretching vibrations of the N–H groups.

The spectra of the model compounds show relatively sharp bands, with the maximum at 3324 cm^{-1}, while at 3440 cm^{-1} a weak but nevertheless marked shoulder can be seen. For the polymers in this region broad bands, of a relatively lower intensity than the model compounds, can be observed. For polymer **2** this band is split into two distinct, overlaying maxima, at 3320 and 3380 cm^{-1}, of a slightly lower intensity, but the shoulder at ~ 3440 cm^{-1} is also weakly visible. For polymer **3** this band is broad with the maximum extending from 3320 to 3340 cm^{-1}; however, its shape is different and the band at 3380 cm^{-1} is also just visible. The shoulder at 3440 cm^{-1} is very weak in this case. Another shape for the band in this region can be seen in the spectrum of polymer **1**. It also shows a broad band, but with a wide maximum at ~ 3336 cm^{-1}; again the shoulder at 3440 cm^{-1} is weakly visible.

According to the literature[8], the band with a maximum at 3440 cm^{-1} can be interpreted as being responsible for the vibrations of the 'free' N–H groups. The spectra obtained show that in both the model compounds and the polymers, only a small amount of 'free', non-bonded N–H groups are present. Most of these are recorded as being associated with hydrogen-bonding groups. In the models, relatively sharp bands at ~ 3320 cm^{-1}, corresponding to the associated groups, can be seen. In the polymers these bands are broad, with overlaying shoulders. These differences seem to confirm that in the model compounds one main type of hydrogen bond, with a certain definite length for the N–H bonds is formed.

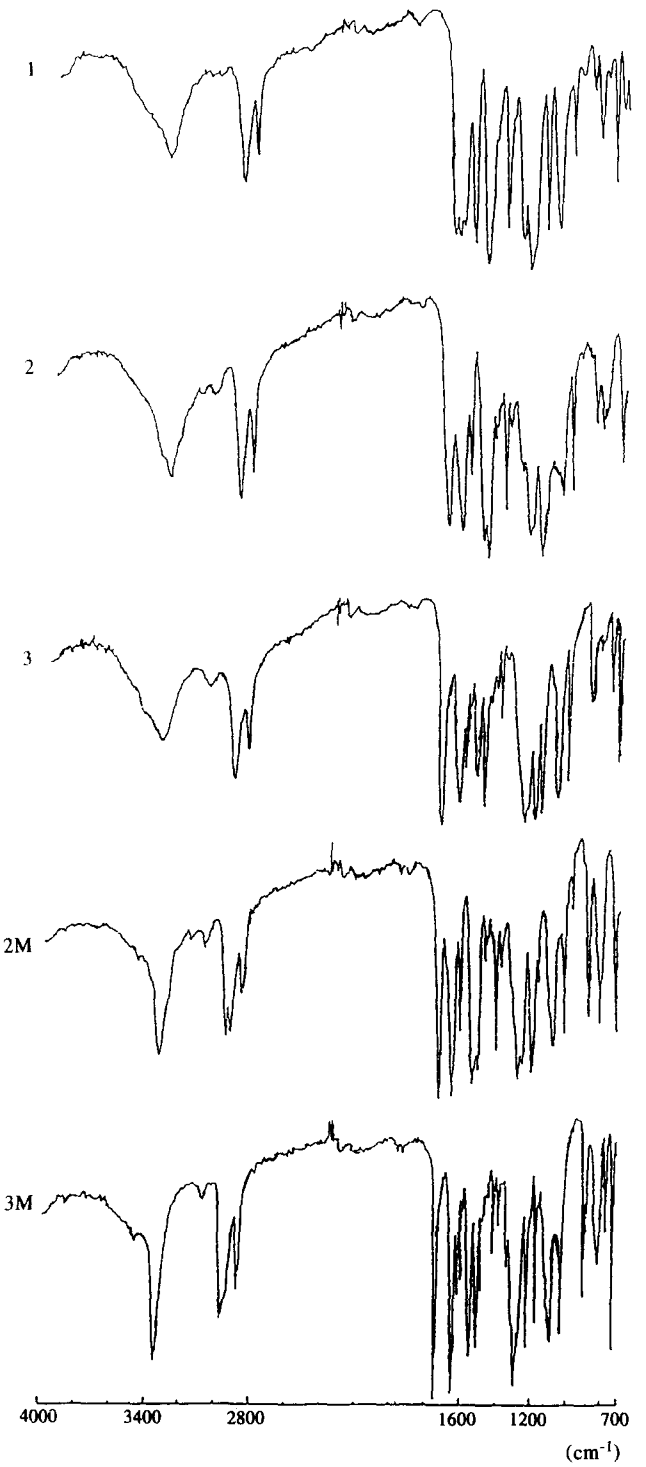


Figure 1 I.r. spectra of the polymers **1**, **2** and **3**, and the model compounds **2M** and **3M**

In contrast, for the polymers the existence of broad bands with overlaying shoulders indicate that in this case more types of hydrogen bond, with different bond distances for the N–H groups, are formed.

Absorption bands in the region 1800–1500 cm^{-1}

The absorption bands in the region from 1800 to 1500 cm^{-1} are associated with the amide I and II bands. According to data in the literature[9], the amide I band consists of the C=O stretching (~ 75%), C–N stretching (~ 15%) and C–C–N deformation (~ 10%) vibrations. For the model compounds **2M** and **3M** this band appears

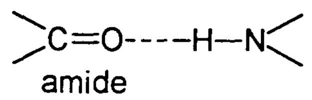
Table 2 Characteristic i.r. bands for the poly(ester amide)s and their model compounds[a]

	Characteristic vibration (cm^{-1})							
No.	N–H stretch		C=O ester stretch	Amide I band		Amide II band	Amide III band C=O ester stretch	
Polymers								
1	3600–3400	3336	1712	1684	1660	1550–1540	1280–1250	
2	3600–3400	3320, 3380	1732	1680(sh)	1656	1550–1540	1270–1250	
3	3600–3400	3340	1732	1690(sh)	1636	1550–1540	1270–1240	
Model compounds								
2M	3440(sh)	3324	1732		1656	1544	1284	1260
3M	3440(sh)	3324	1728		1632	1536	1284	1260

[a] sh = shoulder

in this characteristic region for hydrogen-bonded C=O amide groups at 1656 and 1632 cm^{-1}, respectively. Both bands are sharp, and lack any shoulders.

In the case of the poly(ester amide)s the amide I bands have lower intensities, but they are broader and shoulders can be seen. These shoulders appear at 1684, 1680 and 1690 cm^{-1} for polymers **1**, **2** and **3**, respectively, i.e. in the region of 'free' C=O amide groups. These results confirm that in the polymers some of the C=O amide groups remain as being non-bonded by hydrogen. The broadening of the main band can be caused by the various bond distances in the following system:



The amide II band consists of the N–H bending (~ 45%), C–N stretching (~ 35%) and C–C stretching (~ 15%) vibrations[9]. For the model compounds this band (as with the amide I band) is sharp, with maxima at 1544 and 1536 cm^{-1} for the **2M** and **3M** model compounds, respectively, i.e. in the region characteristic of hydrogen bonding.

For the poly(ester amide)s this band is smaller and also broader, and shoulders can be seen. However, these shoulders are not in the region characteristic of non-bonded amide II bands, but appear in the region corresponding to associated groups.

All of the results obtained seem to confirm the supposition that in the case of the poly(ester amide)s two different types of hydrogen bonds are formed, namely amide–amide and ester–amide bonds which correspond to the bonds between the hydrogen of the amide group and the oxygen of the C=O amide group, or that between the hydrogen of the amide group and the oxygen of the C=O ester group. This is the reason why some of the C=O amide groups in these types of polymers stay 'free', i.e. non-bonded by hydrogen (the amide I bands), whereas the N–H groups are identified as being bonded (in the 3600–3000 cm^{-1} region, amide II bands). The above features are most clearly seen in polymer **1** and confirm that in this case more amide–ester hydrogen bonds are formed. The poly(ester amide)s investigated here, consist of stiff rod-like aromatic segments and flexible aliphatic ones. These segments are connected by ester or amide groups.

In poly(ester amide) **1** the ester is the connecting group, while in polymers **2** and **3** the amide groups link the stiff and flexible segments. It therefore seems that the positions of certain groups along the polymer chain may have an influence on the nature of the hydrogen-bond formation.

Thermal investigations

In order to achieve a better idea of the nature of the hydrogen bonds in both the models and the polymers, investigations in the temperature range from 20 to 240°C have been made. The KBr pellets were heated and spectra at 50, 100, 150, 200 and 240°C were recorded. As the melting points of the models and the polyesteramides are higher than 240°C, the changes observed are, unfortunately, not the final ones.

Absorption bands in the region 3600–3000 cm^{-1}. The most interesting changes seem to be for the model compound **3M** (*Figure 2a*). The band at 3324 cm^{-1} gets broader during heating and the shoulder at 3440 cm^{-1} disappears. However, this band in the spectrum recorded at 20°C, after cooling the sample, had quite a different shape. Now two overlaying bands with maxima at 3320 and 3300 cm^{-1} could be observed. To check this result, the pellet was again heated to 240°C and then cooled. The shape of the bands was the same as that seen after the first heating, i.e. with maxima at 3320 and 3300 cm^{-1}.

During heating of the model compound **3M** at 100°C (*Figure 2b*) the band at 3440 cm^{-1} disappeared and the band at 3324 cm^{-1} gradually broadened, with a simultaneous decrease in its intensity. The spectrum recorded at room temperature after cooling the sample was the same, in this region, as before heating, but without the shoulder at 3450 cm^{-1}. Therefore, the behaviour of the model compound **3M** is different to that of the model compound **2M**.

Changes in the absorption bands during heating of the poly(ester amide)s were also observed. For polymer **1** (*Figure 3a*), upon increasing the temperature the band with a maximum at 3336 cm^{-1} shifts to 3352 cm^{-1}. In the spectrum recorded at 20°C, after cooling the sample, the band at 3352 cm^{-1} had a slightly different shape to that observed in the spectrum recorded during heating at 240°C.

The spectrum of polymer **2** (*Figure 3b*) recorded at room temperature before heating, had two distinct

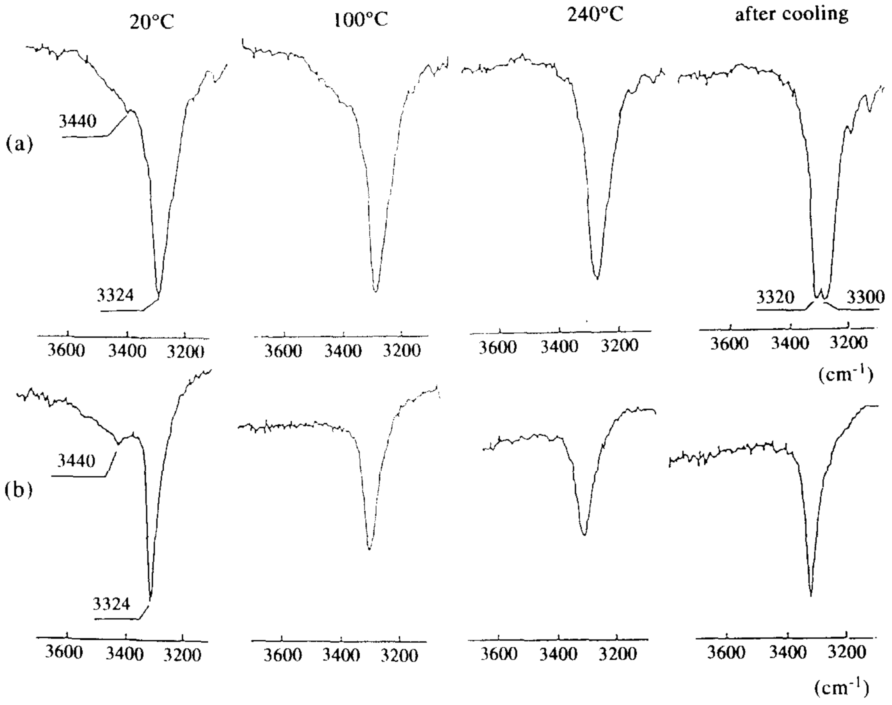


Figure 2 I.r. spectra in the region 3600–3000 cm^{-1} of the model compounds at temperatures of 20, 100 and 240°C, and after cooling: (a) **2M**; (b) **3M**

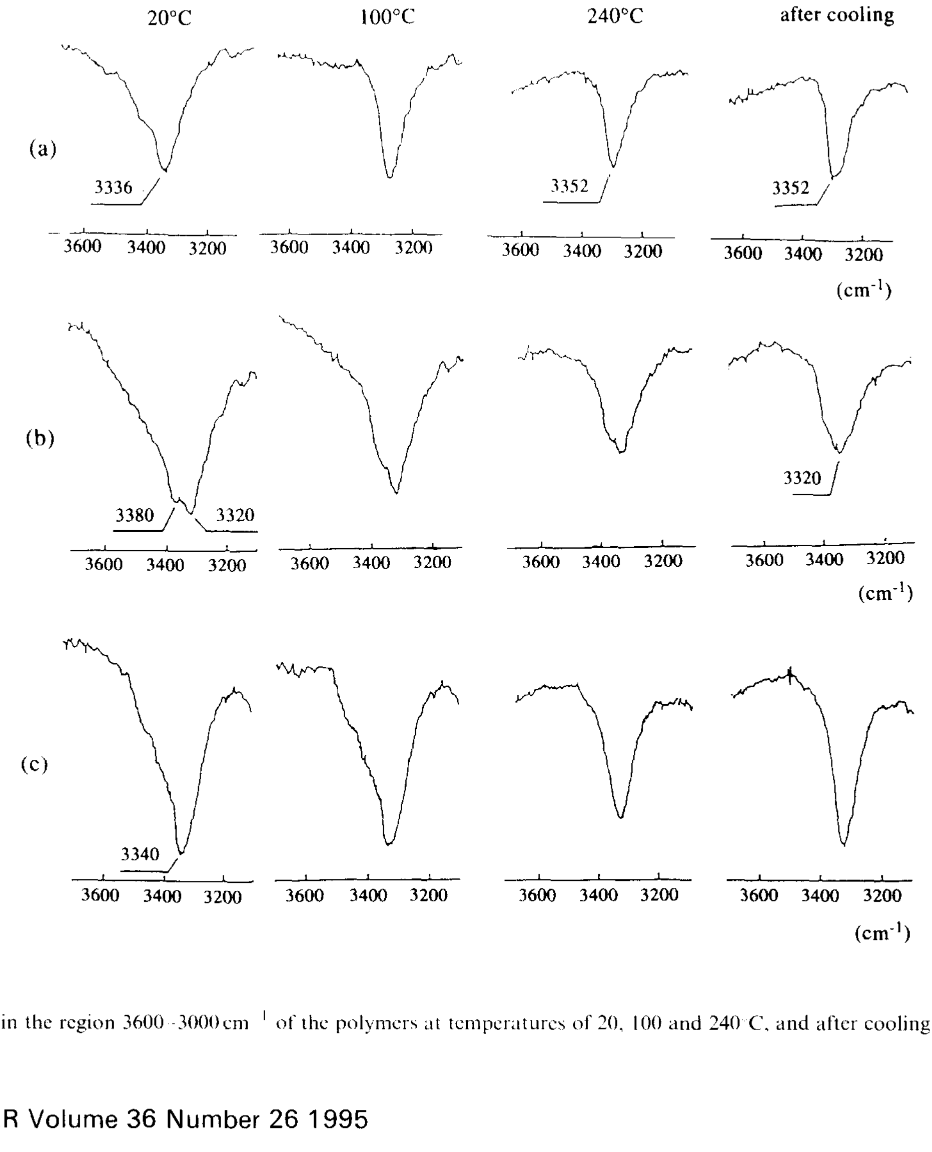


Figure 3 I.r. spectra in the region 3600–3000 cm^{-1} of the polymers at temperatures of 20, 100 and 240°C, and after cooling: (a) **1**; (b) **2**; (c) **3**

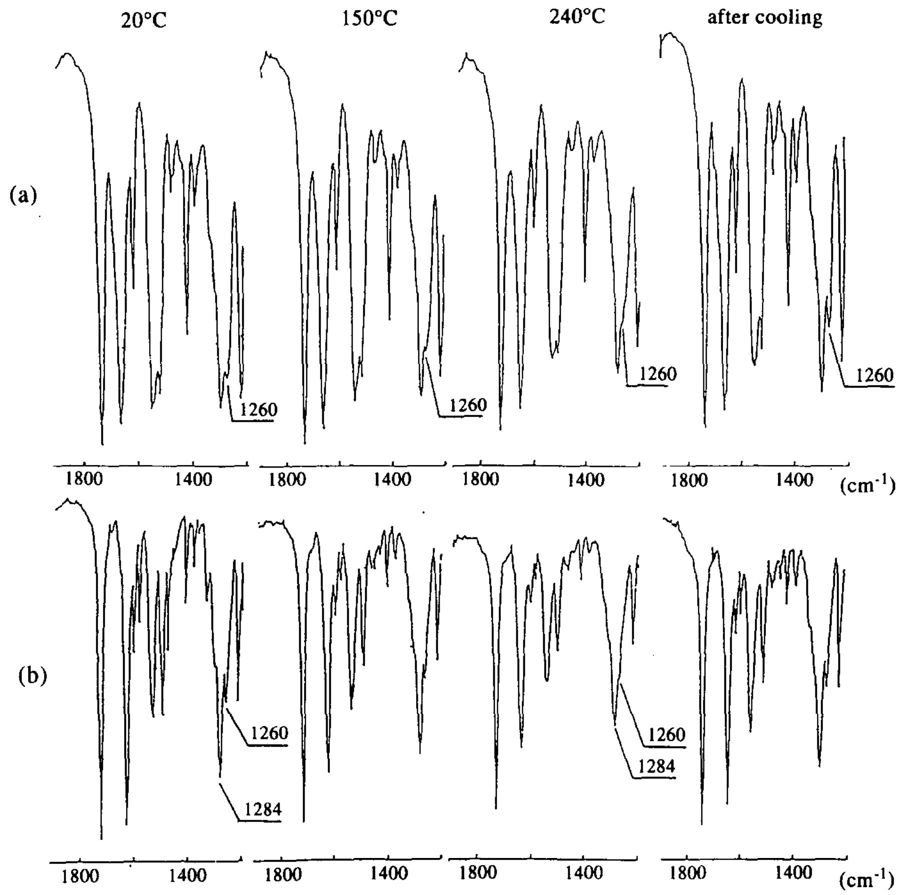


Figure 4 I.r. spectra in the region 1800–1200 cm^{-1} of the model compounds at temperatures of 20, 150 and 240°C, and after cooling: (a) **2M**; (b) **3M**

maxima, i.e. at 3320 and 3380 cm^{-1}. During heating, a decrease in the band at 3380 cm^{-1} could be observed, while at 240°C it appeared only as a shoulder. After cooling the sample, this band did not return to its initial state.

Considerably fewer changes could be observed for polymer **3** (*Figure 3c*), with the band at 3340 cm^{-1} changing its intensity only very little during heating to 240°C.

Absorption bands in the region 1800–1200 cm^{-1}. For the model compound **2M** (*Figure 4a*) no changes were observed for the amide I and II bands, or for the C=O ester band, during heating to 240°C. However, above 150°C the band at 1260 cm^{-1} (the amide III band) gradually decreased and at 240°C was present as a small shoulder. After cooling the sample, the band at 1260 cm^{-1} in the spectrum measured at 20°C had a slightly lower intensity.

There were also changes in the absorption bands in the amide III region during heating of the model compound **3M** (*Figure 4b*). At 150°C a broadening of the band at 1284 cm^{-1} was observed, accompanied by the disappearance of the band at 1260 cm^{-1}, which at 240°C was present only as a weak shoulder.

For the poly(ester amide) **1** (*Figure 5a*) the following changes in the absorptions were detected in the amide I and II regions during heating: a significant decrease in the bands at 1684 cm^{-1}, a slight decrease in the band at 1712 cm^{-1}, and an increase in the bands at 1660 and 1540 cm^{-1}. In the case of poly(ester amide) **2** (*Figure 5b*), the heating treatment caused both a broadening and a decrease in the bands at 1656 and 1540 cm^{-1}. In contrast, very few changes were observed for the bands at 1636 and 1540 cm^{-1} during heating of the poly(ester amide) **3** (*Figure 5c*).

In the poly(ester amide)s, in contrast to the model compounds, the band at 1260 cm^{-1} is recorded only as a shoulder and this partly overlaps the band at 1280 cm^{-1}, which is characteristic of esters. The band at 1260 cm^{-1} can be assigned to the deformation vibrations of the amide–amide bonded N–H (the amide III band). In the polymers there is not just one strictly defined type of hydrogen bond, so any changes in the band at 1260 cm^{-1} during heating are not visible.

The above results confirm that in the poly(ester amide)s both amide–amide and amide–ester hydrogen bonds are formed, with their respective amounts being related to the polymer chain structure. This feature is best observed in the poly(ester amide) **1**. For this polymer, after heating and cooling a small decrease in the band at 1712 cm^{-1}, with simultaneous increases in the bands at 1660 and 1540 cm^{-1}, could be observed. This confirms the fact that during heating, some of the amide–ester hydrogen bonds change into amide–amide hydrogen bonds. The change of the shape of the bands in the region from 3500 to 3200 cm^{-1} also confirms the above conclusion.

The poly(ester amide)s **2** and **3** contain smaller amounts of the amide–ester hydrogen bonds, as illustrated by broad amide I and II bands displaying

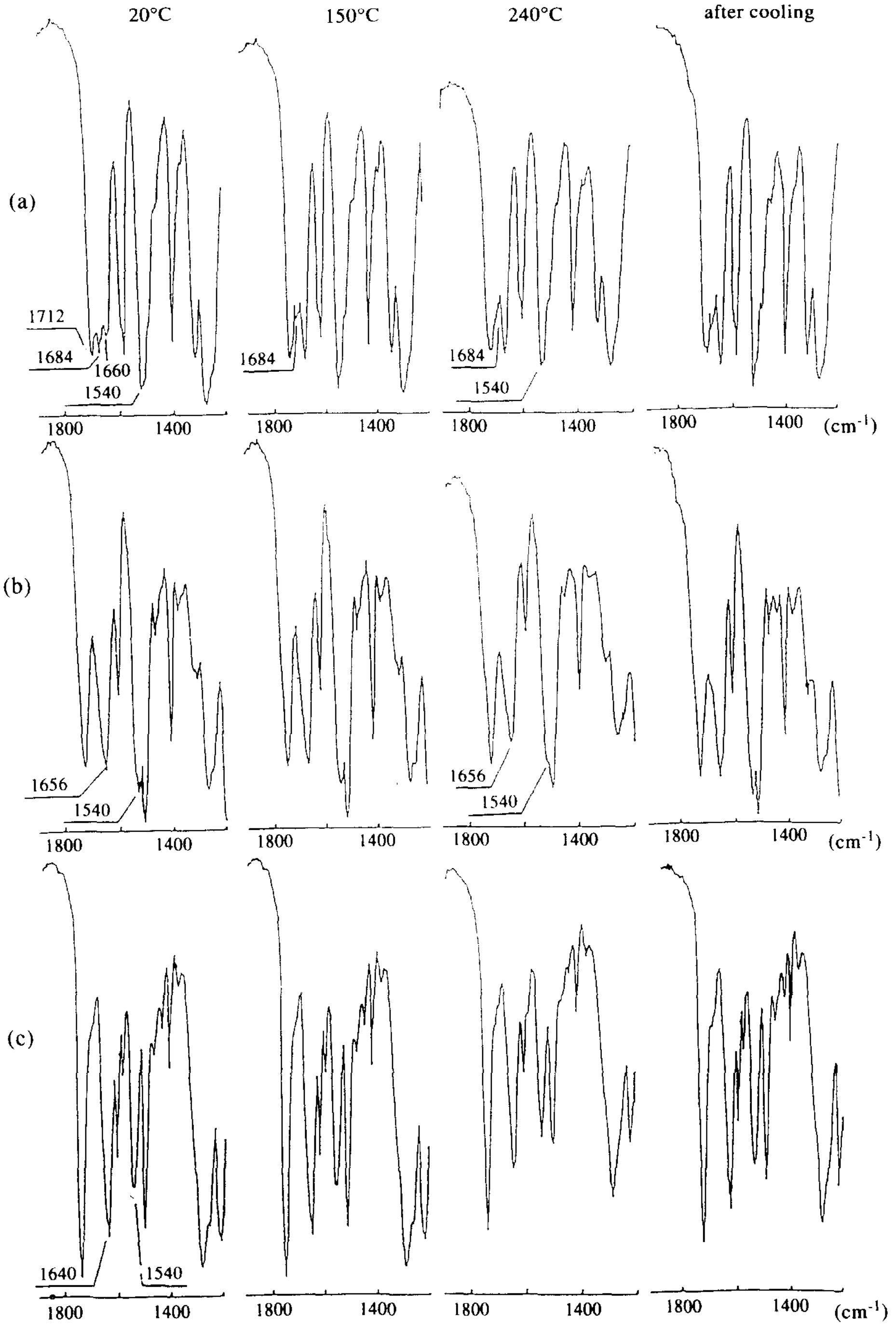


Figure 5 I.r. spectra in the region 1800–1200 cm^{-1} of the polymers at temperatures of 20, 150, 240°C, and after cooling: (a) **1**; (b) **2**; (c) **3**

only shoulders, and not separated bands as seen in poly(ester amide) **1**. It is for this reason that during the heating process, the changes are not so evident. Nevertheless, the increase in the band at 1660 cm^{-1} and the decrease in the band at 3380 cm^{-1}, may also confirm a reduction in the amide–ester hydrogen-bond content in these polymers.

The i.r. spectra confirm that in the model compounds only amide–amide hydrogen bonds are formed. To prove this point, the spectra of benzanilide and acetanilide were recorded while heating from 20 to 240°C, and compared with the spectra of the model compounds **2M** and **3M**. The results obtained confirmed that the nature of the hydrogen bonds in the model compounds **2M** and **3M** is the same as in the amides. The changes observed in the spectrum of model compound **2M** after cooling are similar to those observed for the acetanilide and relate only to changes in the interaction of the amide group.

CONCLUSIONS

In the aromatic-aliphatic poly(ester amide)s having stiff rod-like and flexible units, the formation of amide–amide and amide–ester hydrogen bonds has been detected by using i.r. spectroscopy. The amounts of the various types of hydrogen bonds depends on the structure of the poly(ester amide)s, i.e. the positions of the amide and ester groups. Heating of these polymers causes a decrease in the amide–ester hydrogen-bond content.

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