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Formation and stability of hydrogen bonds and ionic complexes in polyacetamidine and its mixtures with proton donors—a vibrational spectroscopy study

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Abstract

FT-IR spectroscopy was used to study the specific interactions in an aliphatic polyacetamidine and its mixtures with a dicarboxylic acid. In the pure polyacetamidine, hydrogen bonds between the amidine groups were observed. After heating, considerable changes in the position of the interacting group vibration bands were found. These changes were reversible on cooling. In mixtures with glutaric acid strong acid base interactions resulting in the formation of ionic polymer networks were observed. These networks have proven stable up to at least 150 °C.

Keywords: Polyamidine; Hydrogen bondings; Ionic complexes

1. Introduction

It is well known that low molecular weight amidines of the common structure $R^1{-}N{=}C(R^2){-}NR^3R^4$ are strong organic bases which are able to form salts with various mineral or organic acids [1]. Depending on the substituents R^1–R^4, pK_a values higher than 12 were found [2]. Especially, aliphatic substituents on the amidine group increase the basicity of amidines distinctly.

It was our aim to transfer this behavior to polymers. Polyamidines with both nitrogen atoms in the main chain $-(R^1{-}N{=}C(R^2){-}NH)_n-$ are available by the conversion of diamines with orthoesters [3–6]. Among a series of aromatic and aliphatic polyamidines prepared by this procedure, those with aliphatic residues R^1 and R^2 have proved to be most basic [7]. With pK_a values higher than 11, their basicity is comparable with that of aliphatic low molecular weight amidines.

The pronounced basicity enables aliphatic polyamidines to interact with proton donors such as carboxylic acids or phenolic groups. The nature of interaction depends on the acidic strength of the proton donors. It could be shown by NMR spectroscopy that an aliphatic polyacetamidine in the presence of a strong acidic solvent (CF_3COOD) exists as polymeric amidinium salt in which the amidinium groups adopt an asymmetric *ZE* conformation [6]. In another approach, mixtures of chromophores containing aromatic hydroxy groups with aliphatic polyacetamidines were investigated by UV/Vis spectroscopy [8–10]. A strong bathochromic shift of the chromophore's longest UV absorption band by more than 100 nm was observed. This could be explained by deprotonation of the chromophores by the polymer.

Using bifunctional proton donors, ionic network formation can be assumed. This could be proved in case of chromophores with two aromatic hydroxy groups [8]. Although deprotonation of the chromophores was not complete, a strong influence on the glass transition of the polymer was observed. Interactions of carboxylic acids with polyamidines are even stronger. Hence, ionic network formation should be pronounced when using dicarboxylic acids.

Our interest is to study the polymer network formation of aliphatic polyamidines with aliphatic dicarboxylic acids. It is widely accepted that FT-IR spectroscopy is a sensitive tool for studying specific interactions, particularly hydrogen bonds in polymer blends. Here, the influence of temperature

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and composition on interactions in mixtures of poly(1,8-octamethyleneacetamidine) $-((CH_2)_8-N{=}C(CH_3)-NH)_n-$ with glutaric acid is described by means of FT-IR spectroscopy.

2. Experimental

2.1. Materials

Commercially available 1,8-octanediamine (Fluka), phenol (Fluka), and glutaric acid (Fluka) were used without further purification. Triethyl orthoacetate were stored over molecular sieves and purified by distillation prior to use.

2.2. Poly(1,8-octamethyleneacetamidine) (POA)

The phenol catalyzed preparation of POA by conversion of 1,8-octanediamine with triethyl orthoacetate was described earlier [6].

2.3. Temperature-dependent Fourier transform infrared spectroscopy (FT-IR)

The samples were prepared as thin films between two potassium bromide discs by solvent casting from methanol. All discs were carefully dried under vacuum in a desiccator prior to use. A variable temperature cell equipped with a temperature control unit (SPECAC) was used for the temperature-dependent IR transmission measurements in a Bruker spectrometer IFS 66 with DTGS detector. The spectra were recorded in the spectral range of 4000–600 cm^{-1} with a resolution of 2 cm^{-1}, 16 scans/spectrum were co-added. The heating runs were done stepwise (in steps of 10 K, heating rate 10 K/min) from 25 to 150 °C. The spectra were measured in steady-state under the given temperature. The processes were reversible, and after cooling the same spectrum was obtained as in the beginning. In some cases a decrease of the signal intensities was observed which was attributed to a reduction of the film thickness during melting. It could not be prevented completely that a small part of the polymer flowed out. Therefore, the discussion is mainly focused on the alterations of the band positions and not on the intensities.

3. Results and discussion

In order to understand physical network formation in mixtures of POA with glutaric acid, the interactions of the single components have to be taken into account. It is well known that acetamidine groups are able to form single hydrogen bridged chain-like associates [11] and that carboxylic acid groups form dimers with two hydrogen bonds [12,13]. In order to be able to separate interactions between amidine groups and carboxylic groups from those mentioned before, temperature-dependent IR spectra of the single components and their mixtures were recorded. The different interactions under discussion are summerized in Scheme 1.

3.1. Polyacetamidine

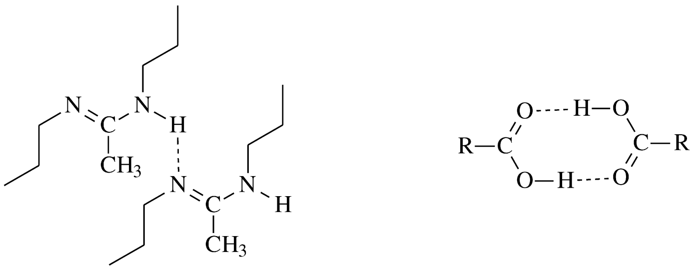
Fig. 1 shows the IR spectra of pure POA in the range of 1200–1800 and 2600–3500 cm^{-1}. The polymer possesses absorption bands at 3277, 2925, 2853, 1636, 1539, 1457, 1362, and 1296 cm^{-1}, which are attributed to the $\nu(NH_{assoc})$, $\nu_{as}(CH_2)$, $\nu_s(CH_2)$, $\nu(C{=}N)$, $\delta(NH)$, $\delta(CH_2)$, and (C–N) vibrations, respectively.

With increasing temperature, some spectral alterations were observed. The wide intensity decrease of the spectra at higher temperatures is most probably caused by a decrease in the thickness of the films after melting. Loss of physically absorbed residual water has an additional influence on the intensity in the region above 3000 cm^{-1}. The distinct shift of the bending vibration band of the NH groups at 1539 cm^{-1} to the lower wave number region (1497 cm^{-1}) can be explained by the destruction of initial carbaminat structures, which were formed at room temperature with CO_2 in air. These structures break at higher temperature, as described in Scheme 2 and do not appear again after cooling the samples in the CO_2 free heating cell.

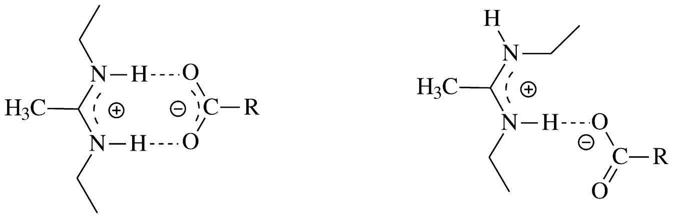
Apart from the before mentioned influences, real temperature depending structural changes that include association effects of the amidine groups could be observed. Thus, the small shift in the stretching vibration band of C=N at 1636 cm^{-1} to the higher wave number region can be attributed to the breaking of hydrogen bonds between the amidine groups in the polymer. The maximum shift was seen at 130 °C. The loss of association at higher temperature results in an increase of the C=N bond strength that explains easily the band shift to higher wavenumbers. The corresponding complex C–N band at 1296 cm^{-1} shifts to lower wavenumbers since, its partial double bond character in a hydrogen bond disappears. At the same time the band at 3277 cm^{-1} corresponding to the stretching vibration of associated NH groups decreases and shifts to higher wavenumbers. At a temperature of 130 °C a small absorption band corresponding to free NH groups appears at 3445 cm^{-1}. This temperature behavior is reversible and clearly indicates the existence of hydrogen bonds in the polymer, which are weaker at elevated temperatures.

3.2. Glutaric acid

Fig. 2 shows the IR spectra of glutaric acid at three different temperatures (room temperature, 70 and 100 °C). The spectra are clearly influenced by intermolecular hydrogen bondings between the carboxylic acid groups resulting in the formation of cyclic dimers, and their destruction near the melting point at 98 °C. Comparing the spectra obtained at room temperature and at 70 °C, it



H-bonds in acetamidines H-bonds between carboxylic acid groups



H-bonds in ionic complexes of amidines and carboxylic acid groups

Scheme 1.

becomes evident that two different solid phase structures must exist. We assume differences in the sample crystallinity, which influence especially the spectrum in the fingerprint region.

When the temperature is increased, the peak at 3047 cm^{-1} corresponding to the O–H stretching vibration of the carboxyl groups in association (intermolecular hydrogen bonding) shifts to higher wavenumbers. At 100 °C, the spectrum of the molten acid shows a band at 3250 cm^{-1} corresponding to free carboxylic acid groups. Simultaneously, the C=O stretching band of the carboxyl groups at 1697 cm^{-1} shifts to higher wavenumbers (1710 cm^{-1}) and a shoulder appears at 1730 cm^{-1} which also comes from free carboxyl groups. So, breaking of the intermolecular hydrogen bonds at higher temperature was indicated clearly.

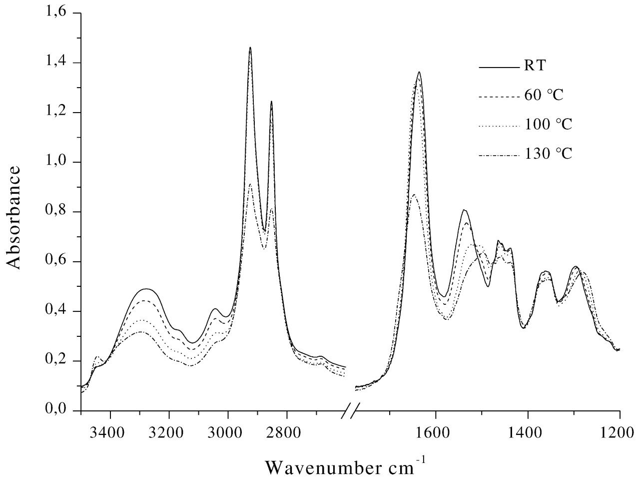
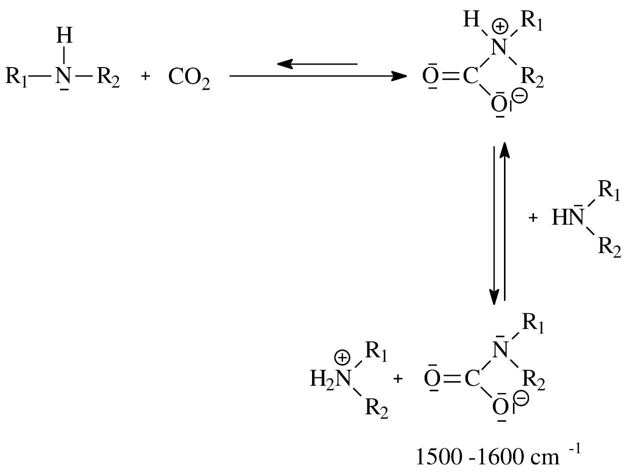


Fig. 1. IR spectra of POA in the range of 1200–1800 and 2600–3500 cm^{-1} at room temperature, 60, 100, and 130 °C.

After cooling glutaric acid back to room temperature, the initial structure could not be recovered. Instead of this, the solid phase structure already observed at 70 °C was obtained. At least the re-formation of hydrogen bondings occurred unambiguously.

3.3. Mixtures of polyacetamidine with glutaric acid

Mixtures of POA and glutaric acid were prepared by dissolving both components in ethanol and subsequent evaporation of the solvent. Related to the number of amidine groups, the equivalent concentration of glutaric acid in the mixtures was 0.80 and 1.6, respectively. That



Scheme 2.

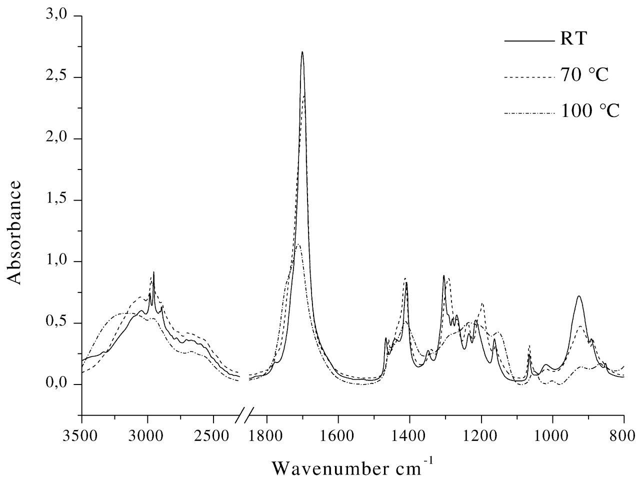


Fig. 2. IR spectra of glutaric acid recorded at room temperature, 70, and 100 °C.

means the content of carboxylic acid groups in the first mixture was below the equimolar ratio whereas in the second one it was above. In the following discussion these mixtures are referred as M0.8 and M1.6.

Fig. 3 shows the IR spectra of the single components and the mixtures at room temperature in the range from 1350 to 1800 cm^{-1}. Comparing the spectrum of the pure polymer (a) with those of the mixtures (b) and (c), a distinct shift of the C=N stretching vibration at about 1635 cm^{-1} to higher wavelengths (ca 1657 cm^{-1}) can be seen. Obviously, the interactions strongly influence the vibration behavior of the amidine group.

Even more pronounced is the influence on the C=O stretching vibration of glutaric acid at 1697 cm^{-1} is even more pronounced (d). In the spectrum of the mixture M0.8 (b), this band completely disappears. Instead of this, two new bands at 1563 and 1393 cm^{-1} corresponding to the antisymmetric and symmetric stretching vibration of the carboxylate anion can be seen. The complete disappearance of the C=O stretching vibration points to the complete deprotonation of glutaric acid by the polymer. In case of the mixture M1.6 (c), the C=O stretching vibration can be seen beside the carboxylate bands. Compared to pure glutaric acid, the slightly shifted position of the C=O stretching vibration to higher wavenumbers indicate a reduced self-association of the remaining carboxylic acid groups. This is not surprising since, the carboxylic acid groups are diluted by the polymer, hence association is reduced. Further bands of the excess acid were found at 2963, 1446 and 1068 cm^{-1}. From these results it can be concluded that the entire amidine groups present in the system are in interaction with the carboxylic acid groups and the excess of carboxylic groups exists as unassociated free carboxylic acid.

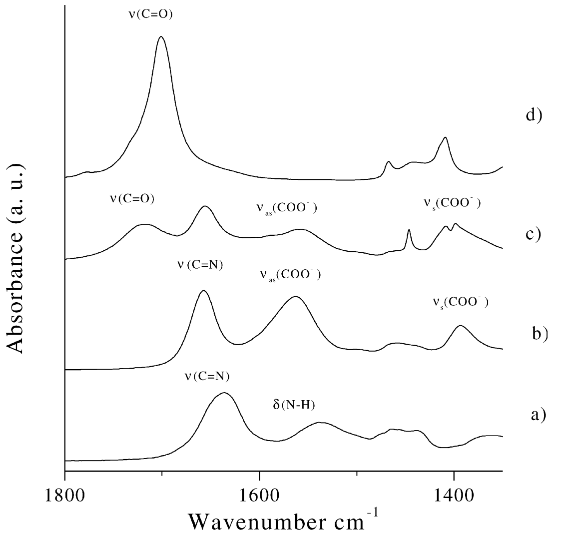


Fig. 3. IR spectra of (a) POA, (b) M0.8, (c) M1.6, and (d) glutaric acid.

Additional hints for the formation of carboxylate anions are the disappearance of the typical broad band of the associated carboxyl groups in the 3000–3500 cm^{-1} region, and the disappearance of the N–H stretching and deformation bands at 3277 and 1539 cm^{-1}. On the other hand, there is a new shape of the absorptions in the range from 2500 to 3500 cm^{-1} with two peaks at 3194 and 3060 cm^{-1}, beside the methylene stretching bands. This comes from the amidinium ion structures formed by the interaction.

Fig. 4 shows the IR spectra of M0.8 in the range from 1350 to 1800 and 2500 to 3600 cm^{-1} at different temperatures. The temperature was increased stepwise from room temperature to 150 °C with a heating rate of 10 K/min. The bands in the spectra do not show any considerable shifts in their positions, which shows the stability of the ionic complexes formed up to at least 150 °C. Additionally, there is no evidence for free carboxylic acid, the vibration band of which would be expected at 3200 cm^{-1}. This supports the idea that all carboxylic acid groups present in the system are bonded ionically with the amidine groups.

The mixture M1.6 containing an excess of carboxylic acid groups behaves similarly. The positions of the bands do

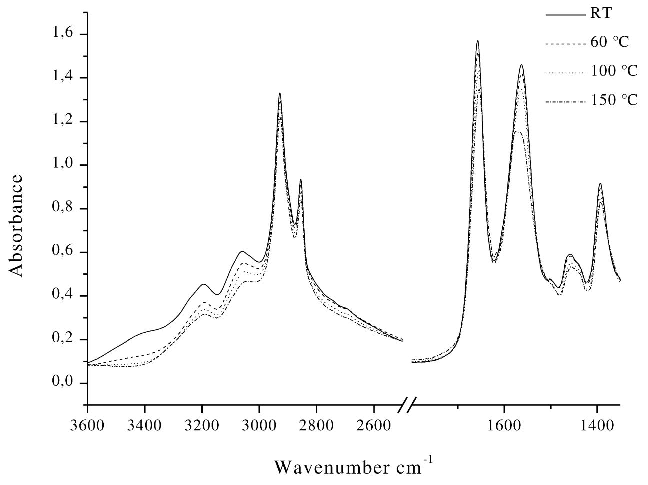


Fig. 4. IR spectra of M0.8 recorded at room temperature, 60, 100, and 150 °C.

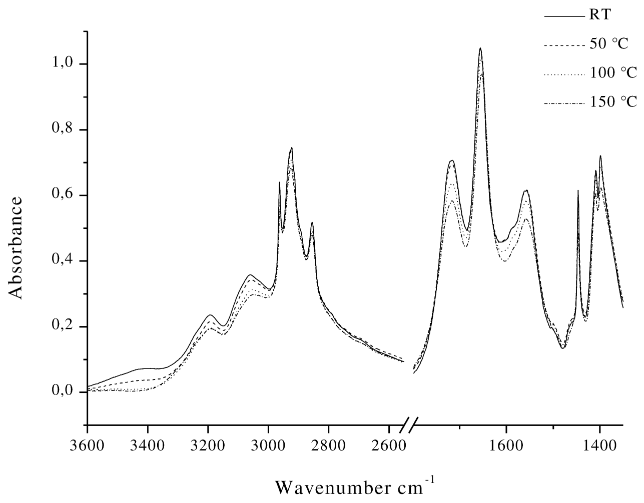


Fig. 5. IR spectra of M1.6 recorded at room temperature, 50, 100, and 150 °C.

not change strongly with either of the increasing temperatures (see Fig. 5). This also concerns the bands of the carboxylic acid groups, which are not in complex with amidine groups, e.g. at 2962 and 1716 cm^{-1}. The small temperature sensitivity of these bands supports the assumption that the excess of carboxylic acid is not self-associated and exists as a free carboxylic acid irrespective of the temperature.

4. Conclusions

IR measurements showed that both polyacetamidine POA and glutaric acid form distinct hydrogen bondings between their molecules. These investigations confirm the association behavior of acetamidine and carboxylic acid groups, which are known to interact via single hydrogen bridged chain-like associates and dimers with two hydrogen bonds, respectively. These interactions break at higher temperatures, which could be concluded from temperature-dependent IR measurements.

In mixtures of POA and glutaric acid, the intermolecular interactions between the components predominate, whereas, the interactions of the single components are completely suppressed. As concluded from the IR spectra, the strongly basic polymer abstracts protons from glutaric acid resulting in the formation of ionic complexes. This deprotonation is nearly quantitative as long as the number of amidine groups exceeds the number of acidic groups. In a mixture with an excess of glutaric acid, unassociated free carboxylic acid groups could be evidenced. The ionic complexes formed between amidine and carboxylic acid groups are stable up to at least 150 °C.

The structure of the ionic complexes cannot be drawn from the IR spectra. For similar complexes of the low molecular weight *N*,*N*-diphenylacetamidine with various carboxylic acid compounds, interactions through one or two parallel intramolecular N–H···O bonds are discussed [14, 15]. Own NMR investigations [6] on POA in solution of trifluoroacetic acid rather point to the formation of a single N–H···O bond in our system, since the adopted *ZE* conformation of the amidinium group does not allow to form two parallel bonds. About the situation in the solid phase or in melt no information is available.

Since the formation of the complexes is quantitative and the glutaric acid is dibasic, one can conclude that an ionic network has to be formed in which the glutaric acid acts as cross-linker between the polyamidine chains. The influence of these interactions on the polymer properties will be the subject of further investigations.

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