

Hydrogen bonding in aliphatic poly(amides)

Dependence of infra-red spectra and density on chemical composition

M. Wöbkemeier and G. Hinrichsen*

Technical University of Berlin, Institute of Nonmetallic Materials, Polymer Physics,
Englische Strasse 20, D-1000 Berlin 12

Summary

A great number of aliphatic poly(amides) was investigated by i.r. spectroscopy and density measurements. The relative integral intensity of the characteristic NH stretching vibration shows a quantitative dependence on the chemical composition of the respective poly(amide) and can be used for the identification of an unknown material. The density varies systematically with the concentration of the hydrogen bonds.

Introduction

Structural characteristic of both aliphatic and aromatic poly(amides) is the existence of a three-dimensional network of hydrogen bonds which is formed by the carbonamide groups within the crystalline as well as the amorphous regions. The concentration of the carbonamide groups and according to this number of possible hydrogen bonds is fixed by the chemical structure of the respective aliphatic poly(amide). The concentration is expressed by the ratio of the carbonamide groups to the number of the carbon atoms in the methylene sequences between the CONH-groups and influences e.g. the melting point, heat of fusion, crystal structure, absorption of water, and many other properties (1,2).

In general, i.r. spectra of various aliphatic poly(amides) dominated by the symmetrical and asymmetrical vibrations of the CH₂-groups and the band of the hydrogen bonded NH-stretching vibration differ not very much from each other with regard to the wavenumber of the respective vibration. The relative peak area of the NH-vibrations within the i.r. absorbance spectra can be considered as a measure of the concentration of hydrogen bonds. A more precise characterization of the nature of hydrogen bonds in poly(amides) is given by Coleman and coworkers (3 - 5).

Experimental

13 different aliphatic poly(amides) which are listed in Table 1 were kindly supplied by ATO, BAYER AG, DSM, EMS CHEMIE, and HUELS AG, resp.

Samples for i.r. spectroscopical investigations were prepared by casting films from a solution of the polymer in trifluoroacetic acid or 2,2,2-trifluoroethanol onto the bottom of a quartz cuvette, which was kept at constant temperature (315 K) for 24 h under vacuum. Subsequently, the films were stripped off, annealed for 1 h at 373 K, dried at 333 K for 23 h, and finally stored for 4 weeks in a mini-desiccator over silica gel. The thickness of the films ranged from 1 to 4 μm .

Spectra were acquired on a Nicolet model 10 DX Fourier transform infra-red spectrometer at a resolution of 4 cm^{-1} . A minimum of 64 scans was signal averaged and the absorbance spectra were stored on magnetic discs.

*To whom offprint requests should be sent

Spectra could be observed in the temperature interval between 140 and 450 K using a special temperature chamber which is described elsewhere (6). The spectra were recorded in steps of 10 K.

Densities of the dry specimens were measured using a density gradient column filled with mixtures of carbon tetrachloride and cyclohexane at 297 K.

Results and discussion

i.r. spectroscopy

The concentration of the carbonamide groups in aliphatic poly(amides) is given by the character z which is defined by the quotient of the number of the carbon atoms of the CH_2 -sequences and the number of the carbonamide groups, see Table 1.

Table 1. Characteristic values of the investigated poly(amides)

poly(amide)	composition z	density g/cm^3	melting point K
4	3	1,2300	533
4,6	4	1,1805	567
6	5	1,1535	496
6,6	5	-	538
4,8	5	1,1470	529
4,10	6	1,1045	523
11,6	7,5	1,0660	491
12,6	8	-	509
8,10	8	1,0701	481
9	8	1,0690	-
11	10	1,0425	463
12	11	1,0065	452
12,12	11	1,0105	457
12,20	15	1,0040	442

As can be recognized from Table 2 the characteristic i.r. bands of the poly(amides) do not shift very much for the specimens of different chemical structure.

Table 2. Wavenumbers (cm^{-1}) of characteristic bands of different poly(amides)

PA 6	PA 11,6	PA 11	PA 12,12	Vibration
3296	3295	3295	3306	NH stretching
2937	2921	2921	2920	CH_2 asymmetrical
2870	2851	2851	2850	CH_2 symmetrical
1641	1638	1639	1640	Amide I
1544	1546	1555	1545	Amide II
1464	1466	1466	1468	σ (CH_2)
1265	1275	1260	1273	Amide III
720	722	720	721	Amide V
690	696		696	Amide V

In order to analyze the spectra quantitatively the peak area under the NH stretching vibration ($3150 - 3500 \text{ cm}^{-1}$) and the CH_2 vibrations ($2700 - 3000 \text{ cm}^{-1}$) resp. was calculated by a computer program after se-

paration of underground intensity by a basis (straight) line (6), see Figure 1. The relative intensity of the NH stretching vibrations, R , is defined by

$$R = \frac{\text{Integrated intensity of NH stretching vibrations}}{\text{Integrated intensity of CH}_2 \text{ vibrations}} \quad (1)$$

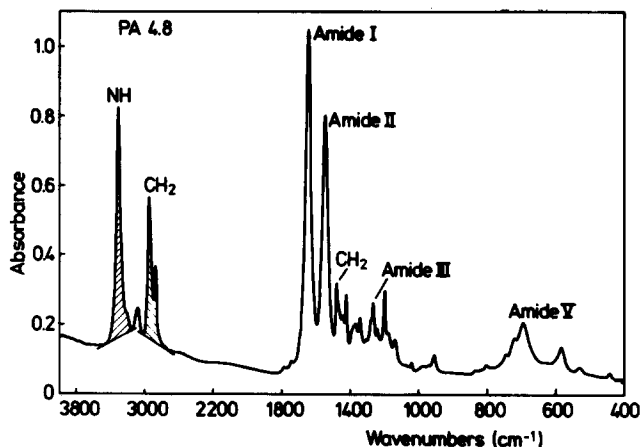


Figure 1: Infra-red absorbance spectrum of poly(amide) 4,8 showing the characteristic vibrations. The dotted areas are used in order to calculate the relative intensity of the NH stretching vibrations, R , (see text)

In the simplest model this quantity, R , is supposed to be proportional to the concentration of the carbonamide groups, i.e. inversely proportional to the character z .

$$R = A \cdot \frac{1}{z}, \quad A = \text{constant} \quad (2)$$

By logarithmation one gets

$$\begin{aligned} \ln R &= -\ln z + \ln A \\ &= -\ln z + C, \quad C = \text{constant} \end{aligned} \quad (3)$$

Therefore in Figure 2 $\ln z$ is plotted in dependence of $\ln R$. Within the limits of experimental error a straight line is obtained with a slope of -1.69 which differs from the theoretical value of -1.00 demanded by equation (3). Thus, the experimental data at room temperature can be represented by the following equations

$$\ln R = -1.69 \cdot \ln z + 3.08 \quad (4)$$

$$\text{or} \quad R = 21,76 \cdot \frac{1}{z^{1.69}} \quad (5)$$

The deviation of the observed exponent from the theoretical value may be due to the fact that the absorption coefficient of the different aliphatic poly(amides) varies from species to species in a systematic manner. This means that the absorbance A has to be expressed by

$$A(z) = a(z) \cdot b \cdot c \quad (6)$$

where $a(z)$ molar absorptivity depending on the chemical composition of the respective poly(amide)

- b path length of radiation within the sample
 c molar concentration of NH groups.

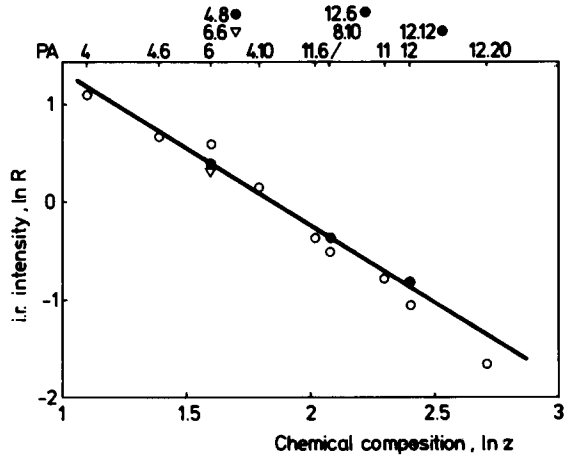


Figure 2. Dependence of relative integral i.r. intensity of NH stretching vibrations, R , on the chemical composition of aliphatic poly(amides) characterized by quantity z (see text). Measurements were performed at room temperature.

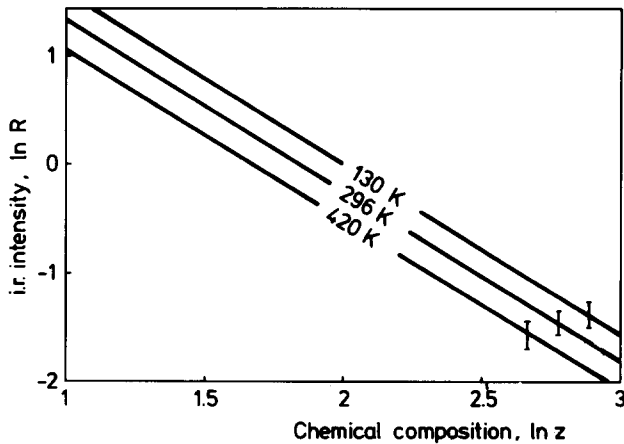


Figure 3. Same plotting as in Figure 2. The measurements were performed at different temperature (130, 296 and 420 K resp.)

Analogous results on CH_3 groups containing linear low density poly (ethylene) with different types of branching (methyl, ethyl, n-butyl, n-hexyl, iso-butyl) showing the dependence of the molar absorptivity on the type of branching have been reported recently (7).

Coming to other temperatures than room temperature it is observed that equation (4) remains valid at very low temperature (~ 130 K) and high temperature (~ 420 K) with the exception of the absolute value of constant C, as shown in Figure 3. Equation (4) does not hold within the temperature intervals around 200 and 310 K resp. where mechanical relaxation takes place.

Equation (4) can be used in order to identify the chemical composition of any aliphatic poly(amide) by i.r. spectroscopy.

Density

The density of the investigated poly(amides) is plotted in Figure 4 as a function of the concentration of carbonamide groups, characterized by the quantity z. This figure confirms the well-known fact that the molecules are aligned closer by increasing concentration of hydrogen bonds and that the density reaches that of poly(ethylene) if the quantity z tends to very high numbers (8). Besides the chemical composition the actual density of each poly(amide) is influenced by the crystallinity in a minor degree (9).

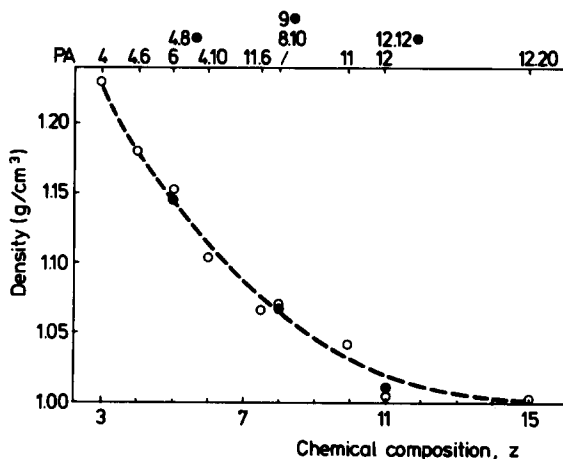


Figure 4: Dependence of density of aliphatic poly(amides) on the chemical composition, characterized by quantity z (see text)

Acknowledgement

The financial support of the Deutsche Forschungsgemeinschaft (DFG) is greatly appreciated. The authors also wish to thank ATO, BAYER AG, DSM, EMS CHEMIE, and HUELS AG for supplying the poly(amides) used in this study.

References

1. J. Brandrup, H.E. Immergut, (Eds.), Polymer Handbook, J. Wiley & Sons, New York 1975

2. R. Vieweg, A. Müller, (Eds.), *Kunststoff-Handbuch*, Vol. VI, Polyamide, Hanser-Verlag, München 1966
3. M.M. Coleman, D.J. Skrovanek, P.C. Painter, *Makromol. Chem., Makromol. Symp.* 5, 21 (1986)
4. D.J. Skrovanek, S.E. Howe, P.C. Painter, M.M. Coleman, *Macromolecules* 18, 1676 (1985)
5. D.J. Skrovanek, P.C. Painter, M.M. Coleman, *Macromolecules* 19, 699 (1986)
6. M. Wöbkemeier, G. Hinrichsen, H.J. Jahr, to be published
7. T. Usami, S. Takayama, *Polym. J.* 16, 731 (1984)
8. A. Müller, R. Pflüger, *Kunststoffe* 50, 203 (1960)
9. G. Hinrichsen, *Coll. & Polym.Sci.* 256, 9 (1978)

Accepted April 10, 1989 C