Structural Investigation of Polyurethanes: Infrared Spectroscopic Investigations of Monomeric and Polymeric *N,N'*-Diaryl Ureas

J. HOCKER, *Zentralbereich Zentrale Forschung und Entwicklung Bayer AG, D-5090 Leverkusen-Bayerwerk, Federal Republic of Germany*

Synopsis

The carbonyl stretching vibration of crystalline *N,N'*-diaryl ureas at 1640 cm^{-1} undergoes a very considerable shift to 1700 cm^{-1} when these compounds are in solution. This finding is of particular significance in connection with the hard segments of polyurethane elastomers. The absence of a carbonyl band at 1640 cm^{-1} in polyurethane–polyurea systems does not indicate the absence of urea groups or the reaction of urea groups to biuret groups. Urea groups may instead be present in the dissolved, i.e., noncrystalline, form. On the other hand, the absorption at 1640 cm^{-1} is suitable for the determination of crystallization kinetics.

INTRODUCTION

The spectroscopic properties of ureas appear to be fairly well known. However, a number of discrepancies in the literature redirected our attention to this class of compounds, whose importance in the chemistry of polyurethanes is so great. For instance, Merten et al.[1–3] found no absorption at 1640 cm^{-1} in the infrared spectrum of a polyurethane foam produced with the aid of water and attributed this to a secondary reaction of the polyurea with isocyanate to form the biuret. An attempt, using model compounds and analogous conditions, to reproduce such a secondary reaction to form the biuret was, however, unsuccessful. Rossmy et al.,[4] on the other hand, attributed the absence of the typical urea absorption at 1640 cm^{-1} in the spectrum of a water-expanded polyurethane–polyurea foam to the intermediate formation of carbamic acids. This assumption would not explain the continuous polymerization (and consequent increase in viscosity) or the evolution of carbon dioxide, which already begins at the start of the reaction.

Our own investigations of the reactivity of electron-rich olefins[5] or of the imidazolinium salts obtainable therefrom led us to a 1:1 molecule complex consisting of 1,3-diphenylimidazolinium chloride I and diphenyl urea II, which had no band in the infrared spectrum at 1640 cm^{-1}.
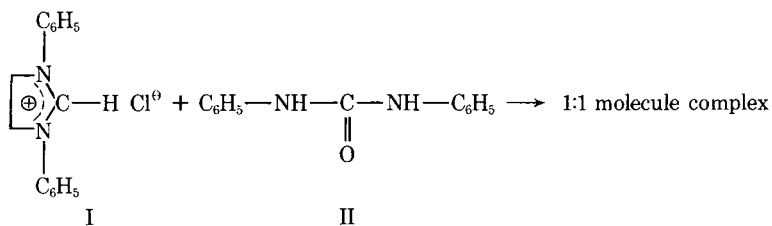
On the other hand, absorption was found to occur within a range that is entirely exceptional where solid aromatic ureas are concerned, namely at 1697 cm^{-1} with a side band at 1718 cm^{-1} (KBr pellet).

As polyureas are of great importance in the chemistry of polyurethanes, especially in connection with the hard segments of polyurethane elastomers, it appeared to us that the infrared-spectroscopic behavior of the ureas ought to be investigated in detail with the aid of model substances.

EXPERIMENTAL METHODS

The IR spectra were determined with the Perkin–Elmer Infrared Grating Spectrophotometer 521 and NaCl Spectrophotometer 157. The crystalline substances were measured as KBr pellets. The spectra of the solutions were determined in NaCl cuvets with compensation of solvent. The Fourier-transformed infrared (FT-IR) spectra of very dilute solutions were determined with the Digilab Fourier IR Spectrophotometer FTS-14 with mathematical subtraction of the solvent.

MONOMERIC *N,N'*-DIARYL-SUBSTITUTED UREAS

N,N'-Diphenyl Urea

The simplest representative of the *N,N'*-diaryl-substituted ureas is diphenyl urea. As many aromatic polyureas may be regarded as substituted diphenyl ureas, this compound is particularly suitable as a model substance for the study of IR-spectroscopic properties.

The IR spectrum of crystalline diphenyl urea, examined as a KBr pellet, contains the characteristic and familiar absorptions [Fig. 1(a)]: The C=O stretching vibration appears as expected, at 1640 cm^{-1}, the amide band II (—C—N—H) at 1543 cm^{-1}, and the NH stretching vibrations at 3275–3325 cm^{-1}. The last mentioned are the vibrations of associated NH groups:

If the NH protons are replaced by deuterium (completely deuterized diphenyl urea is obtained most simply by reacting phenyl isocyanate with D$_2$O), the absorptions are shifted—to some extent considerably—in the following manner[6] [Fig. 1(b)]: The N—D stretching vibration now appears at 2400–2500 cm^{-1} and the amide band II is shifted from 1543 to ca. 1460 cm^{-1}, a shift which indicates the important contribution made by the proton to the —C—N—H— or —C—N—D— vibration. In the spectrum of the deuterized diphenyl urea the C=O stretching vibration is shifted in the direction of longer wavelengths from 1640 to 1630 cm^{-1}, which indicates that this is influenced by a proton and that the vibration is either not exclusively a C=O stretching vibration (case a) or that it is influenced by hydrogen bridges (case b):

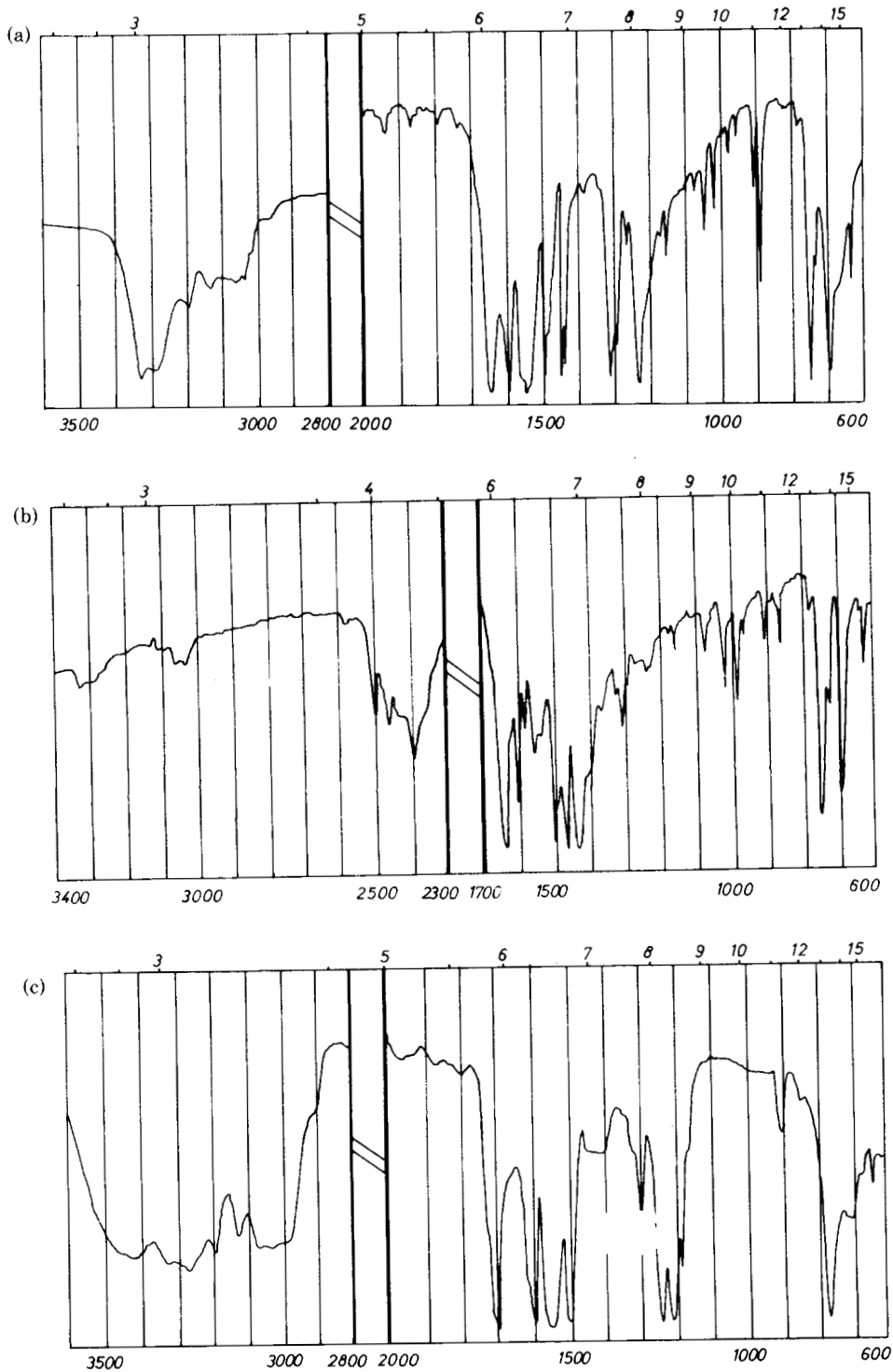Regarding the interpretation of additional bands see ref. 6.

Fig. 1. (a) Characteristic and familiar absorption of IR spectrum examined as Kr pellet. (b) NH protons replaced by deuterium showing shifted absorptions. (c) IR spectrum of diphenyl urea in dimethyl sulfoxide.

With a view to finding out more about the nature of the intermolecular and intramolecular binding, we determined the spectra of solutions. Although the IR spectra of solutions of aliphatic substituted ureas have been investigated in detail, there is almost no literature on the solution spectra of aromatic substituted ureas—presumably owing to the poor solubility of the compounds.

One of the few good solvents for diphenyl urea is dimethyl sulfoxide (DMSO). If, now, one determines the IR spectrum of diphenyl urea in dimethyl sulfoxide [Fig. 1(c)], one finds, unexpectedly, that the carbonyl band is shifted from 1640 (KBr) to 1697 cm^{-1} (main band) and 1720 cm^{-1} (shoulder) (in the case of a ~2% by weight solution in DMSO, 0.05 mm NaCl cuvette). Within the range 0.1–10% by weight, the position of these bands is independent of the concentration. The spectrum permits no conclusions regarding the NH absorptions because a broad absorption (DMSO, H$_2$O) covers the range 3000–3500 cm^{-1}. Much the same can be said of a solution of diphenyl urea in pyridine-d_5: The C=O stretching vibration is even shifted to 1702 cm^{-1} (with a shoulder at 1720 cm^{-1}).[7]

Since the solubilities of the urea in the less polar solvents CCl$_4$ and CHCl$_3$ were inadequate, it was not possible to obtain solution spectra in the normal way. It was found, however, that the Fourier transformation method gives satisfactory spectra in both CCl$_4$ and CHCl$_3$: in the spectrum of a saturated solution in CCl$_4$ the carbonyl absorption occurs at 1705 cm^{-1}.

In the case of a saturated solution in CHCl$_3$ (Fig. 2) the carbonyl absorption likewise occurs at 1705 cm^{-1}, but it is accompanied by a shoulder at 1687 cm^{-1}. In addition, a fairly distinct absorption appears in the NH range at 3425 cm^{-1}.

This absorption must be assigned to the stretching vibration of a *non*associated NH group. It follows that as a solution in CCl$_4$ or CHCl$_3$, diphenyl urea is not associated. An association of the carbonyl group in DMSO or pyridine solution (self-association or association with the solvent) likewise appears unlikely in view of the position of the carbonyl absorption. As no distinct absorptions were observed above 3400 cm^{-1}, an association of the NH group with the solvent cannot be ruled out.
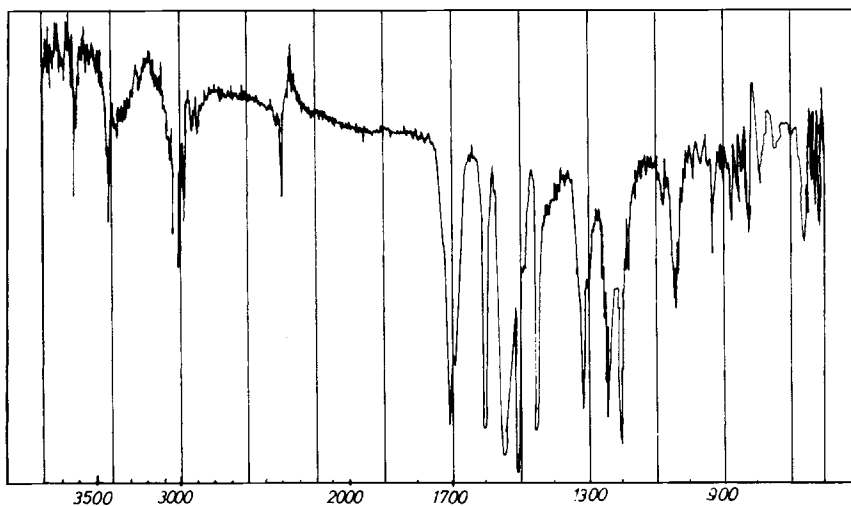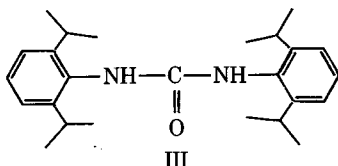

Fig. 2. Saturated solution in CHCl$_3$.

N,N'-Di-(2,6-Diisopropylphenyl) Urea

The behavior of di-(2,6-diisopropylphenyl) urea III, which, in view of the sterical hindrance, was expected to show a reduced tendency to form hydrogen bridges, is similar to that of diphenyl urea:

In the IR spectrum of the crystalline substance [KBr, Fig. 3(a)] the carbonyl band appears at 1635 cm^{-1}, the amide band II at 1540 cm^{-1}, and the NH absorption at 3315 cm^{-1}. The positions of the carbonyl and NH absorptions indicate the presence of associates. In the spectrum of a saturated solution in DMSO (0.05 mm, NaCl cuvet) the carbonyl absorption appears at 1682 cm^{-1} and the amide band II is shifted to 1523 cm^{-1}. The NH zone again permits no conclusions regarding the NH stretching vibration (there is a broad absorption band and possibly association of NH with DMSO). The IR spectrum of a solution in chloroform is more informative [Fig. 3(b)]: The carbonyl absorption appears at 1670 cm^{-1}, the amide band II is shifted still more (to 1490 cm^{-1}), and the NH absorptions occur at 3404–3410 cm$^{-1\cdot}$ The latter are attributable to the *unassociated* urea. Cis–trans conformers are possibly responsible for the occurrence of two NH absorptions. Especially remarkable is the position of the amide band
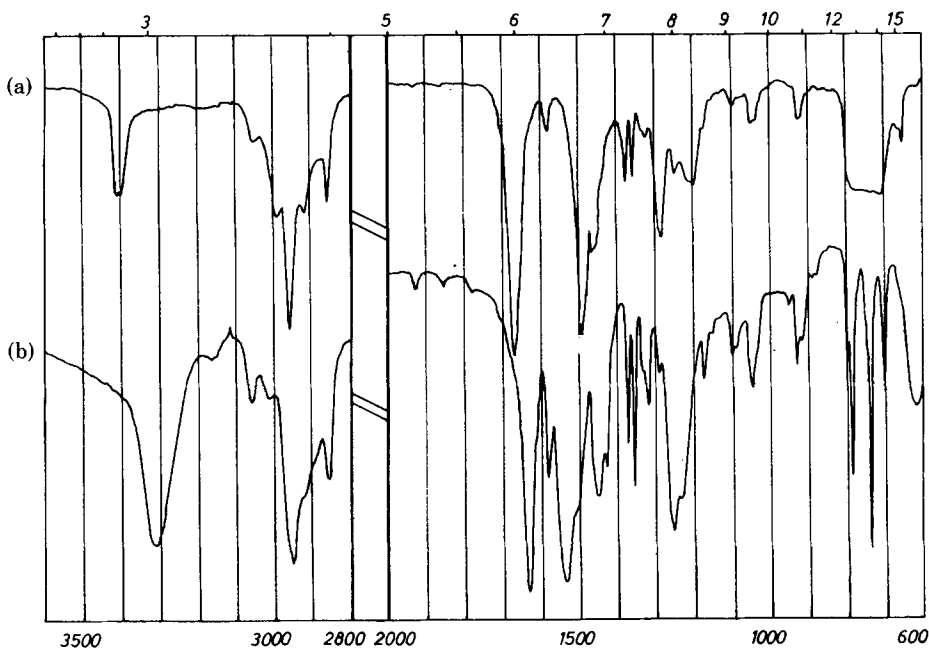

Fig. 3. IR spectrum of N,N'-di-(2,6-diisopropylphenyl)urea: (a) KBr pellet; (b) solution in chloroform.

II <1500 cm^{-1} (it normally appears at ~1550 cm^{-1}). Within the concentration range (0.1–5.0% by weight) the positions of the bands do not change.

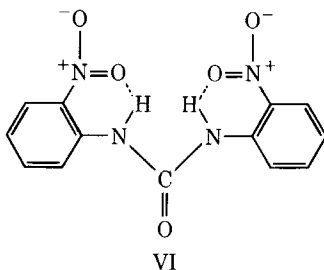### 4,4′-Diethoxydiphenyl Urea and 4,4′-Dinitrodiphenyl Urea

To investigate the influences of electron-donating and electron-accepting groups on symmetrical diaryl ureas we determined the spectra of 4,4′-diethoxydiphenyl urea IV and 4,4′-dinitrodiphenyl urea V:
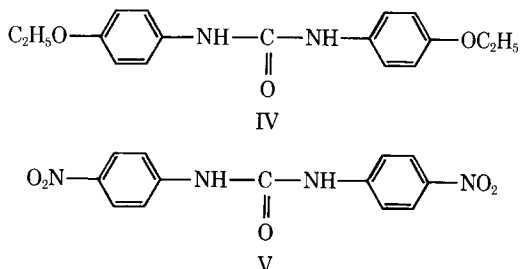
In the spectrum of IV as a KBr pellet [Fig. 4(a)] there is an absorption for the associated carbonyl group at 1630 cm^{-1}, to which the absorption for the associated NH group at 3285 cm^{-1} corresponds. The amide band II appears, as expected, at 1550 cm^{-1}. If, however, the spectrum is determined by the FT method in DMSO, the carbonyl frequency is shifted to 1702 cm^{-1}. (A fairly broad band at 1663 cm^{-1} is possibly attributable to the water contained in DMSO.) The absorption for nonassociated NH appears (despite the possible presence of water in DMSO) at 3450 and 3500 cm^{-1}.

A somewhat more complex picture is presented by compound V: In addition to an absorption at 1618 cm^{-1} the IR spectrum of the crystalline compound [KBr, Fig. 4(b)] has a double band at 1730 and 1738 cm^{-1}. In the NH zone there are two absorptions, attributable to the associated NH vibration, at 3335 and 3363 cm^{-1}.

Here it is possible that intermolecular hydrogen bridges are present in addition to the "normal" —NH . . . O=C association. That would also explain the occurrence at extremely short wavelengths (1730 and 1738 cm^{-1}) of "genuine" free urea carbonyl absorptions. But this finding is not in direct agreement with the IR data of 2,2′-dinitrodiphenyl urea VI [Fig. 4(c)]. The carbonyl absorption of compound VI, in which both NH groups ought to be fixed by intramolecular hydrogen bridges, occurs at 1652 cm^{-1}, and is therefore shifted in the direction of shorter wavelengths, but this position does not agree with that of a free carbonyl group:
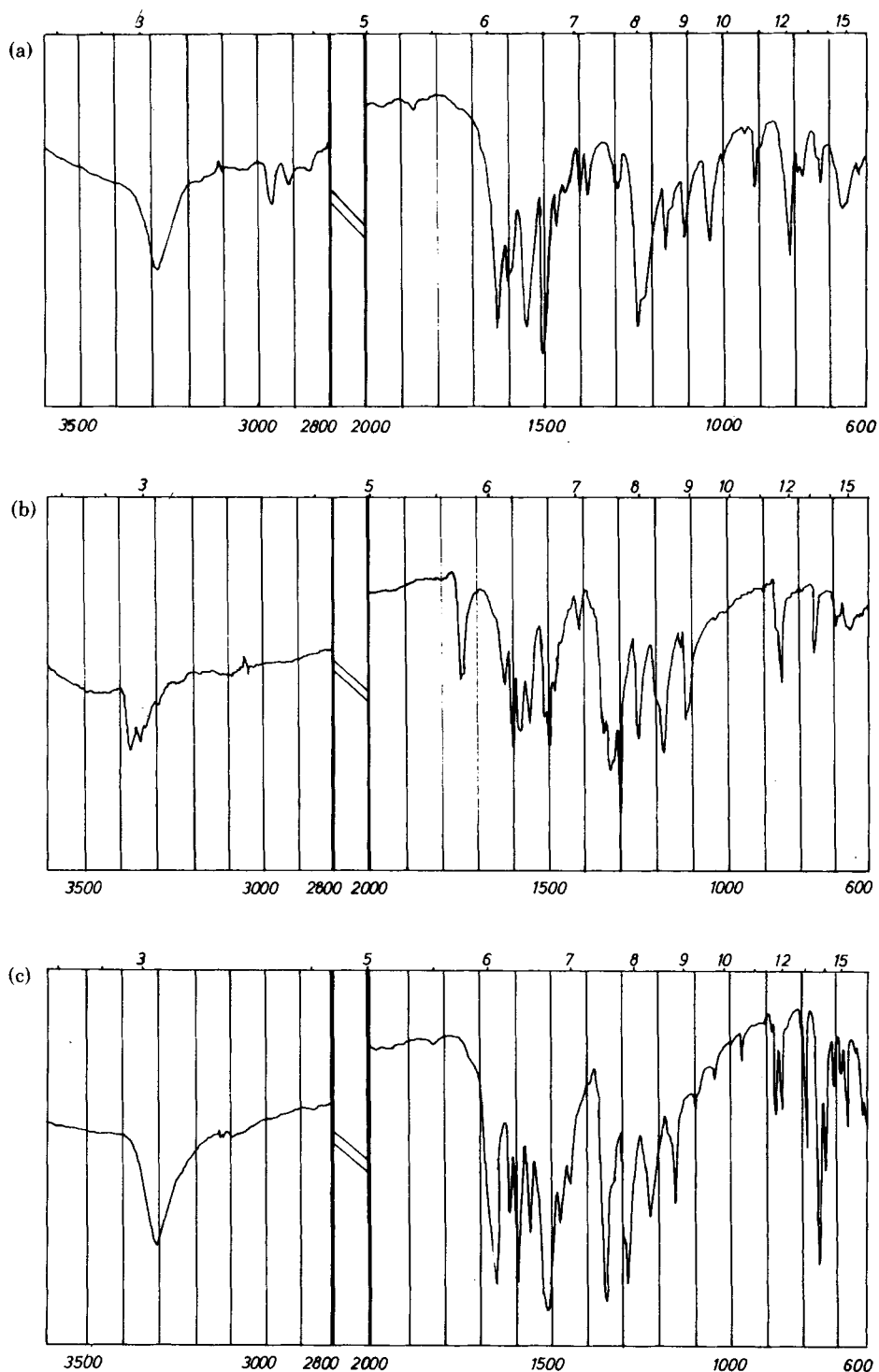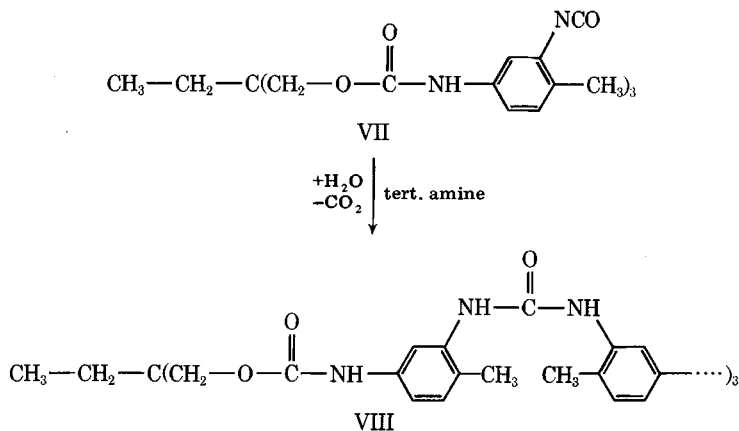
Fig. 4. (a) Spectrum of 4,4'-diethoxydiphenyl urea IV as a KBr pellet. (b) Spectrum of 4,4'-dinitrodiphenyl urea V as a KBr pellet. (c) IR data of 2,2'-dinitrodiphenyl urea VI as a KBr pellet.

POLYMERIC DIARYL UREAS

We first obtained evidence to suggest that the findings for monomeric ureas are also applicable to polyureas when we reacted triisocyanate VII with water:

$$CH_3-CH_2-C(CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\text{[aryl]}-CH_3)_3 \quad (\text{NCO})$$

VII

$$\begin{array}{c} +H_2O \\ -CO_2 \end{array} \Big| \text{ tert. amine}$$

$$CH_3-CH_2-C(CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\text{[aryl]}-CH_3 \quad CH_3-\text{[aryl]}-\cdots)_3$$

VIII

If a thin layer of a mixture of triisocyanate VII[8] with 1% of tertiary amine, serving as a catalyst, is exposed to atmospheric humidity, a clear film VIII is obtained within a few minutes.   An IR spectrum, from which there is surprisingly no absorption in the "urea zone" around 1640 cm^{-1} [Fig. 5(a)], is easily obtained for this film.

In view of the following experiment it appeared to us improbable that urea groups participate in a further reaction to form biuret groups as several authors have assumed[1-3]:
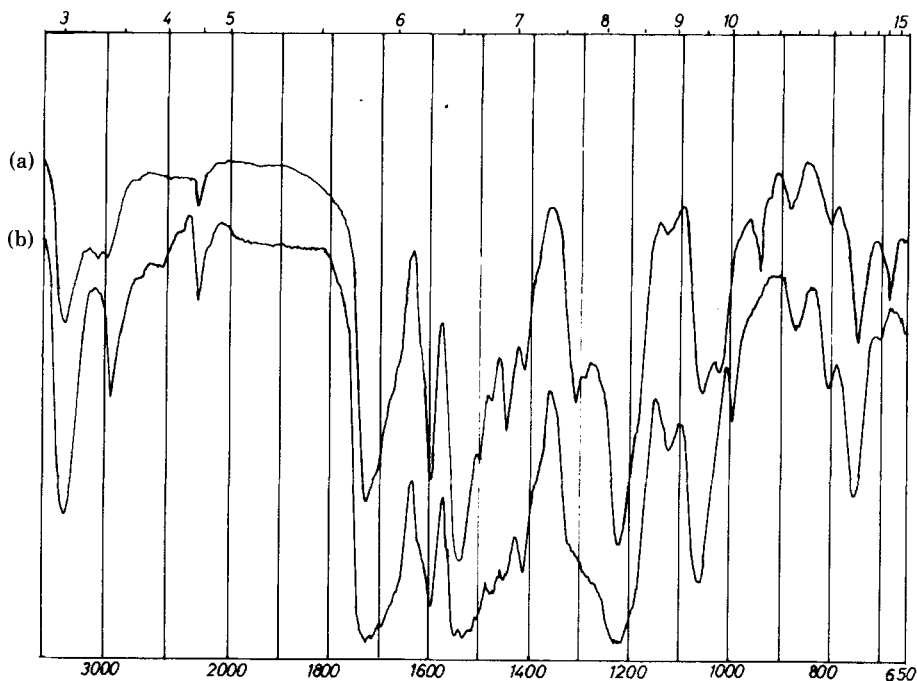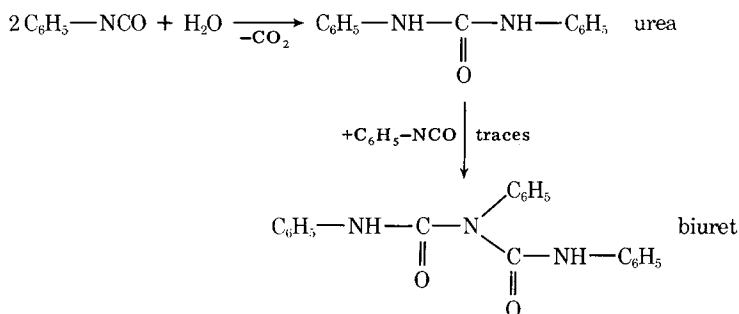

Fig. 5. (a) Compound VIII, a clear film. (b) Result of mixing VIII with diphenyl urea.

After several milliliters of phenyl isocyanate had been mixed with several mg of an amine catalyst in an open dish a crystal slurry was obtained within a few minutes. IR-spectroscopic and thin layer chromatographic determinations showed that diphenyl urea had been formed almost exclusively. Only traces of diphenyl biuret were detected. These two observations showed us that the IR absorption of aromatic polyureas is definitely not restricted to the zone around 1640 cm^{-1}. On the contrary, it varies within wide limits[9]—according to the degree of association:

$$2\,C_6H_5\text{—NCO} + H_2O \xrightarrow[-CO_2]{} C_6H_5\text{—NH—}\underset{\underset{O}{\|}}{C}\text{—NH—}C_6H_5 \quad \text{urea}$$

$$+C_6H_5\text{-NCO} \Big| \text{traces}$$

$$C_6H_5\text{—NH—}\underset{\underset{O}{\|}}{C}\text{—N}\underset{\underset{\underset{O}{\|}}{C}\text{—NH—}C_6H_5}{\overset{C_6H_5}{}} \quad \text{biuret}$$

Proof that urea groups that are "present" in the film do not absorb at 1640 cm^{-1} was provided by the following experiment. When 8.75 g of triisocyanate VII (0.01 mole VII $\hat{=}$ 0.03 mole NCO $\hat{=}$ 0.015 mole urea groups) are mixed with 10 ml of ethyl acetate, 50 mg of amine catalyst, and 1.5 g (0.0075 mole) of diphenyl urea and 5 ml of DMSO is added, a clear solution is obtained, which can be cast and which solidifies in air to form a film. The IR spectrum of this film [Fig. 5(b)] shows no absorption at 1640 cm^{-1} despite the addition of the diphenyl urea.

This band still does not appear when the film has been dried under a high vacuum at 100°C for several hours. To make sure that the added diphenyl urea could not react with the NCO groups of VII to form biuret, the film was extracted in a Soxhlet apparatus with methanol for 20 hr: The diphenyl urea was recovered quantitatively and unchanged. With regard to the reaction products of triisocyanate VII the zone around 1700 cm^{-1}, that is to say the zone in which we expected the urea absorptions, was "occupied" by broad urethane bands. We therefore chose another model substance in order to demonstrate that in polymeric ureas, too, the urea band must be expected primarily, i.e., in the unorientated state, at ~1700 cm^{-1}.

If 20 ml of DMSO is mixed with 1 ml of water and 3 ml of a toluene diisocyanate[10] is added, the formation of the polyurea, accompanied by CO$_2$ formation, begins immediately. After 5 min isocyanate is no longer detectable in the IR spectrum [Fig. 6(a)]. There is, however, a pronounced absorption at 1702 cm^{-1} and an extremely weak absorption at 1650 cm^{-1}. Now, if this solution is poured onto a sodium chloride plate and the resulting film is "precipitated" with a little chloroform, the film becomes opaque. The IR spectrum [Fig. 6(b)] now has two absorptions of approximately equal strength at 1640 cm^{-1} (oriented/crystalline urea portions) and 1702 cm^{-1} (noncrystalline urea portions).

If the same sodium chloride plate is immersed in chloroform for 10 min, an opaque film is obtained, in whose IR spectrum [Fig. 6(c)] only the absorption of orientated urea groups at 1640 cm^{-1} appears. Two conclusions of importance
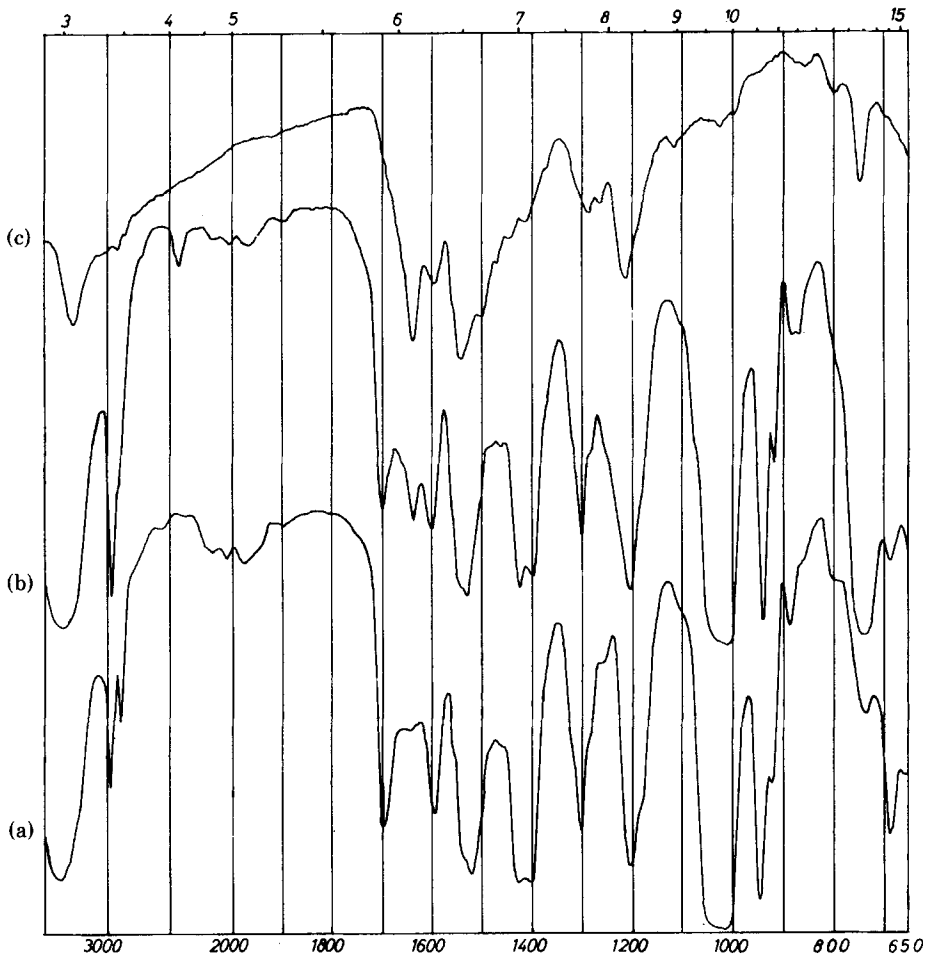
Fig. 6. (a) Polyurea in solution; (b) equal amounts of dissolved and crystalline polyurea; (c) crystalline polyurea.

to the chemistry of polyurethanes can be drawn from the results of the experiments just described.

(1) The fact that the spectra of the "polyurethanes" described in the literature[1-3] showed no absorption at 1640 cm^{-1} does not justify the assumption that the intermediately formed ureas had undergone a further reaction to form biuret. In fact the polyureas are present in the unorientated state and absorb at ~1700 cm^{-1}. Similarly, the methods for the IR-spectroscopic determination of groups in polyurethanes described in *Analytical Chemistry of Polyurethanes*[11] are in need of revision.

(2) The band at 1640 cm^{-1} is wholly unsuitable for the determination of the urea formation kinetics because it is entirely absent from the spectra of unorientated ureas.

In fact all that this band does is to indicate "crystallization kinetics." That also explains why, as frequently happens, the CO_2 formation (expansion reaction) in polyurethane foam reactions is observed, whereas the band in the IR spectrum at 1640 cm^{-1} is absent or does not appear until later.

References

1. R. Merten, G. Braun, and D. Lauerer, *Kunststoffe,* **55,** 249 (1965).

2. R. Merten, D. Lauerer, G. Braun, and M. Dahm, *Makromol. Chem.,* **101,** 337 (1967).

3. R. Merten, D. Lauerer, and M. Dahm, *J. Cell. Plast.,* 262 (1968).

4. G. Rossmy, H. J. Kollmeier, W. Lidy, H. Schator, and M. Wiemann, *Proceedings of the 4th SPI International Cellular Plastics Conference,* Montreal, Technomic, Westport, CT, 1976, p. 166.

5. J. Hocker and R. Merten, *Liebigs Ann. Chem.,* 16 (1978), and previous publications concerning the reactivity of electron-rich olefins.

6. Confer C. I. Jose, *Spectrochim. Acta Part A,* **25,** 111 (1969).

7. A Russian publication (which has not been translated into English) mentions also that diphenyl urea as a solution in THF or polyoxypropylene polyol absorbs at 1715 cm^{-1}; V. V. Zharkov and N. K. Rudnevskii, *Vysokomol. Soedin., Ser. B,* **10,** 29 (1968); in another Russian publication, it is mentioned that "free urea groups have an absorption band in the vicinity of 1710 cm^{-1}." (No experimental evidence is given.); L. I. Kopusov and V. V. Zharkov, *Plast. Massy,* **9,** 66 (1972).

8. As a 75% solution in ethyl acetate.

9. A recent Japanese publication attributes a band at 1695 cm^{-1} to an unassociated urea group in a polyurea. Unlike the present publication, however, it reports no measurements on low-molecular model substances in solution. Our study reports for the first time the simultaneous existence of free and bound carbonyl groups in polyureas and the transition of one form to the other; H. Ishihara, I. Kimura, K. Saito, and H. Ono, *J. Macromol. Sci. Phys.* **10**(4), 591 (1974).

10. Mixture of 80% toluene diisocyanate-(2,4) and 20% toluene diisocyanate-(2,6).

11. D. F. David and H. B. Stanley, "High Polymers," *Analytical Chemistry of Polyurethanes,* Vol. XVI, Part 3, Wiley-Interscience, New York, London, Sydney, Toronto, 1969, p. 335 ff.