Infrared Spectra and Structure of Polyurethane Elastomers from Polytetrahydrofuran, Diphenylmethane-4, 4'-diisocyanate, and Ethylenediamine

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SUMMARY

The infrared spectra (4000–650 cm^{-1}) of a series of polyurethane elastomers synthesized from polytetrahydrofuran, diphenylmethane-4,4$'$-diisocyanate, and ethylenediamine were examined. By comparing the spectra with those of the constituent polytetrahydrofuran and of the model compounds for the hard segments of the elastomers containing the urea, urethane, and diphenylmethane groups, most of the stronger bands could be assigned with reasonable assurance to the vibrations of each constituent part. The frequencies of the urea and the urethane characteristic bands correspond to complete association of the polar groups in the polymers. The spectral changes produced by uniaxially stretching polyurethane films can be interpreted as due to the induced crystallization of the polyether blocks in the elastomer, which remain amorphous in the undistorted state. Polarization measurements on stretched samples confirmed that the polyether chains are oriented parallel to the direction of the stretch.

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INTRODUCTION

Polyurethane linear elastomers are physicochemically interesting materials because they exhibit good elastomeric properties but contain no chemically cross-linked structures. These materials can be generally regarded as a kind of block copolymer consisting of the alternating hard and soft segments. The hard segments constitute a localized, regular intermolecular structure through a strong interaction such as hydrogen bonding between polar groups belonging to different molecules, and the secondary structure thus formed may play a dominant role analogous to that of chemical cross-linking, which restrains the motions of macromolecular chains past one another when some external forces are applied to the material.

In order to investigate the relationship between the chemical structure and the physical properties of the polyurethane linear elastomers, it is necessary first of all to establish the method to specify the chemical compositions of the compounds. From this point of view, some typical polyether-urethane samples were synthesized, and their infrared spectra were examined in comparison with the spectra of several model compounds and with some established data on related materials. In this paper the results of the vibrational analysis of the polyurethane elastomers are reported.

EXPERIMENTAL

Preparation of Polyurethane Elastomers

Polyurethane samples were synthesized from polytetrahydrofuran (PTHF) with two hydroxyl end groups, diphenylmethane-4,4'-diisocyanate (MDI) and ethylenediamine (EDA). An excess of MDI was added to PTHF, and the mixture was held at 80°C for 2 hr, while being stirred under nitrogen stream. The molar ratio of MDI to PTHF was 2 to 1, and the number average molecular weights ($\bar{M}_n$) of the PTHF used were 2100, 3300, 8390, and 10,600. The product obtained was polyether-urethane-diisocyanate, the so-called prepolymer, which was dissolved into N,N-dimethylformamide (DMF) to form a 30% solution and thereafter chain-extended with an equimolar amount of EDA in DMF at 0–5°C. Films suitable for infrared measurements were prepared by casting the solution onto a glass plate and evaporating off the solvent in vacuo.

Synthesis of Model Compounds

Some low-molecular-weight model compounds for polyurethane elastomers were synthesized as described below. These compounds contain the urethane, $-NHCOO-$, or the urea, $-NHCONH-$, groups and have chemical structures similar to the hard segments of the polyurethane elastomers.

N-phenyl-N′-ethylurea. Melting point 99–100°C.

$$\langle\!\!\!\bigcirc\!\!\!\rangle\!-NHCONHC_2H_5$$
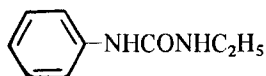
(I)

An equimolar amount of phenylisocyanate was added dropwise during 3 hr to ethylamine dissolved in purified benzene at 10°C. The precipitate was separated from the solution, washed with benzene, and dried.

4,4′-di-3-ethylureidodiphenylmethane. Melting point >300°C.

$$C_2H_5NHCONH\!-\!\langle\!\!\!\bigcirc\!\!\!\rangle\!-CH_2\!-\!\langle\!\!\!\bigcirc\!\!\!\rangle\!-NHCONHC_2H_5$$
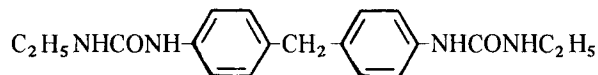
(II)

An excess ethylamine was added to purified MDI which had been melted on a water bath and suspended in benzene at 10°C. After the reaction had been completed, residual ethylamine and benzene were evaporated under reduced pressure. The white crystals deposited were washed with benzene and dried in vacuo.

N-phenyl-ethylcarbamate. Melting point 52–53°C.

$$\langle\!\!\!\bigcirc\!\!\!\rangle\!-NHCOOC_2H_5$$
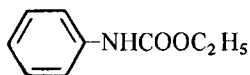
(III)

Equimolar amounts of phenylisocyanate and ethyl alcohol were mixed and the mixture was stirred during 3.5 hr at 70°C. After the reaction had been completed, the product was kept overnight at room temperature.

Needle crystals were precipitated, separated from the solution, washed with ethyl alcohol, and dried in vacuo.

N,N'-diethoxycarbonyl-4,4'-diaminodiphenylmethane. Melting point 128-128.5°C.

$$C_2H_5OCONH-\langle\!\bigcirc\!\rangle-CH_2-\langle\!\bigcirc\!\rangle-NHCOOC_2H_5$$

(IV)

Melted MDI was added dropwise into excess ethyl alcohol and the mixture was held at 70°C for 30 min. The excess ethyl alcohol was then evaporated, and the residual white crystals were dried in vacuo.

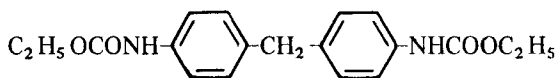## Measurement of Infrared Spectra

Measurements of the infrared spectra in the 4000–650 cm^{-1} region were made by using a Japan Spectroscopic Model DS-402G spectrophotometer with grating optics. A silver chloride polarizer was used in examining the dichroic properties of oriented specimens. The spectra of the model compounds were measured using the potassium bromide disk method.

RESULTS AND DISCUSSION

The polyurethane samples are considered to have essentially a linear structure because these materials are easily dissolved in DMF and their infrared spectra exhibit no absorption band at 1645 cm^{-1}, which is known from the spectra of model compounds to be characteristic of the biuret group, $-NHCON\overset{|}{C}ONH-$ [1].

The infrared spectra of the polyurethane samples from PTHF of $\bar{M}_n$ = 2100, 3300, and 8390 are shown in Fig. 1a–c, respectively. Figure 2 shows the polarized infrared spectrum of a polyurethane sample from PTHF of $\bar{M}_n$ = 3300 which has been uniaxially stretched fivefold. The wave numbers and the relative intensities of the observed bands are listed in Table 1. The table also contains the infrared dichroic data of the bands obtained on oriented specimens and the results of the vibrational analyses of the bands, discussed below.

Because the polyurethane elastomers consist of the polyether (PTHF), the
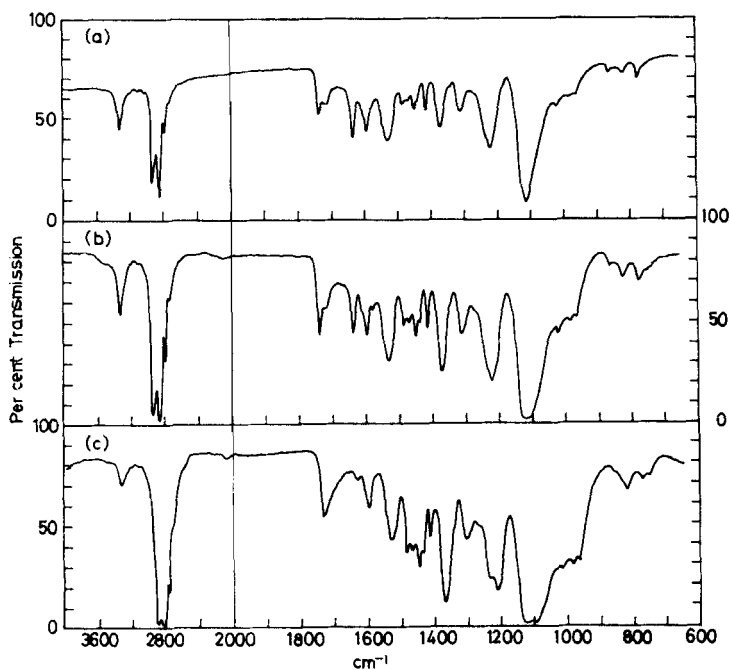
Fig. 1. IR spectra of polyurethane elastomers from polytetrahydrofuran, diphenylmethane-4,4'-diisocyanate, and ethylenediamine. $\overline{M}_n$ of polytetrahydrofuran = (a) 2100, (b) 3300, and (c) 8390.

substituted diphenylmethane group, and the polar groups such as the urethane and the urea, the whole spectrum of the elastomers can be interpreted in first approximation as the superposition of the characteristic absorption bands of each constituent part. The following are the results of the empirical vibrational assignments of the bands which have been made by comparing the spectra of the polyurethanes with those of the constituent groups and of the corresponding model compounds.

Characteristic Bands of Urethane and Urea Groups

The absorption bands of the urethane, $-NHCOO-$, and the urea, $-NHCONH-$, groups are typical of the spectra of the polyurethane elastomers. Since both groups contain the N-monosubstituted amide unit, $-NHCO-$, the spectra of these groups can be interpreted in terms of the

amide characteristic vibrations, which have been studied extensively by many authors [2, 3]. Pauling et al. [4] found that the C−N bond of the amide group is shorter and the C=O bond longer than in the case of normal valence bond structures, and attributed these facts to the presence of the resonance structures, O=C−N⇌O⁻−C=N⁺. Thus, the frequency of the amide I band, which mainly consists of the C=O stretching mode, is usually smaller than the C=O stretching frequency of the ketones.

In the case of the urea group, the amide I frequency becomes lower and the amide II frequency higher relative to the amide −NHCO− group, because of the added effects of the adjacent NH group [3]. Figures 3a
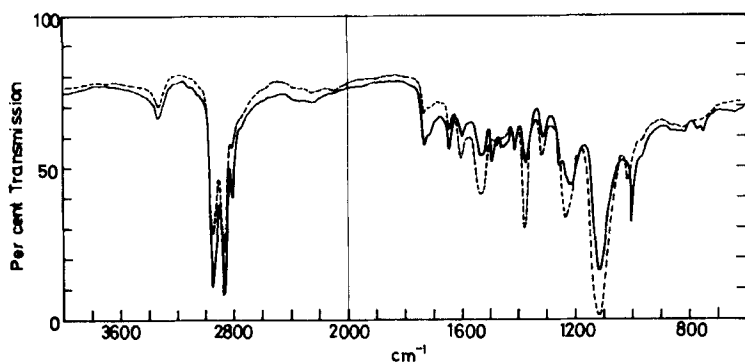
Fig. 2. Polarized IR spectrum of a uniaxially stretched polyurethane elastomer from polytetrahydrofuran of $\overline{M}_n$ = 3300, diphenylmethane-4,4'-diisocyanate, and ethylenediamine. (———) electric vector perpendicular to stretching direction; (- - - - -) electric vector parallel to stretching direction.

and 3b show the infrared spectra of the compounds (I) and (II), respectively, as typical model compounds for the hard segments of the polyurethanes containing the urea group. The strong bands observed at about 1635 and 1560 cm⁻¹ in these spectra are, respectively, assigned to amides I and II of the urea group. The band around 1240 cm⁻¹ is ascribed to amide III and that at 3320 cm⁻¹ to the N−H stretching mode. The vibrational frequencies of (II) are tabulated in Table 2 together with the assignments. Referring to these results, the bands at 1635 and 1575 cm⁻¹ of the polyurethanes are clearly assigned to amides I and II of the urea group, respectively. The band at 1232 cm⁻¹ is assigned to amide III and the one at 3325 cm⁻¹ to the N−H stretching vibration of the urea group, but these bands are considered to have contributions from the corresponding vibrational modes of the urethane group, as described below.
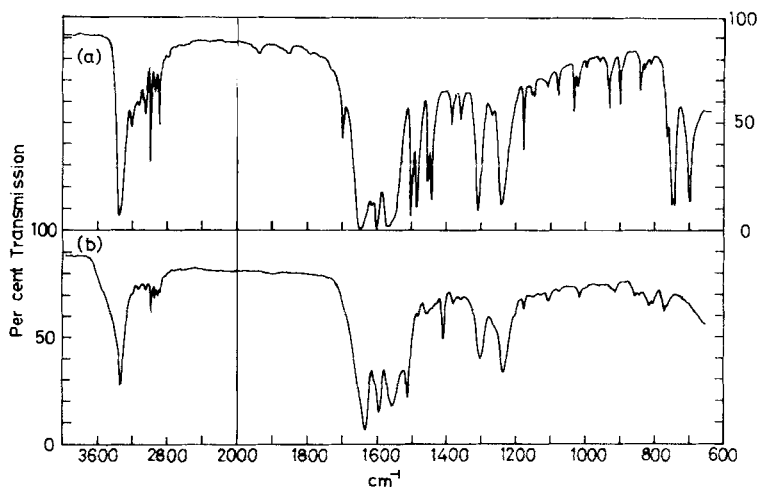
Fig. 3. IR spectra of the model compounds for the hard segments of poly-urethane elastomers containing the urea group. (a) N-phenyl-N'-ethylurea (I), (b) 4,4'-di-3-ethylureidodiphenylmethane (II).

In the case of the urethane group, the frequency of the amide I band is increased up to the region of the C=O stretching vibrations in esters or ketones [3, 5]. In Figs. 4a and 4b are shown the spectra of compounds (III) and (IV), respectively, as typical model compounds for the hard segments of the polyurethanes containing the urethane group. These spectra exhibit intense absorption bands around 1700 and 1530 cm^{-1}, which are ascribed, respectively, to amides I and II of the urethane group. The amide III band appears at 1225 cm^{-1}, and the N–H stretching band at 3320 cm^{-1}. The vibrational frequencies of (IV) are given in Table 2 together with the assignments. On the basis of these results, the bands observed at 1727 and 1530 cm^{-1} in the spectra of the polyurethane elastomers can be assigned to the amide I and II vibrations of the urethane group, respectively. The band at 1217 cm^{-1} may be ascribed to amide III and that at 3325 cm^{-1} to the N–H stretching mode. The band observed at 1705 cm^{-1} as a shoulder to the 1727 cm^{-1} band is considered to be of the same origin as amide I of the urethane group, though it is rather difficult to give a more detailed assignment at the present stage. These assignments were also confirmed by examining the infrared spectra of a series of polyurethane samples which differ in the molar ratio of the urethane to the urea group [1].

The frequencies of the urethane and the urea characteristic bands fall within the regions expected for the fully associated state of the polymers, in

Table 1. IR Spectrum of Polyurethane Elastomers

Frequency, cm^{-1}	Relative intensity [a]	Dichroism [b]	Phase [c]	Urea, urethane [e]	P T H F	Benzene ring
					Assignment [d]	
3325	m	σ		U: UT:} ν(N–H)		
3190	vw	σ				
3110	vw	σ				ν(C–H)
2944	vs	σ			$\nu_a(CH_2)$, B$_{1}$u	
2854	vs	σ			$\nu_s(CH_2)$, B$_{2}$u	
2790	m	σ			$\nu_s(CH_2)$, B$_{2}$u	
2730	vw	σ				
1727	m	σ	{	UT: amide **I**		
1705	m	σ				
1635	m	σ		U: amide **I**		
1592	m	π				ν(C–C)
1575	w	π		U: amide **II**		
1543	sh	—				
1530	s	π		UT: amide **II**		
1513	sh	—				ν(C–C)
1491	m	σ	C		$\delta(CH_2)$, B$_{1}$u	
1483	w	σ	A		$\delta(CH_2)$	
1473	w	π	C		$\delta(CH_2)$, B$_{3}$u	
1466	w	π	A		$\delta(CH_2)$	
1459	w	σ	C		$\delta(CH_2)$, B$_{1}$u	
1446	m	σ	A		$\delta(CH_2)$	
1435	w	σ				

cm⁻¹	Intensity	Orientation	Phase	Urea/urethane	Assignment	Assignment
1412	m	σ				ν(C–C)
1370	s	π			w(CH$_2$), B$_{3u}$	
1342	sh	π				β(C–H)
1310	m	σ			w(CH$_2$), B$_{2u}$	
1250	w	σ	C			
1232	sh	π		U: amide **III**		
1217	s	π		UT: $\Big\{$ amide **III** ν_a(CO–O–C)		
1207	sh	σ			t(CH$_2$), B$_{1u}$	
1112	vs	π		UT: ν_s(CO–O–C)	ν_a(C–O–C), B$_{3u}$	
1040	sh	—				
1017	w	π				β(C–H)
1008	w	π	C		ν(C–C), B$_{3u}$	
996	m	σ	C		ν_s(C–O–C), B$_{2u}$	
985	w	σ	A		ν_s(C–O–C)	
965	w	σ				
917	sh	—				γ(C–H)
866	w	σ				
820	w	σ				γ(C–H)
800	sh	σ				
773	w	σ	C	UT: γ(O=C–O)		
747	w	σ			r(CH$_2$), B$_{1u}$	

aRelative intensity refers to the sample made from PTHF of $\bar{M}_n = 3300$;
s = strong, m = medium, w = weak, v = very, sh = shoulder.

b π = parallel, σ = perpendicular.

c A = amorphous, C = crystalline.

d ν = stretching, ν_a = antisymmetric stretching, ν_s = symmetric stretching, δ = bending, w = wagging,
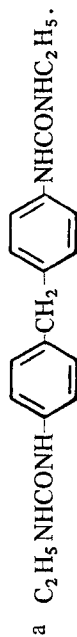t = twisting, r = rocking, β = in-plane bending, γ = out-of-plane bending.

e U = urea, UT = urethane.

Table 2. IR Spectra of Model Compounds for Polyurethane Elastomers

Compound (II)[a]		Compound (IV)[b]		Assignment[d]		
Frequency, cm^{-1}	Relative intensity[c]	Frequency, cm^{-1}	Relative intensity[c]	Urea, urethane[e]	Benzene ring	Others
3320	s	3325	s	U : UT: } ν(N–H)		
3185	sh	3190	sh			
3100	vw	3110	vw			
3026	vw	3030	vw		ν(C–H)	
2970	m	2980	m			ν_a(CH$_3$)
2926	w	2930	w			ν_a(CH$_2$)
2900	w	2900	w			ν_s(CH$_3$)
2870	vw	2870	sh			ν_s(CH$_2$)
—		1728	m	UT: amide **I**		
—		1700	vs	U: amide **I**		
1635	vs	—				
—		1607	sh			
1596	vs	1593	s		ν(C–C)	
1555	vs	—		U: amide **II**		
—		1530	vs	UT: amide **II**		
1510	s	1506	sh		ν(C–C)	
1483	w	1475	w			
1458	w	1455	vw			
1447	sh	—				} δ_a(CH$_3$)
1437	vw	1434	vw			
1410	m	1413	s		ν(C–C)	

a		b		Assignment
1380	w	1388	w	$\delta_s(CH_3)$
1359	vw	1365	vw	
1307	s	1310	s	$\beta(C–H)$
1260	sh	—		
1238	s	—		U: amide **III**
—		1227	vs	UT: $\Big\{$ amide **III** / $\nu_a(CO–O–C)$
1177	w	—		
1104	w	1110	sh	
1074	vw	—		
—		1069	s	UT: $\nu_s(CO–O–C)$
1018	w	1018	w	$\beta(C–H)$
915	w	918	vw	$\gamma(C–H)$
860	w	860	w	$r(CH_2)$
818	w	818	m	$\gamma(C–H)$
806	w	—		
773	m	772	m	U: $\gamma(N–H)$ / UT: $\gamma(O=C–O)$
—		—		

a $C_2H_5NHCONH$—⟨ring⟩—CH_2—⟨ring⟩—$NHCONHC_2H_5$.

b C_2H_5OCONH—⟨ring⟩—CH_2—⟨ring⟩—$NHCOOC_2H_5$.

c s = strong, m = medium, w = weak, v = very, sh = shoulder.

d ν = stretching, ν_a = antisymmetric stretching, ν_s = symmetric stretching, δ_a = antisymmetric deformation, δ_s = symmetric deformation, β = in-plane bending, γ = out-of-plane bending, r = rocking.
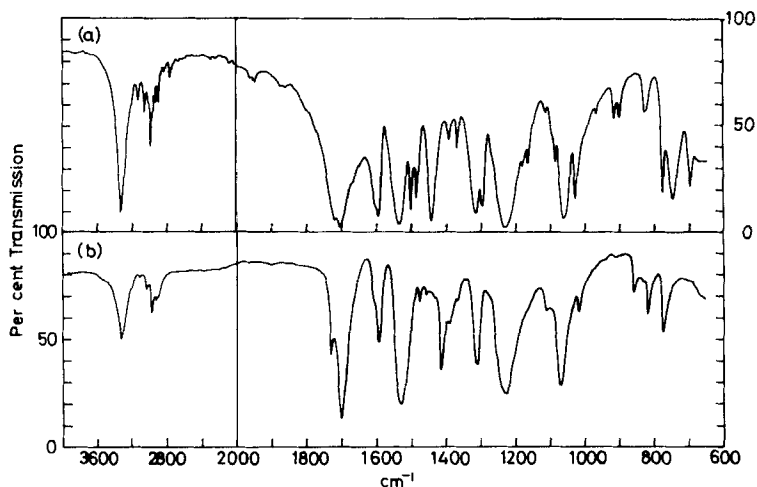
e U = urea, UT = urethane.

Fig. 4. IR spectra of the model compounds for the hard segments of poly-
urethane elastomers containing the urethane group. (a) N-phenyl-
ethylcarbamate (III), (b) N,N'-diethoxycarbonyl-4,4'-diaminodiphenylmethane
(IV).

which the urethane and the urea groups belonging to different molecules are
linked with each other through hydrogen bonding. No absorptions corre-
sponding to the N—H stretching vibrations of the unassociated urethane and
urea groups were observed. The details of these points will be discussed in
later papers.

 Besides the amide characteristic bands of the urethane group, the anti-
symmetric and the symmetric stretching vibrations of the CO—O—C group
of the urethane are expected to appear as absorptions around 1240 cm^{-1} and
in the 1200–1000 cm^{-1} region, respectively. The band at 1225 cm^{-1} of the
model compounds, which has been assigned to amide **III** of the urethane
group (Table 2), is considered to have contributions from the CO—O—C
antisymmetric stretching mode, while the band at 1070 cm^{-1} can be assigned
to the CO—O—C symmetric stretching vibration. By analogy, the 1217 cm^{-1}
band of the polyurethanes is considered the superposition of the amide **III**
and the CO—O—C antisymmetric modes, and the CO—O—C symmetric
stretching band is probably overlapped by the strong polyether band at 1112
cm^{-1}. The band observed around 770 cm^{-1} in the spectra of the model com-
pounds and polyurethane elastomers may be assigned to the O=C—O out-of-
plane bending mode of the urethane group [5].

Characteristic Bands of PTHF Blocks

In the infrared spectra of the polyurethane samples shown in Fig. 1, some of the bands, such as those observed at 2944, 2854, 2790, 1483, 1466, 1446, 1370, and 1112 cm^{-1}, increase in relative intensities with the $\overline{M}_n$ of the PTHF component, $-\!\!\!\left(-CH_2 CH_2 CH_2 CH_2 O-\right)_{\overline{n}}-$. These bands are, therefore, ascribed to the vibrations of the PTHF blocks in the polyurethanes. Figure 5 shows the infrared spectra of PTHF in the amorphous and the crystalline states. The spectral changes observed with the change in state of
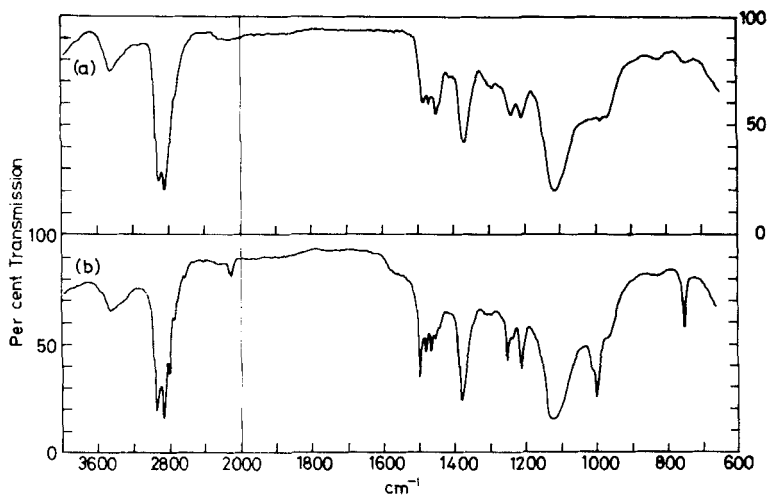
Fig. 5. IR spectra of polytetrahydrofuran. (a) Amorphous, (b) crystalline.

the polymer are essentially the same as those reported by Imada et al. [6]. The PTHF blocks in the unstretched polyurethane elastomers are considered to exist in the amorphous state, because the samples possess good elastomeric properties and also exhibit only the amorphous halos in their X-ray diffraction diagrams. In fact, the aforementioned infrared bands of the polyurethanes, which become stronger the larger the $\overline{M}_n$ of the PTHF component, agree quite well both in frequency and in relative intensity with the bands of the amorphous PTHF. This is strong evidence that the PTHF chains in the polyurethane elastomers assume random conformations in the undistorted state.

The infrared spectra of a polyurethane film made from PTHF of $\overline{M}_n$ = 3300 in the unstretched and the stretched states are shown in Fig. 6. The stretched polyurethane film exhibits new absorptions at 996 and 747 cm^{-1},
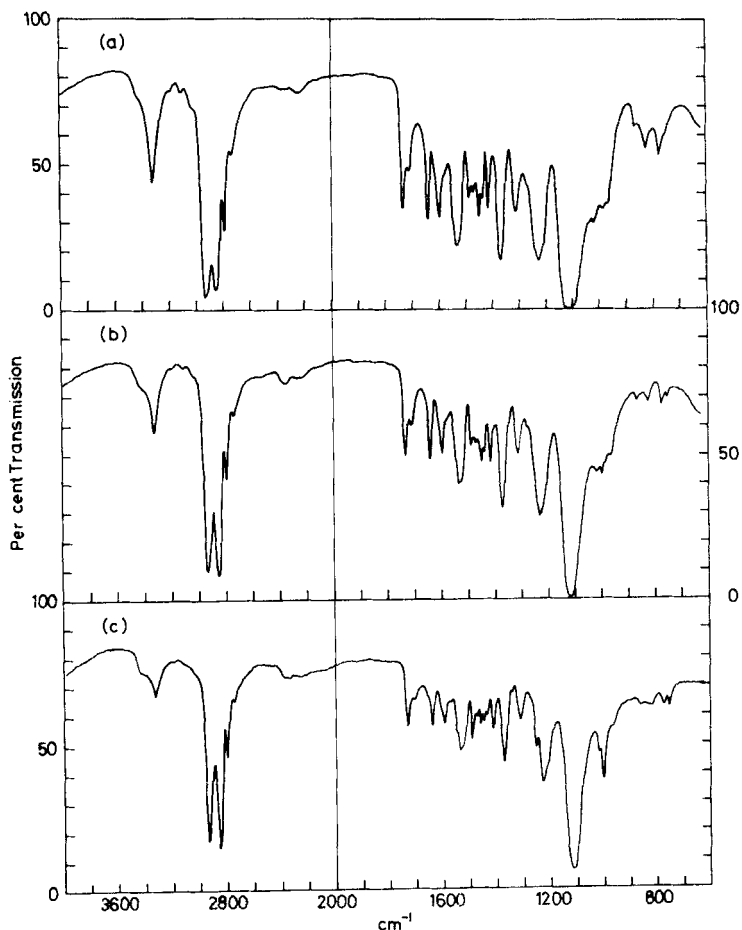
Fig. 6. IR spectra of a polyurethane elastomer from polytetrahydrofuran of $\overline{M}_n$ = 3300, diphenylmethane-4,4′-diisocyanate, and ethylenediamine. (a) Unstretched, (b) stretched threefold, (c) stretched sixfold.

which were not observed in the spectrum of unstretched specimens. These bands correspond to the crystallization-sensitive bands of PTHF at 995 and 745 cm⁻¹, which are strong in the crystalline state, but become extremely weak and broad in the amorphous state. The vibrational spectrum of the crystalline PTHF has been analyzed by Imada et al. [6] on the basis of the normal coordinate treatment. According to their results, the 995 and 745

cm^{-1} bands are characteristic of the planar zigzag conformation of the PTHF chain in the crystalline state. These results, together with the fact that the X-ray diagrams of stretched polyurethane samples exhibit crystalline reflections of PTHF, are evidence that the PTHF blocks in the polyurethane elastomers become crystallized by uniaxially stretching the specimen. From the infrared dichroic behavior of the PTHF bands in the polarized spectrum of a stretched polyurethane sample (Fig. 2), we conclude that the PTHF chains are oriented along the direction of the stretch.

Characteristic Bands of Substituted Diphenylmethane Group

The absorption bands characteristic of the benzene ring in the substituted diphenylmethane group
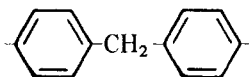
can be interpreted in first approximation by analogy with the spectra of various p-disubstituted benzenes
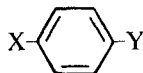
for which detailed vibrational analyses have been done by many workers [7-9]. In Table 2 are listed the absorption bands of compounds (II) and (IV), and the bands common to both the compounds are assigned to the vibrations of the p-disubstituted benzene ring as shown in the table. The bands at about 1600, 1510, and 1410 cm^{-1} are assigned to the stretching vibrations of the benzene ring, those observed around 1310 and 1020 cm^{-1} to the C—H in-plane bending modes, and the bands at about 920 and 820 cm^{-1} are ascribed to the C—H out-of-plane bending modes. As shown in Fig. 1, the absorptions of the polyurethane elastomers which are characteristic of the substituted benzene ring appear at almost the same positions as those of the model compounds.

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