Inversion of infra-red dichroism in linear crystallizable polyurethanes

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Infar-red spectroscopic and calorimetric data for a number of linear crystallizable polyurethanes based on n-tetramethylene glycol oligomers ($n=1,2,3,4$) and hexamethylene diisocyanate are given. A degree of similarity has been found in the orientation behaviour of stretching vibration bands of NH groups (inversion of dichroism with elongation) and of CH_2 groups (no inversion) in the spectra of polyurethanes studied and in the spectra of segmented polyurethanes. It is concluded that in polyurethanes with a glycol ether component of relatively small length a somewhat independent behaviour of segments of different nature localized in separate micro-regions may take place. A supposition is made that the polyurethanes examined, except for the first member of a series ($n=1$), can be considered as segregated systems with an ether glycol unit enriched amorphous phase in which crystallites formed mainly by urethane chain fragments are distributed.

Keywords Inversion; infra-red dichroism; crystallizable polyurethanes; segmented polyurethanes; chain fragment orientation; micro-segregation; segregation

INTRODUCTION

Segregation processes taking place in segmented polyurethanes are known to affect strongly the strain behaviour of the latter. This is manifested, in particular, in the orientation behaviour of absorption bands characterizing vibrations of functional groups in hard and soft segments. For example, for segmented polyurethanes with oligooxytetramethylene glycol as a soft unit, with partly crystalline hard domains the elongation increase usually results in inversion of dichroism of the stretching vibration bands of NH and CO (associated) groups, while for the stretching vibration bands of CH_2 groups no inversion occurs[1–4]. We observed a similar change of dichroism of bands associated with group vibrations in diisocyanate and ether glycol chain fragments when examining crystallizable tri(tetramethylene glycol) and hexamethylene diisocyanate based polyurethane (see ref. 5 and also *Table 1*).

The behaviour of ν NH and ν CH_2 bands is essentially different, for example, from that of the bands in the nylon-6,6 spectrum. As is seen in *Table 2* (taken from ref. 6) the stretching vibration bands of NH and CH_2 groups here change their dichroism with elongation in unison, i.e. dichroism inversion is observed both for ν NH and ν CH_2. This could be expected because the corresponding transition moments are directed identically with respect to the chain backbone. It should be noted that the change of band polarization with elongation (dichroism inversion) was also observed in spectra of other crystallizable polymers (PVC, PE, PET) and can be attributed to a transition from the orientation of crystallites as a whole at small elongations to the orientation of molecular chains at large elongations[7–9].

It seems to be especially remarkable that the results for linear crystallizable polyurethane[5] proved to be similar in many respects to the results found for segmented polyurethanes. At the same time they differ essentially from those for nylon-6,6. It allows one to suppose that even in polyurethanes with a relatively small length of ether

Table 1 Comparison of dichroic ratios of stretching vibration bands of NH and CH_2 groups at small and large elongations for PU-3

		Dichroic ratio $A_{\parallel}/A_{\perp}$ at different elongations	
ν (cm^{-1})	Band assignment	100%	300%
3340	νNH	1.25	0.75
2945	ν_aCH_2	0.88	0.66
2870	ν_sCH_2	0.74	0.59

$A_{\parallel}$ is the absorbance for linearly polarized light parallel to the direction of strain.
$A_{\perp}$ is the corresponding measurement perpendicular to the direction of strain

Table 2 Dichroic ratios for ν NH and ν CH_2 bands at different elongations of nylon-6,6 (from ref. 6)

	Dichroic ratio $A_{\parallel}/A_{\perp}$ at different elongations				
ν (cm^{-1})	1	2.02	2.99	3.99	5.02
3310	0.98	1.35	1.25	0.92	0.79
2930	0.92	1.23	1.20	0.96	0.90
2860	0.98	1.34	1.13	0.80	0.77

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Table 3 Comparison of dichroic ratios for stretching vibration bands of NH and CH_2 groups for PU-1, PU-2 and PU-3 (quenched)

Sample history	Dichroic ratio $A_{\parallel}/A_{\perp}$ for bands		
	2870 cm^{-1}	2950 cm^{-1}	3340 cm^{-1}
PU-1, 200% elongation	0.83	0.78	0.72
The same sample relaxed for a year	0.83	0.83	0.80
PU-2, 350% elongation	0.60	0.64	0.38
PU-3, 300% elongation	0.70	0.76	0.42
The same sample relaxed for a year	0.99	1.00	0.65

glycol component a somewhat independent behaviour of segments of different nature, apparently localized in separate micro-regions, may take place.

EXPERIMENTAL

To check this supposition, we made comparative i.r. spectroscopic and calorimetric studies on a number of linear crystallizable polyurethanes based on n-tetramethylene glycol oligomers and hexamethylene diisocyanate of the general formula $\{\text{–OCHN}(CH_2)_6\text{NHCO}[O(CH_2)_4]_n\text{–O–}\}$ where $n = 1,2,3,4$ (PU-1, PU-2, PU-3, PU-4 respectively). The first member of this series (PU-1) is the well known Perlon-U[10,11], being an analogue of polyamide nylon-6,6. The synthetic procedure of the polyurethanes used in this study was described elsewhere[12]. The viscosity-averaged molecular weight was 5.0×10^4. Oriented polyurethane films obtained by extension of both isotropic amorphous samples prepared by melt quenching in ice water and crystalline ones obtained by casting from dimethylformamide solution on a glass plate at 373 K were examined.

Spectra were recorded by a spectrophotometer UR-20 in frequency ranges 1500–1800 cm^{-1} and 2700–3600 cm^{-1} using AgCl polarizer. The slit programme of conventional spectra recording was 4, that of differential spectra recording was 8, scanning rates being 25 and 64 cm^{-1} min^{-1}. For differential spectra recording a sample was placed inside the instrument at 45° at the point of mixing of both light beams; polarizers with mutually perpendicular directions of polarization were fitted in the normal sample and reference positions. To characterize the urethane fragment orientations, dichroism of the stretching vibration bands of NH and CO groups was chosen.

The orientation behaviour of ether glycol fragments in PU-2 and PU-3 was judged by the change of dichroism of the stretching vibration bands of CH_2 groups. Though the presence of CH_2 groups in urethane chain fragments affects the value of dichroism, the sign of the latter will apparently be determined by the orientation of CH_2 groups in the ether glycol fragments owing to their greater number. The absorbance coefficients of CH_2 groups in urethane and ether glycol links are assumed to be similar to each other. The angle between the transition moment and local axis of the chain for CH_2 and NH groups is taken to be 90°. Calorimetric measurements were made on a microcalorimeter described elsewhere[13].

RESULTS AND DISCUSSION

Table 3 lists data on 3340 cm^{-1} (ν NH), 2870 cm^{-1} and 2950 cm^{-1} (νCH_2) band dichroism at large elongations of amorphous PU-1, PU-2 and PU-3 films. These data were obtained directly after film extension, and for PU-1 and PU-3 samples additional data were obtained after their relaxation for a year with stress being removed. It should be noted that for such films the stretching vibration band of NH groups is perpendicular both at large (200–300%) and small (50–100%) elongations.

It is seen from *Table 3* that unlike PU-1 for which the dichroism values of ν NH and ν CH_2 bands are nearly identical, for PU-2 and PU-3 films a distinct difference in dichroic ratios of these bands is observed. Of particular interest is the fact that with stress being removed the flexible PU-3 segments relax nearly completely, while the rigid ones show residual orientation. Similar data obtained for segmented polyurethanes with non-crystallizable hard domains were used[1–4] to support the assumption of a two-phase structure of segmented polyurethanes and are in good agreement with established concepts of micro-segregation of units of different structures. The data from *Table 3* can be considered as additional evidence in favour of the fact that segments of different mobilities in linear crystallizable polyurethanes of such structure are located in different micro-regions, responding somewhat independently to stress application and removal. These data demonstrate that one may observe the differences in dichroic ratios of ν NH and ν CH_2 bands even passing from PU-1 to PU-2, the latter being in its orientation behaviour closer to PU-3. This also follows from the results obtained when the crystalline PU-2 sample was strained. The structure of such films is described in ref. 14. It is essential to note that no spectral variations characterizing the conformational change of the chain were observed when PU-2 film was strained.

Figure 1 presents spectra for PU-2 films recorded with electric vector parallel and perpendicular to the axis of strain at small (50 and 100%) and large (200%) elongations. Differential spectra are shown in *Figure 2*. As well as for PU-3 (*Table 1*), the stretching vibration bands of CH_2 groups in spectra of oriented crystalline PU-2 films are perpendicular both at small and large elongations, whereas for the stretching vibration band (3345 cm^{-1}) of NH groups inversion of dichroism is observed: at small elongations the band is parallel, while at larger elongations (200%) it becomes perpendicular (*Figures 1a* and *2*).

In the frequency range of the stretching vibrations of CO groups at 100% elongation two bands of opposite polarization are observed, namely 1690 cm^{-1} (parallel) and 1725 cm^{-1} (perpendicular) (*Figures 1b* and *2*). Strain behaviour of the former band is similar to that of stretching vibration band of NH groups with $\nu = 3340$ cm^{-1}, for which inversion of dichroism is also observed. This band corresponds to the stretching vibrations of CO groups, forming hydrogen bonds of the NH ... OC type in ordered regions. The $\nu = 1725$ cm^{-1} band is perpendicular both at small and large elongations and seems to correspond to the stretching vibrations of those CO groups that are incorporated in chain fragments where NH groups are hydrogen-bound to an oxygen atom of an ether fragment.

Thus even in PU-2 behaviour one may trace a degree of similarity to segmented polyurethanes in which hard

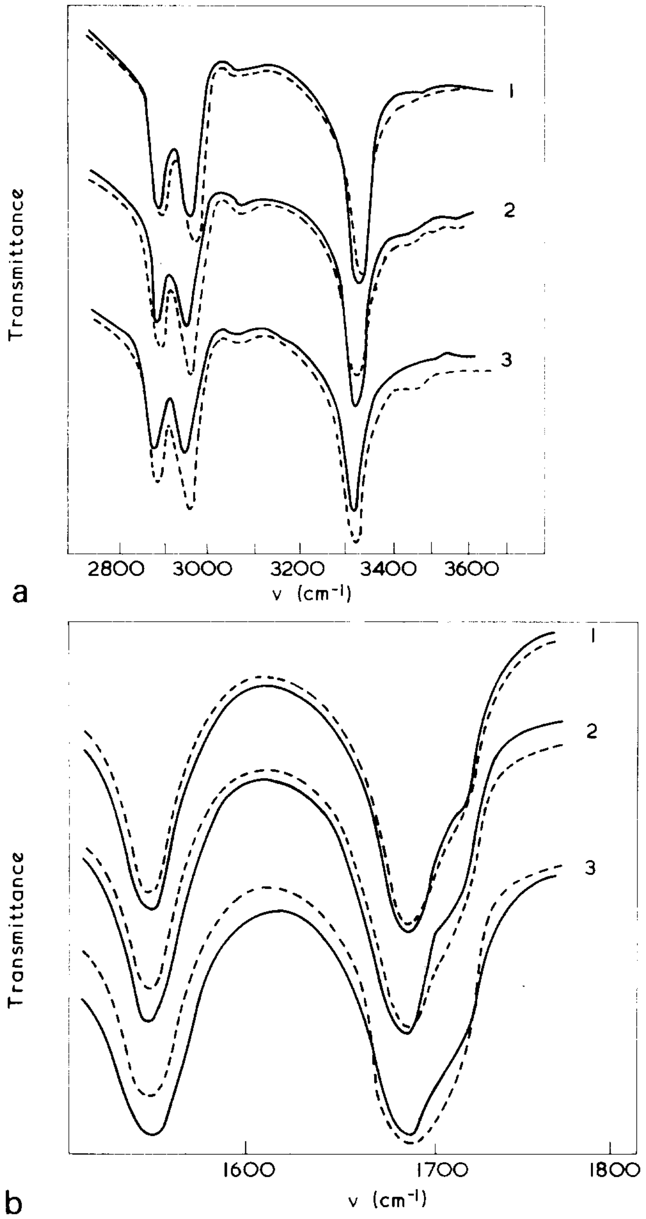

Figure 1 I.r. transmission spectra of oriented ditetramethylene glycol and hexamethylene diisocyanate based polyurethane film (PU-2) at elongations of 50% (1), 100% (2) and 200% (3) in ν CH$_2$ and ν NH range (a) and in ν CO range (b). The full curves are the parallel components and broken curves the perpendicular components

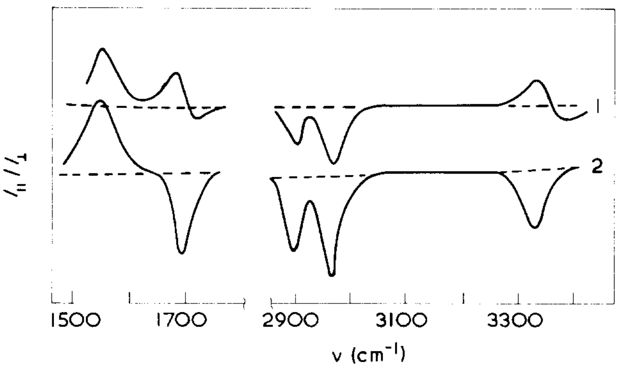

Figure 2 Intensity ratio of two beams polarized parallel and perpendicular to the direction of PU-2 sample strain at elongations of 100% (1) and 200% (2). Broken lines are base lines obtained from the two polarizers with no sample present

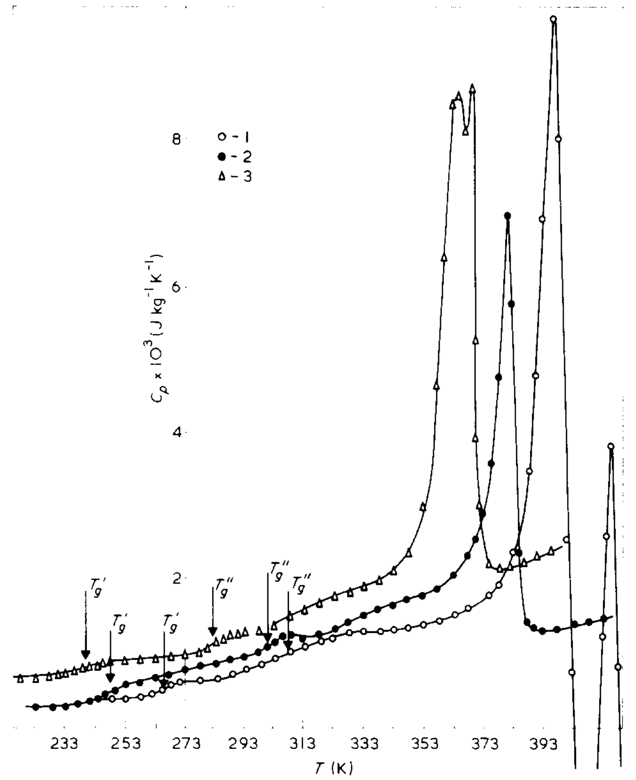

Figure 3 Heat capacity as a function of temperature for PU-2 (1), PU-3 (2) and PU-4 (3)

domains are able to crystallize: the stretching vibration bands of NH and associated carbonyl groups reverse the dichroism sign when passing from small to large elongation, while the stretching vibration bands of CH$_2$ and non-associated carbonyl groups remain perpendicular both at small and large elongations.

Plots of heat capacity vs. temperature based on calorimetric data indicate that all polyurethanes studied are crystallizable. As regards the phenomenon considered, the most interesting effect is a higher temperature transition (T_g'') appearing on temperature dependence curves of heat capacity for PU-2, PU-3 and PU-4 in the range 275–325 K together with a low temperature transition (T_g') in the range 235–250 K (*Figure 3*). The above are characteristic of glass transition in the polyurethanes in question.

In *Figure 4* T_g' and T_g'' values are plotted against molar concentration of urethane groups in polyurethane. As can be seen, the points clearly give straight lines, one being for T_g', the other for T_g''. An important point is that extrapolation of data for low temperature transition T_g' to zero concentration of urethane groups gives the T_g value for high polymer homologue of glycol component, i.e. for polyoxytetramethylene glycol[15]. In its turn the T_g value for PU-1 falls on the second glass transition line (curve 2).

This allows the conclusion that T' and T'' characterize segmental mobilities in micro-regions enriched by either ether glycol or urethane-containing unit respectively.

The calorimetric data being accounted for, it appears that a certain similarity of behaviour in the stretching vibration bands of NH groups (dichroism inversion with elongation) and CH$_2$ groups (no dichroism inversion) in crystallizable polyurethanes spectra, studied by us, and those of segmented polyurethanes reflects the generality

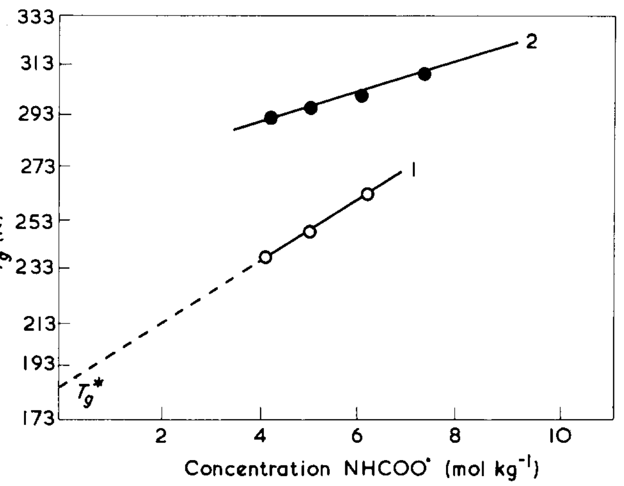

Figure 4 Glass transition temperatures as a function of concentration of urethane groups in polyurethanes: 1, T_g'; 2, T_g''. T_g^* is the glass transition temperature of polyoxytetramethylene glycol

of phenomena in both systems and in its turn gives evidence of a relatively independent behaviour of ether glycol segments in a polyurethane chain despite their small length.

Thus the examined polyurethanes except for PU-1 may be considered, according to concepts developed in ref. 16, as segregated systems with glycol ether unit enriched amorphous phase, in which crystallites formed mainly by urethane chain fragments are distributed.

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