Vibrational spectroscopic characterization of rigid rod polymers:
3. Microstructural changes in stressed polymers

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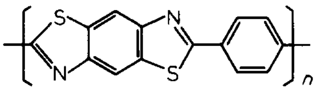
Highly oriented poly(*p*-phenylene benzobisthiazole) films were stressed in a miniature hydraulic tensile tester interfaced to a fast scanning Fourier transform infra-red spectrometer. The changes in relative intensity, polarization, frequency and shape of infrared bands have been useful in the elucidation of microstructures. With the short time resolution achievable, vibrational bandshape and frequency have been shown to change at different rates when an external stress was applied.

Keywords Spectroscopy; vibrational; rigid rod; stressed polymer; microstructure

INTRODUCTION

Heterocyclic rigid-rod polymers, exhibiting properties such as high tensile strength, high modulus, thermal and oxidative resistance have attracted considerable interest[1-3]. In particular, poly(*p*-phenylene benzobisthiazole) (PBT), with repeat unit



has shown desirable mechanical properties superior to the well known poly(*p*-phenylene terephthalamide) (Kevlar). Until recently, the study of rigid rod polymers arose mainly from the practical point of view, there have been few structural characterizations. X-ray[5,6], electron diffraction coupled with dark field imaging[7], theoretical conformational analysis[8], and vibrational spectroscopic studies[9,10] have provided a substantial amount of structural data for PBT and its model compounds. It is known that solutions of this type of polymer can exist in either optically isotropic or anisotropic liquid crystalline phases, depending on temperature, concentration or molecular weight. The high strength of these polymers arise from the ability to achieve a high degree of molecular order during processing.

In our laboratory, mechanical behaviour of these rigid rod polymers has been studied extensively. Several recent studies have shown the utility of vibrational spectroscopy in order to gain greater insight into the microstructural response when an external stress is applied. Spectroscopic features such as band polarization, frequency, intensity and shape can all be sensitive to an external stress[11-17]. Their changes have been associated with changes in chain conformation, orientation and packing. This type of information supplements the macroscopic performance data, ultimately leading to a more accurate description of the structure–property relationship.

However, because of stress relaxation, this type of time dependent spectroscopic analysis is difficult. The multiplex characteristic (the ability to measure all spectral elements) of a Fourier transform infra-red spectrometer (*FT*i.r.) together with the high energy throughput provide *FT*i.r. with a substantial gain in signal to noise ratio for a given measurement time when compared to a dispersive instrument. Therefore, it is feasible to use *FT*i.r. to follow time dependent phenomena. Unlike a dispersive instrument, simultaneous measurements of band position, shape and relative intensity over a wide frequency region are retained in *FT*i.r. studies. We have followed the stress induced structural changes of PBT with our rapid scanning *FT*i.r. The results are presented here.

EXPERIMENTAL

PBT and its model compounds were furnished by the Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Highly oriented fibres or films processed at Celanese Corporation have been characterized and used for these spectroscopic studies[18]. We have also prepared highly oriented films (~ 10 μm thick) in our laboratory from a 6% solution of PBT (intrinsic viscosity ~ 17) in methane sulphonic acid (MSA). The solution was sheared between glass plates, and then coagulated in deionized distilled water. In order to prevent dimensional changes, the films on the glass slide are attached to a frame during the subsequent washing. After continuous washing, the films were dried in air and then in a vacuum oven at room temperature. In all samples the characteristic band of acid

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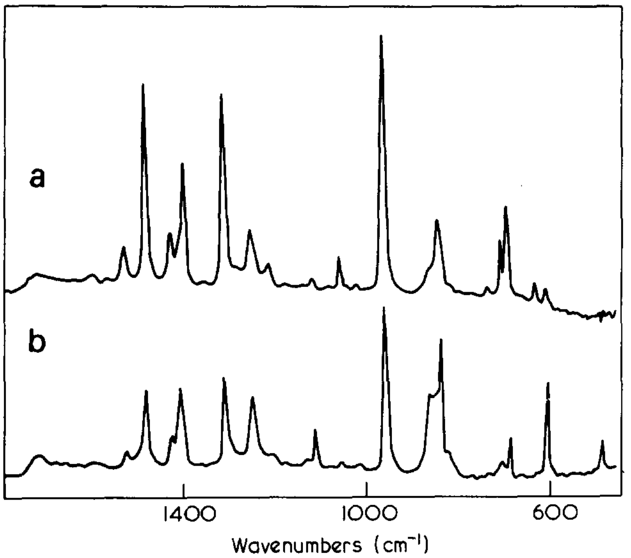


Figure 1 Polarized infra-red spectra obtained from highly oriented PBT film: (a) parallel polarization; (b) perpendicular polarization

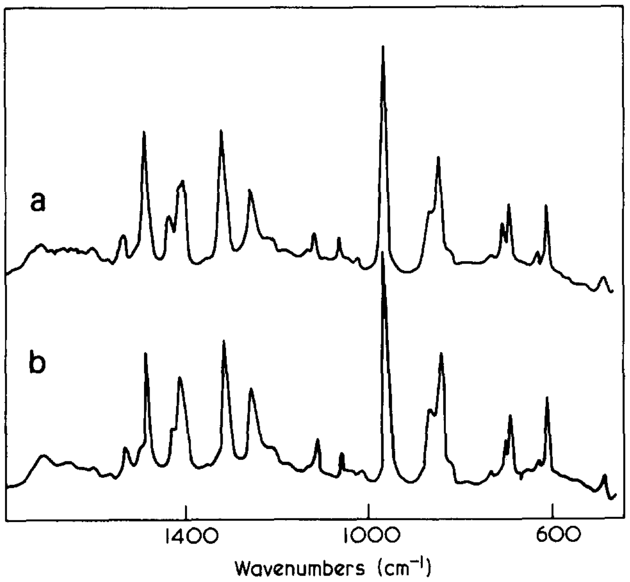


Figure 2 Infra-red spectra obtained from highly oriented PBT films: (a) curve corresponds to spectrum taken with film plane perpendicular to the incident radiation; (b) curve corresponds to a 45° rotation

(located at 1190 cm^{-1}) was absent, indicating a complete elimination of residual acid.

A miniature tensile tester is interfaced to our Nicolet Fourier transform infra-red spectrometer (*FT*i.r.). Both the load and displacement values applied to the sample are available in digitized form and accessible by our *FT*i.r. minicomputer. Accurate macroscopic mechanical information in the form of stress–strain data is collected along with microscopic information in the form of infra-red data. Details of this apparatus are described elsewhere[19]. These highly oriented films were drawn slowly (0.6 mm min^{-1}) until nearly broken. Maximum stress and strain obtainable are approximately 0.22 GPa and 3%, respectively. In some cases, a permanent plastic strain obtained is nearly 0.8%.

Polarized radiation was obtained with a quad-diamond cell[20]. The infra-red spectra were collected using a modified rapid scanning Nicolet 7199 *FT*i.r. Infra-red spectra with time resolution on the order of 700 ms can be stored on a magnetic disc for further analysis.

RESULTS AND DISCUSSION

As expected, the polarization spectra of all the PBT films exhibit high orientation. Polarized spectra of PBT films are shown in *Figure 1*. Since the intermolecular interaction in PBT is strong, biaxial orientation is to be expected. Several recent studies have shown that three dimensional orientation of polymers can be measured by infra-red spectroscopy[21,22]. These measurements generally involve changing the angle of the film plane relative to the polarized incident radiation in order to determine the relative absorptions of transition moments along x and y perpendicular to the chain or z direction. A series of infra-red spectra were measured at angles between 0° and 60°. Representative spectra are shown in *Figure 2*. Prominent infra-red bands and their polarization are listed in *Table 1*. Since these molecules are complicated, accurate vibrational assignments have been difficult to achieve[9,10]. Tentative assignments based on model compounds and the transition moment directions measured, are listed in *Table 1*[9,10,23–27].

From these band assignments and the orientation measurements, one can show several interesting structural aspects of PBT films. The transition moments associated with the out-of-plane deformation vibrations of the heterocyclic ring (605 and 488 cm^{-1}) and of the 1, 2, 4, 5–C_6H_2 (860 cm^{-1}) are normal to the main ring plane. Orientation measurements have shown all of these bands are perpendicular to the film plane, indicating on the average the main heterocyclic ring lie parallel to the film surface.

Table 1 Infrared bands observed for highly oriented PBT film

Frequency (cm^{-1})	Intensity	Polarization directions	Tentative assignment
3076	w	y	20b 1,4–C_6H_4
3050	sh		20a 1,2,4,5–C_6H_2
3027	w	z	20a 1,4–C_6H_4
1605	w	z	8a 1,4–C_6H_4, 1,2,4,5–C_6H_2
1532	m	z	19a 1,4–C_6H_4
1500	sh		19a 1,2,4,5–C_6H_2
1485	vs	z	Hetero ring stretch
1428	m	z	19b 1,2,4,5–C_6H_2
1410	s	y	19b 1,4–C_6H_4
1401	s	z	Hetero ring stretch
1314	vs	z	Hetero ring stretch
1252	s	y	Crystalline band
1211	w	z	C–C stretch
1113	m	y	18b 1,4–C_6H_4
1056	m	z	18a 1,4–C_6H_4
1017	w	x	18a 1,2,4,5–C_6H_2
960	vs	z	Hetero ring 'breathing'
860	s	y	11 1,2,4,5–C_6H_2
837	s	x	11 1,4–C_6H_4
732	w	z	Hetero in-plane ring deformation
705	m	z	12 1,4–C_6H_4
689	s	z	Hetero ring stretch
627	w	z	6b 1,4–C_6H_4
605	s	y	Hetero out-of-plane ring deformation
488	m	y	Hetero out-of-plane ring deformation

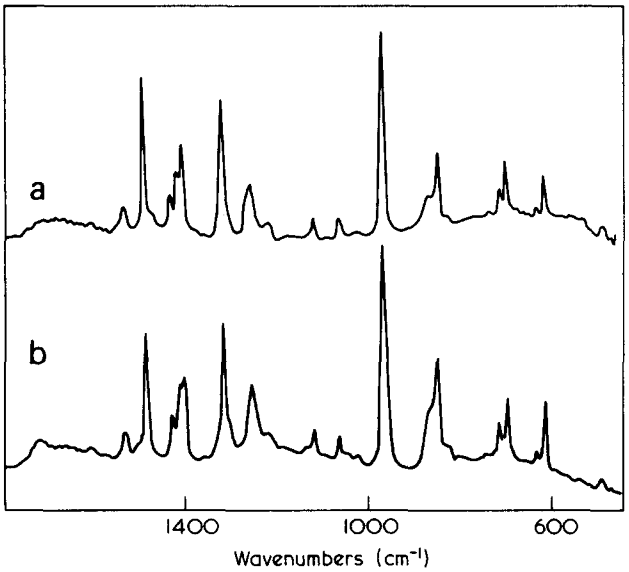


Figure 3 Infra-red spectra of PBT: (a) taken from an unoriented sample; (b) spectrum taken from a highly oriented film

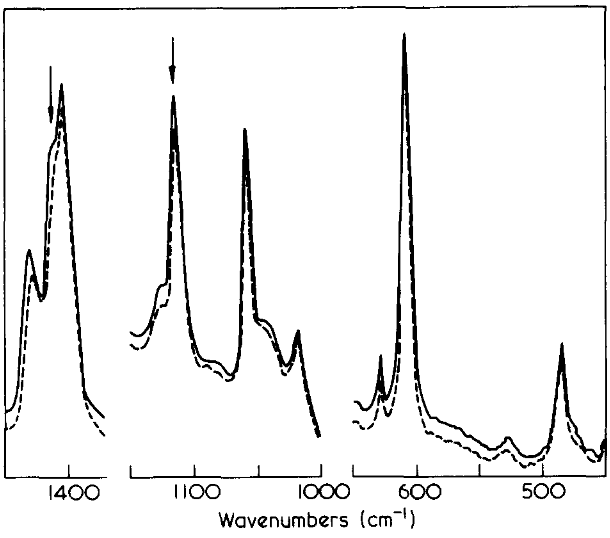


Figure 4 Stress induced relative intensity changes: A (——) no stress; B (– – –) 0.18 GPa stress applied

Based on the model compound studies, one can also establish the transition moments of the in-plane and out-of-plane vibrations of the phenyl ring. Our three dimensional dichroic ratio have shown the in-plane vibrations of the phenyl ring (1113, 1410 and 3075 cm^{-1}) are polarized normal to the film. Furthermore, the CH out-of-plane bending vibration of the phenyl ring (837 cm^{-1}) is predominately in the film plane. These measurements suggest that the phenyl ring is at a fairly large angle with respect to the heterocyclic ring or the film. Surprisingly this angle can be changed by sample preparation, such as the degree of orientational order. Representative spectra of a sheared and an unoriented film coagulated in water are shown in *Figure 3*. One can observe the difference in relative intensity between those bands assigned to the phenyl ring *versus* the ones assignable to the heterocyclic ring.

In addition, the relative intensity of these infra-red bands are sensitive to the external stress applied. Since elongation of the sample is small ($<3\%$), the influence of film thickness variation on band intensity cannot account for these changes observed. For stressed samples, the intensities of parallel bands remain unchanged as expected. However, the intensity of perpendicular bands assignable to phenyl ring exhibited some variation. Because of the large intensity difference associated with the PBT infra-red active bands, the stress induced spectroscopic changes are difficult to observe. Therefore we have plotted selected regions on *Figure 4*. The in-plane vibration at 1410 and 1113 cm^{-1} associated with the phenyl ring decrease significantly in intensity. In contrast, the intensities of the bands assignable to the heterocyclic ring remained unchanged. These results suggest that the coplanarity of the phenyl ring with respect to the heterocyclic group can also be influenced by the external stress. In our previous Raman studies, dramatic intensity changes associated with backbone vibrations observed in various PBT model compounds have been interpreted by variations in this dihedral angle between the plane of the phenyl group and the plane of the central heterocyclic ring, thus affecting the resonance conformation between the two rings. X-ray results have shown the rings are rotated to an angle of 23° or more, owing to the steric hinderance between the S and H on the heterocyclic and phenyl ring, respectively[28]. The angle predicted from conformational energy calculations is 60°[29], larger than actually measured. It appears that intermolecular interactions tend to keep the angle twist low in the solid state[28,29]. When the material is stressed, or in material lacking orientational order, it is reasonable to assign the changing polarization to a disruption of the intermolecular forces or to a direct weakening of the bond connecting two rings, thus affecting the coplanarity of the two rings.

Table 2 lists the frequency shifts caused by an external stress. Nearly all the skeletal vibrations exhibit changes of 1 cm^{-1} or more at a 0.18 GPa load. However, most of the ring deformation and C–H vibrations remained essentially constant as expected. These frequency shifts are reversible and proportional to the stress applied. It is interesting that the macroscopic modulus measured for these films is generally in the 15–22 GPa, much lower than measured for the corresponding PBT fibres[30]. By using the force constant generally associated with the single

Table 2 Frequency shift of PBT infra-red bands under mechanical load (0.18 GPa)

Frequency (cm^{-1})	Shift (cm^{-1})
1532	1.4 ± 0.1
1485	1.0
1428	1.7
1410	0.9
1401	1.1
1314	0.9
1252	2.9
1113	0.6
1056	0.4
1017	0.2
960	1.3
860	0.0
837	0.2
732	0.3
705	0.6
689	1.4
627	0.0
605	0.0

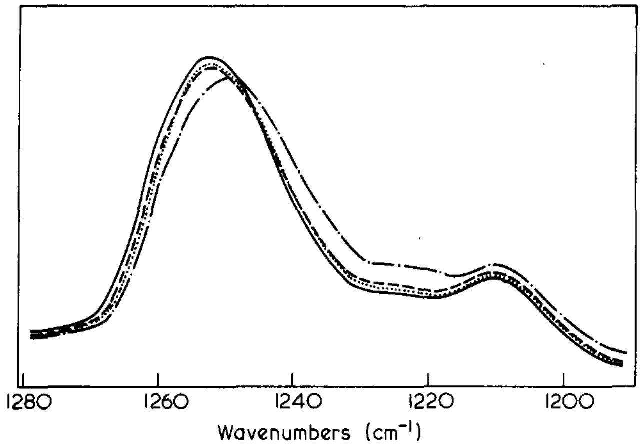
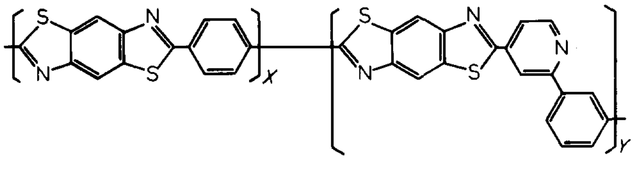


Figure 5 Stress induced spectroscopic changes for the 1252 cm^{-1} band in PBT: A (——) no stress; B (— · —) 0.18 GPa; C (— — — —) spectrum taken immediately after stress is released (<70 s); D(· · · · ·) spectrum taken from a relaxed sample

bond (~5 mdyne Å^{-1}) connecting the phenyl ring to the heterocyclic ring and the cross sectional area (~10 Å)^2 measured for PBT[31], the maximum theoretical modulus is estimated to be ~500 GPa, a value much higher than measured. (This estimate is high because the valence angle deformation should lower this value somewhat.) Nevertheless, these comparisons are important and demonstrate the usual difficulty in relating the macroscopic stress to the changes at the molecular level, even for these highly ordered films processed from anisotropic liquid crystalline state.

The most interesting band is the perpendicular 1252 cm^{-1} band of medium intensity. The frequency of this band lowered to 1249 cm^{-1} when a 0.18 GPa stress is applied. Representative spectra are shown in *Figure 5*. The frequency variation as a function of applied stress is shown in *Figure 6*. It is generally accepted that in stressed polymers, bonds weaken causing a decrease in the force constant; therefore, the frequency shift is observed. The sensitivity of this perpendicular band is surprising since skeletal modes with transition moments parallel to the drawing direction are generally more sensitive to the applied stress[14–16]. Also, although the frequency of this perpendicular band is sensitive to the stress applied, it can also be affected by sample preparation. For sheared PBT films of high orientation, it is located at 1251.8 cm^{-1}, but for PBT as prepared resin (in KBr), it is located at 1249.2 cm^{-1}. In certain experimental polymers, 'swivel' segments are added forming copolymers of PBT. The structure of the copolymer is:



where $x = 0.90$ and $y = 0.10$. As a result, this band in the copolymer is shifted to 1247.6 cm^{-1}. This kind of copolymer in solution does not exhibit an isotropic to anisotropic transition. The film formed is of much lower perfection when compared to PBT. Therefore, our observations suggest a correlation between the frequency of this band and the uniformity and magnitude of intermolecular interaction providing an alternative explanation for the frequency shift in stressed PBT.

Although the frequency shift is the most obvious change measured when the polymers are stressed, it should be noted that the band shape is perturbed as well. For example, the 1249 cm^{-1} band in stressed polymers exhibit a definite increase in the intensity at the low frequency side of the central peak. This is similar to the behaviour observed for typical stress-sensitive infra-red bands in semicrystalline polymers[15,16]. As discussed earlier, the frequency shift, $\Delta\nu$ is proportional to the applied stress σ usually expressed as:

$$\Delta\nu = \alpha\sigma$$

where α is the experimentally determined proportionality constant. The 'tail' of a vibrational band developed in stressed polymer is usually interpreted as being caused by the non-uniform stress distribution at the microstructural or molecular level. Although the macroscopic stress applied is uniform, the actual stress at the microstructural level may be heterogeneous due to conformational or packing defects. For similar strain, some of the bonds or regions may be loaded much more than sample taken as a whole forming the so-called 'overstressed bonds' vibrating at lower frequencies[15,16]. In most semicrystalline polymers, amorphous regions usually contain chain folds, tie chains, cilia, as well as completely unincorporated molecules. The disordered structures (macro or micro) in these PBT films has not been characterized sufficiently to provide a phenomenological mechanism relating macroscopic load to the molecular level in order to explain the frequency changes.

A definite explanation for the changing band shape is still lacking, but we have given particular attention to the time dependence of the spectroscopic changes observed. Although the frequency recovers to the original position almost instantaneously, the band shape does not. In *Figure 5*, the curve C was measured immediately after the load was released. In this case, the frequency of the central peak is 1251.6 cm^{-1} as compared to the 1251.8 cm^{-1} in the original sample. However, the shape does not fully

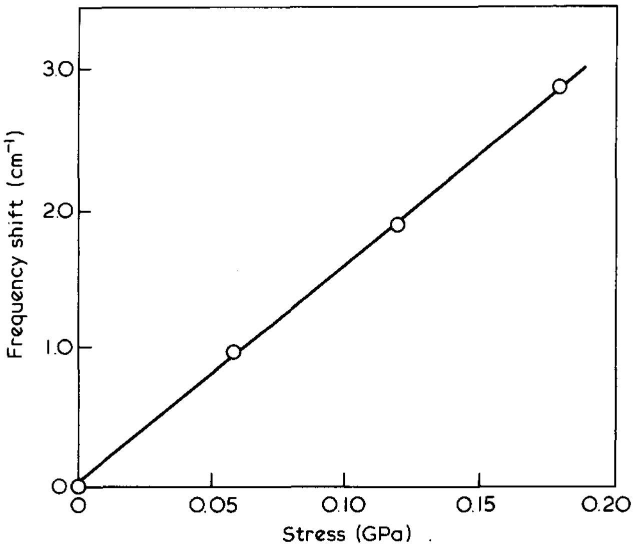


Figure 6 Frequency shift of the 1252 cm^{-1} band as a function of stress

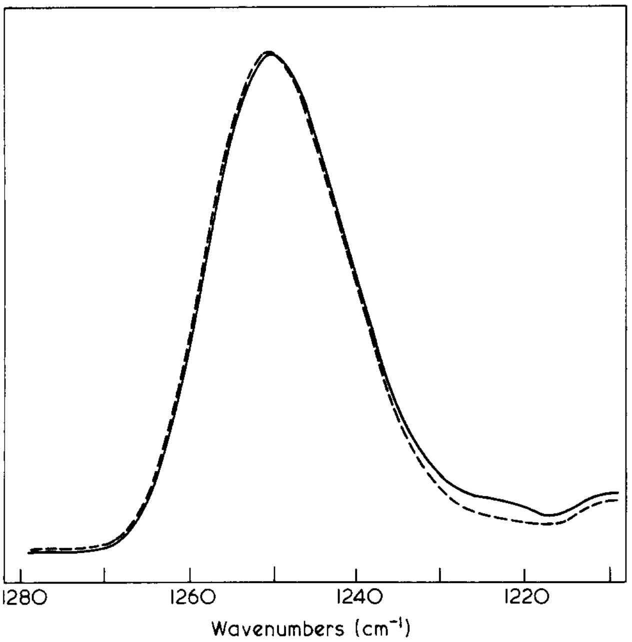


Figure 7 Infra-red spectra taken after the stress is applied: A (———) immediately after the stress is applied (<0.35 s, 0.18 GPa); B (– – – –) taken after 140 s when stress is relaxed to 0.11 GPa

recover until 18 h after the load was released. Similar observations can be seen in the stress–relaxation experiments as shown in *Figure 7*. Curve A was taken immediately (< 140 s) after a load (0.18 GPa) was applied. In this case, the frequency of the central peak shifts to 1249.7 cm^{-1} from the original 1252 cm^{-1}. After 140 s, the central peak shifts slightly to 1249.9 cm^{-1} (curve B). However, the intensity on the low frequency side decreased substantially as a function of time. The precise nature of our spectroscopic changes are still unclear, and are being studied in our laboratory.

CONCLUSION

The infra-red spectra obtained for stressed rigid-rod PBT exhibit a number of changes in band polarization, frequency and shape. The stress-induced polarization changes have been explained in terms of the changing dihedral angle between the phenyl ring and the heterocyclic group. In most cases frequency changes can be explained by a reduction of force constant for polymers in the stressed state. However, the frequency shift of a perpendicularly polarized band has been interpreted to result from a disruption of intermolecular interaction in stressed polymers. This interpretation is supported by the changing frequency of similar magnitude also observed in samples containing much lower degrees of orientational order. Lastly, by using rapid scanning Fourier transform technique, we observed that frequency and bandshape change on a different time scale. The eventual goal is to correlate these changes to the molecular dynamics when a macroscopic stress is applied to the polymers.

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