High-temperature properties of PBZT fibres

K. S. Macturk* and R. K. Eby
Department and Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

and B. L. Farmer
Department of Materials Science and Engineering, The University of Virginia, Charlottesville, VA 22901, USA
(Received 30 November 1992; revised 4 May 1993)

Molecular dynamics simulations were performed in an attempt to elucidate the molecular mechanism of a relaxation measured experimentally in poly(*p*-phenylene benzobisthiazole) (PBZT) fibres. Results for the coefficient of thermal expansion and tensile modulus parallel to the molecular axis agreed favourably with published experimental values. The X-ray peak intensity ratio of (200)/(010) *versus* temperature obtained from the simulations showed a variation qualitatively similar to that from experiments. The torsion angle between the benzobisthiazole and phenyl moieties increased with temperature. A distortion of the phenyl and benzobisthiazole moieties also occurred and the molecules were observed to undergo increased oscillatory ribbon-like motions perpendicular to the (010) plane as the temperature increased. Finally, translational oscillations of the molecules parallel to the *c*-axis occurred. These molecular motions are coupled to the tensile stress and could play a role in the relaxation.

(Keywords: molecular dynamics; PBZT fibres; relaxation)

INTRODUCTION

Poly(*p*-phenylene benzobisthiazole) (PBZT) fibres are well known for their high specific tensile strength and specific modulus. They also have potential for use in high-temperature applications. Therefore, it is necessary to understand their behaviour in these environments. Use of ultrasound to investigate the modulus–temperature relationship of these fibres produced evidence of a relaxation in the 300–400°C temperature range[1]. A change in the ratio of the wide-angle X-ray diffraction peak intensity of (100) (one molecule per unit cell) relative to (010) was also found in this temperature range. In addition, a peak in attenuation of the ultrasonic waves used to make the modulus measurements was found and t.g.a. measurements showed a small weight loss. The combined data suggest a relaxation is occurring. The authors noted that there must be a coupling between the applied stress and the molecular mechanism of the relaxation. A change in the torsion angle between the benzobisthiazole and phenyl moieties was proposed as a possible mechanism. A similar change has been observed in *para*-phenylenes[2]. It was also noted[2] that there is evidence of a mechanical relaxation in other polymers which contain heterocyclic moieties in the backbone[3,4]. The purpose of this paper is to report results from a modelling investigation of the molecular mechanisms that might be involved in the relaxation.

COMPUTATIONAL METHOD

Molecular dynamics simulations were performed using the SYBYL software package from Tripos Associates. The force fields were modified according to published work[5]. The non-primitive unit cell[6] was minimized using a grid search. The experimental unit cell and minimized unit cell dimensions are shown in *Table 1*. The value of γ was 94.0°. An array of chains arranged as shown in *Figure 1* was used for the simulations. The molecules were five monomers in length. Alternating rows of molecules in the array were shifted one-third of a repeat unit in the z-direction. Thus, a unit cell consists of molecules 1–6 in *Figure 1*. Molecules 2, 5 and 8 were shifted one-third of a repeat unit in the z-direction relative to the others. During the dynamics runs, molecules 2, 4, 5, 6 and 8 were allowed to move. The rest of the molecules were held fixed due to memory and speed limitations of the computer. Dynamics simulations 10 000 fs in length were run at temperatures of 27, 197, 277, 347, 427, 497 and 577°C. Time steps of 1 fs were used with data being saved every 25 fs. Since the autocorrelation functions of the properties of interest showed the data were not yet uncorrelated, the simulation at 27°C was extended to 100 000 fs. Even this extended simulation time did not result in uncorrelated data. Since the size of the dynamics history file was very large, the calculation could not be extended. The dimensions of the arrays were expanded with temperature to match experimental values of the unit cell dimensions and γ was held constant[1].

In order to test the validity of the simulations the coefficient of thermal expansion (CTE) and the tensile modulus were calculated. The tensile modulus for the array run at 27°C was found using a published approach[7]:

$$E = 4v^2L^2\rho$$

where E is the tensile modulus, v is the frequency of the longitudinal acoustic mode, L is the length of the molecule and ρ is the density of the unit cell. The frequency of the

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* To whom correspondence should be addressed

0032-3861/94/010053-04

Table 1 Experimental and minimized unit cell dimensions

Unit cell dimension	Experimental unit cell[a] (Å)	Minimized unit cell (Å)
a	11.790	13.150
b	3.539	3.189
c	12.514	12.711

[a] From ref. 6

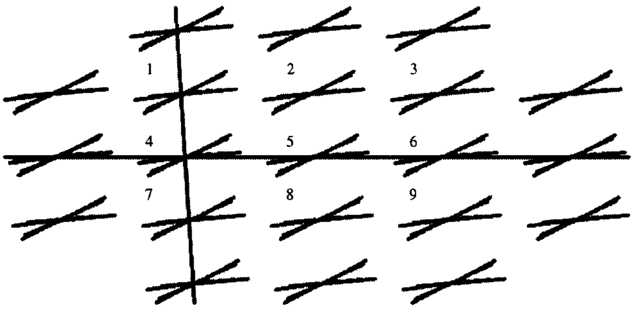

Figure 1 Molecular array used for dynamics simulations. Molecules are five monomers long. The (200) plane is vertical and the (010) plane is horizontal. Benzobisthiazole moieties are parallel to (010) and phenyl moieties are approximately 20° from (010). Molecules 2, 5 and 8 are shifted one-third of a repeat unit into the page

mode was found by doing a Fourier transform of the length of the central molecule *versus* time. The coefficient of thermal expansion was calculated with the time-average lengths at 27, 347 and 427°C.

The X-ray intensities of the relevant peaks were calculated using the following formula:

$$I_{(hkl)} \propto [\{\textstyle\sum f_j e^{-M_j} \cos 2\pi(hu_j+kv_j+lw_j)\}^2 + \{\textstyle\sum f_j e^{-M_j} \sin 2\pi(hu_j+kv_j+lw_j)\}^2]$$

where f_j is the atomic scattering factor for atom j; u_j, v_j and w_j are the fractional coordinates of atom j; $M_j = 8\pi^2\mu^2[(\sin\theta)/\lambda]^2$; μ^2 is the mean squared displacement of atom j normal to the plane with Miller indices (hkl); θ is one-half the scattering angle and λ is the wavelength of radiation used. Molecules 5 and 6 from *Figure 1*, both of which were allowed to move during the simulations, were used to calculate the time-average X-ray intensities. Theoretically it is difficult to accurately estimate μ^2 in anisotropic materials. Using molecular modelling it is a fairly straightforward task.

RESULTS AND DISCUSSION

The thermal expansion coefficient and tensile modulus are given in *Table 2* along with experimental results from the literature. The modelling results compare favourably with the experimental values. In addition, the computed coefficient for 27 to 347°C matched that determined for a modelling time of 3000 fs[8]. Finally, the results for 27°C changed little during the extended simulation time. Thus, the model appears to be reasonable.

The modelling analogue of the experimental X-ray results is given in *Figure 2*. In this figure, as in all others, the errors are less than or equal to the size of the symbols themselves. The curve exhibits an increase in the peak intensity ratio in the 300–400°C range which is qualitatively similar to the experimental curve. In addition the magnitude of the curve is correct. Examination in further detail of the change in intensity ratio shows that the intensity of the (200) peak remains essentially constant over the temperature range studied (*Figure 3*), while the intensity of the (010) peak decreases as the temperature increases (*Figure 4*). This accounts for the increase in the ratio of the peak intensities (200)/(010). Thus, the molecular mechanism responsible for this decrease must increase the displacement of the atoms relative to the (010) planes while leaving the distance from the (200) planes relatively unchanged. *Figure 4* also shows that the decrease in (010) intensity is due mainly to the motion of the aromatic carbon and sulfur atoms. The labels in *Figures 3* and *4* indicate the atom types which were considered to be moving in the calculation, i.e. the atom types for which the e^{-M} term was included. Thus, the curves labelled by atom type in *Figures 3* and *4* must be examined mainly for changes in intensity since the magnitude of the intensity has been altered because the motion of only the specified types of atoms was taken into account.

Table 2 Comparison of experimental and modelling results

Property	Experimental	Modelling
10^{-6} CTE (K^{-1}) (27–427°C)	−7[a] (oriented film)	−6
Tensile modulus (GPa)	450[b]	370

[a] From ref. 12
[b] From ref. 1

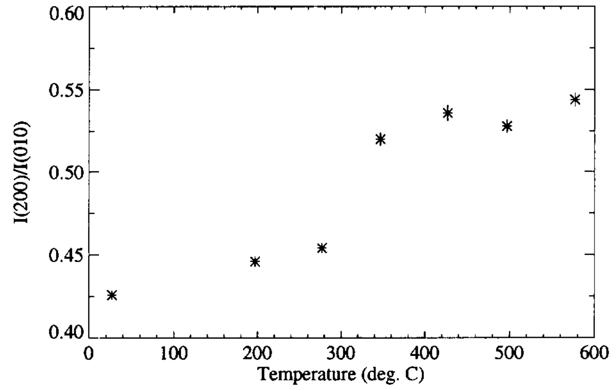

Figure 2 Modelled X-ray intensity ratio (200)/(010) *versus* temperature

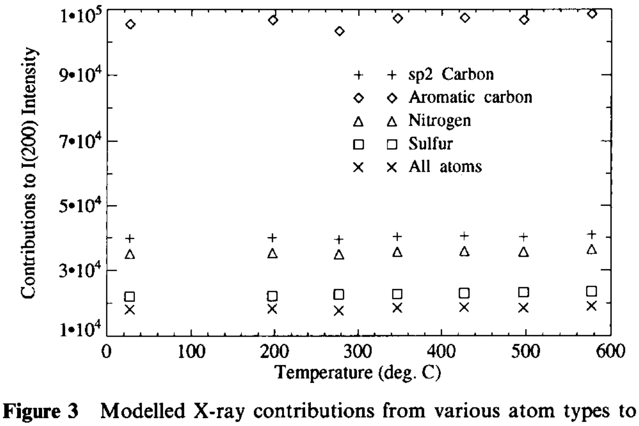

Figure 3 Modelled X-ray contributions from various atom types to (200) intensity *versus* temperature

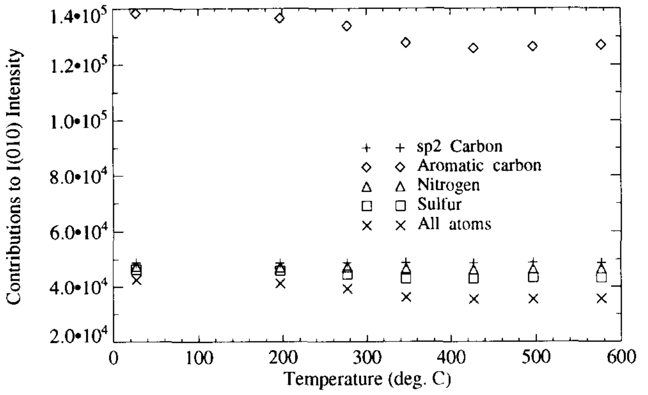

Figure 4 Modelled X-ray contributions from various atom types to (010) intensity *versus* temperature

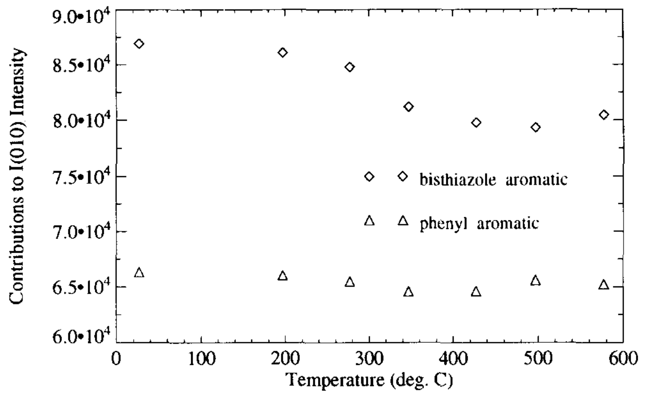

Figure 5 Modelled X-ray contributions from aromatic carbons for (010) intensity *versus* temperature

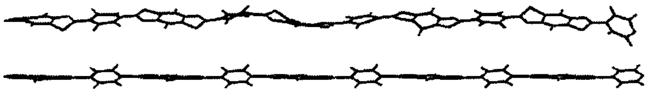

Figure 6 Ribbon-like distortion of molecule at 277°C. The bottom molecule is undistorted

A further investigation of the aromatic carbon atoms shows that the decrease in (010) intensity is due mainly to a decrease in the intensity contributions from the aromatic carbons in the benzobisthiazole moieties (*Figure 5*). Thus, the molecular mechanism of the increase in the peak intensity ratio would seem to be an increase in the displacement of the aromatic carbon and sulfur atoms with the aromatic carbon atoms in the benzobisthiazole moieties experiencing a larger increase in displacement than do those in the phenyl moieties.

The exact nature of the molecular mechanism is difficult to discern. The increase in r.m.s. torsion angle between the phenyl and benzobisthiazole moieties was mentioned earlier. In addition, examination of the molecules during dynamics playbacks showed another displacement mechanism to be a combination of an increase in ribbon-like oscillatory motion of the molecules as a whole perpendicular to the (010) plane and a puckering of the phenyl and benzobisthiazole moieties as the temperature increases. *Figure 6* shows an example of this for a simulation at 277°C. In general, the shape of the molecules at any given moment appears similar to that reported previously to account for the negative coefficient of thermal expansion parallel to the molecular axis[8]. The effects of the torsion angle and ribbon-like motions are difficult to separate.

In addition, mean square displacements of ~0.1 Å^2 along the *c*-axis were found at room temperature. The mean square displacements increased with temperature. These displacements would be affected by the finite size of the model. For example, the magnitude of the barrier that must be surmounted for a given translation could be reduced. Therefore, the magnitude should be viewed qualitatively. Nevertheless, the array is ordered at the start of the simulation and the *c*-axis displacements can be thought of as axial translational disorders. These disorders will have the effect of reducing intensities of spots on the upper layer lines of a fibre diffraction pattern[9,10] and, thus, help to explain the limited number of reflections seen on the upper layer lines in PBZT.

It is possible that the above motions are involved in the relaxation. The axial translations will be coupled to tensile stress applied along the fibre axis. Since the ribbon-like motion shortens the molecule, it too will be coupled to the tensile stress. Finally, the torsional oscillations of the moieties are also coupled to the tensile stress[11]. Provided that the molecules rearrange with a resulting strain at a relaxation time τ under an applied stress and that the frequency of the applied stress is equal to $1/(2\pi\tau)$, a relaxation will be observed. For the experimental frequency used, the relaxation time in the 300–400°C range would be of the order of 3×10^{-7} s, which is considerably longer than the simulation time. However, the motions are coupled to the stress and could be involved in the relaxation. This possibility is strengthened by the good agreement between experimental and modelled results for X-ray, modulus and thermal expansion data.

CONCLUSIONS

The results of the dynamics simulations show the same general behaviour for the X-ray intensity ratio *versus* temperature as experiment. The mechanism appears to be due to an increase in displacement relative to the (010) planes of the aromatic carbons, mainly those in the benzobisthiazole moieties, and the sulfur atoms. The displacement results from a combination of torsional oscillations between the phenyl and benzobisthiazole moieties, a ribbon-like motion of the molecule as a whole perpendicular to the (010) plane and out-of-plane distortions of the phenyl and benzobisthiazole moieties themselves. Finally, translational motions of the molecules parallel to the *c*-axis were observed. These motions might play a role in the mechanical relaxation which has been observed.

ACKNOWLEDGEMENTS

This work was funded by the Petroleum Research Fund, the University of Akron Research Committee and the Robert C. Musson Endowment. The help of Howard Fisher and Philip Klunzinger is gratefully acknowledged.

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