Solid-state thermochromic transition in poly(2-methoxyphenylene vinylene)

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The crystalline, conjugated polymer poly(2-methoxyphenylene vinylene) undergoes a solid-state thermochromic transition at about 350°C. The optical absorption maximum shifts hypochromically as the colour of the film changes from orange to olive-green during the transition. This effect can be correlated with an endothermic event, as seen in differential scanning calorimetric measurements. Polarized infra-red spectra reveal that movements of the phenylene rings about the chain axis are involved in the transition. The polymer deviates from the low-temperature rigid-rod planar structure during the transition, but conjugation is restored at temperatures above the transition. A molecular motion mechanism is proposed that involves phenylene ring wagging motion relative to the ring–ring axis as the temperature increases. At the transition temperature, the rings undergo a 180° flip about the chain axis. This motion causes a temporary and reversible decrease of effective conjugation along the backbone of the polymer, and the colour change is interpreted as a consequence of such phenylene ring motions.

(Keywords: thermochromic transition; poly(2-methoxyphenylene vinylene); film; molecular motion; differential scanning calorimetry; infra-red spectroscopy; X-ray diffraction)

INTRODUCTION

Substituting alkyl or alkoxy groups on an aromatic polymer structure that can assume a rigid-rod (high persistence length) conformation can effectively manipulate the solid-state properties of these polymers (for example, ionization potential, melting point, solubility and crystallinity)[1–4]. Of particular relevance in this context are studies of alkyl-substituted polythiophenes[5–7]. Addition of these substituents to the molecular backbone increases the solubility of the polymer without significantly affecting electronic properties[5]. Thermochromism and solvatochromism have been observed in poly(3-alkylthiophenes) (P3AT), both in the solid state and in solution[6,7]. The length of the side chains affects the related order–disorder chromic transition. The transition associated with colour changes occurs at lower temperatures and is accompanied by a larger shift in the absorption maximum in the polymers as the length of the alkyl side chain increases[7,8]. The chromic transition in conjugated systems is associated with a decrease in the extent of delocalization of the polymer main chains, and it has been suggested that this transition is primarily an intramacromolecular process with minimal intermolecular contributions[9]. A theoretical analysis has been presented in an attempt to correlate the colour transition with segmental tilt or ring-tilt motions in conjugated polymer systems[7,10].

Poly(2,5-dihexyloxyphenylene vinylene) (DH-PPV), also an alkoxy-substituted conjugated polymer, has been synthesized and found to be soluble in common organic solvents[11]. This amorphous PPV derivative shows an electronic absorption spectrum similar to that of highly crystalline poly(2,5-dimethoxyphenylene vinylene) (DMeO–PPV)[12], a result suggesting that extended conjugation is maintained in DH–PPV. Like poly(3-alkylthiophenes) and certain other substituted polydiacetylene derivatives[9,13], DH–PPV exhibits thermochromism and solvatochromism[14].

The aforementioned polymers that exhibit thermochromism are all soluble, non-crystalline or partially crystalline, conjugated systems. In this contribution we show that the crystalline, insoluble, infusible conjugated polymer poly(2-methoxyphenylene vinylene) (MeO–PPV) also exhibits a distinctive thermochromic transition. This transition was observed at about 350°C. The colour changes in the solid film were observed by optical microscopy and further characterized by ultra-violet/visible (u.v.-vis.) spectroscopy. Polarized infra-red spectroscopy, differential scanning calorimetry (d.s.c.) and X-ray diffraction data enabled us to attribute the transition to motions of the phenylene rings located in the chain axis.

EXPERIMENTAL

Samples

Poly(2-methoxyphenylene vinylene) was prepared as previously described[15]. Unoriented thin films of MeO–PPV were cast from aqueous solution of the precursor polyelectrolyte and thermally converted to MeO–PPV under vacuum at 280°C. Stretch-oriented film samples were obtained by using a drawing apparatus as reported previously[16]. Another type of sample was used in d.s.c. measurements and was prepared as follows.

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With vigorous stirring, 500 ml of cold isopropanol was added to 100 ml of a concentrated aqueous solution of MeO-PPV precursor polyelectrolyte. A white, gelatinous precipitate was formed. The precipitate was rinsed first with additional isopropanol and then with a copious amount of diethyl ether. The precipitated polyelectrolyte was dried and thermally converted to MeO-PPV under vacuum at 280°C. This type of sample contained a substantially higher amorphous content than did the film samples.

Measurements

U.v.-vis. spectra were obtained with an IBM-9420 u.v.-vis. spectrophotometer using free-standing films of MeO-PPV mounted on a hot stage. Thermal contact was ensured by using a quartz plate to cover the film samples and the temperature was controlled with an MTS90/TH600 system (Linkam Scientific Instruments). The sample chamber was under a nitrogen blanket during spectral acquisition.

Infra-red spectra were recorded with an IBM IR/30 *FT*i.r. spectrometer. The spectral resolution was set at 2 cm^{-1}, and spectra were signal averaged over 100 scans. A Perkin-Elmer gold wire grid polarizer was used to obtain the polarized spectra. The incident beam was polarized in directions perpendicular and parallel to the film-stretching axis during these measurements. Nitrogen protection and temperature control used for obtaining the u.v.-vis. spectra were employed in the i.r. measurements.

Differential scanning calorimetry (d.s.c.) measurements were performed with a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples for d.s.c. measurements were typically 5 to 10 mg and were scanned up to 400°C.

RESULTS AND DISCUSSION

Optical spectra of MeO-PPV

The MEO-PPV film was examined visually under an optical microscope when the sample was heated from room temperature to 370°C. The visible colour of the MeO-PPV film changed gradually from orange to yellowish orange from room temperature to about 310°C, and then more abruptly to olive-green between 310 and 370°C. The onset of the colour change was observed to start at about 310°C. Upon cooling to below 300°C, the polymer film turned orange again, with residual, frozen-in olive-green regions. This thermochromic process could be repeated two or three times provided the sample was not heated to above 380°C. Furthermore, the polymer film turned orange as well at 380°C (above the transition temperature region) before thermal degradation occurred. If the film was held at 380°C for more than 5 min, however, the film turned orange irreversibly, i.e. no colour changes were observed during subsequent heating-and-cooling cycles.

The visually observed colour change was quantitatively characterized by u.v.-vis. spectroscopy. The major absorption peak located at 460 nm at room temperature shifted to 400 nm at 370°C (*Figure 1*). This shift of the MeO-PPV absorption to higher energies occurred slowly as the temperature was raised to 310°C. Between 310 and 370°C, however, the film exhibited a more rapid change in the absorption maximum location. The optical absorption results thus indicate that a thermochromic transition occurred in the solid film of MeO-PPV.

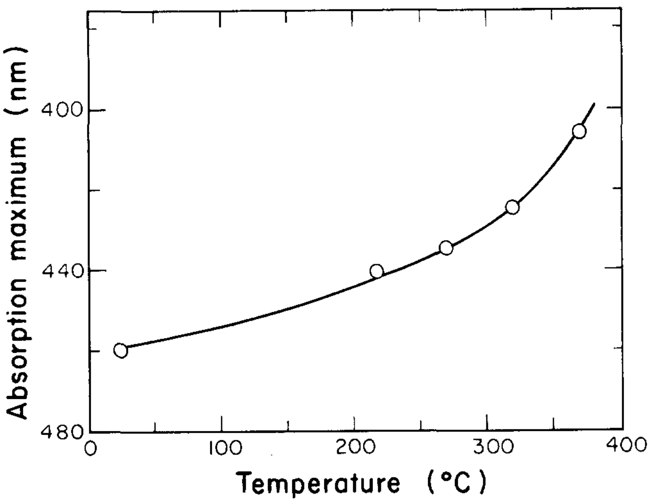

Figure 1 Optical absorption maximum of MeO-PPV shifts as a function of temperature

An X-ray diffraction pattern of the room-temperature sample taken after one heating-and-cooling cycle showed a sharper diffraction pattern than that of an unheated sample, but the unit-cell structure of the heated sample showed no sign of change[17]. This result indicates that the polymer exhibits increased crystallinity after heating to 380°C and that the heating cycle effectively serves as an annealing process.

The thermochromic transition displayed by MeO-PPV is rather unusual because of the crystalline nature of the polymer. Although hypochromic shifts in the optical absorption spectra appear to be a general feature of conjugated polymers when the temperature is increased, such shifts in the absorption maximum are usually small and do not necessarily constitute discrete phase transitions. For example, poly(phenylene vinylene) with a near-perfect crystallinity does not show a distinct thermochromic transition even though a small blue shift is observed as the temperature increases.

Model of molecular motion in MeO-PPV

The shift in optical absorption is apparently a direct consequence of changes in the electronic structure of the conjugated polymer. Previous studies on poly(3-alkylthiophenes) have shown that changes in the electronic structures are strongly associated with single-chain conformational changes of the polymers[7,18]. Tashiro *et al.* proposed that the all-*trans* alkyl side chains of a poly(3-alkylthiophene) undergo disordering conformation motions between *trans* and *gauche* forms as the temperature of the polymer increases[18]. This structural disorder disrupts the regularity of the main-chain conformation and decreases the effective conjugation length of the polythiophene. As a consequence, a decrease in polymer crystallinity and a blue shift in optical absorption are observed at higher temperatures.

This mechanism of molecular motion apparently does not apply to MeO-PPV because, as shown above, the decreased conjugation in MeO-PPV reverts to a more extended conjugation and structural regularity at temperatures above the transition. Therefore, an alternative mechanism of molecular motion is proposed to interpret the observed thermochromic transition in MeO–PPV. The polymer chains of MeO–PPV are proposed to undergo wagging motions at temperatures below 310°C. The gradual blue shift results from such wagging motions of the polymer chains. During the thermochromic transition, the phenylene rings undergo significant 180° flip motions and other associated motions (e.g. near 90° rotations) about the 1,4-ring axis. These motions disrupt the effective conjugation along the polymer chain and, in turn, result in a sharp blue shift in optical absorption of the polymer. The 180° flip motion of the rings may convert the polymer to a more stable conformation and thereby restore extended conjugation.

We have recently studied the chain orientation and molecular motion dynamics of poly(*p*-phenylene vinylene) (PPV)[19,20], a closely related structural derivative of MeO–PPV. It was found that PPV phenylene rings undergo significant 180° jumps about the ring axis in addition to wagging motions. Similar motions are indeed suggested for MeO–PPV based on preliminary ^2H n.m.r.[20] and polarized infra-red absorption studies. On the other hand, MeO–PPV exhibits non-degenerated conformations while PPV involves no energy change before and after a ring flip. As a result, no abrupt phase transition was observed in PPV in this temperature region, whereas a thermochromic transition took place in MeO–PPV. The present model of molecular motion is thus consistent with the optical spectra and X-ray diffraction data and is further corroborated by the i.r. and d.s.c. data, as shown below.

Temperature dependence of infra-red spectra

The infra-red dichroic ratio is sensitive to changes in segmental orientation, which reflects molecular motion in the polymer chain. For example, any rotation or tilting of segments about the chain axis, which is also the stretching axis, will increase the intensity of the perpendicularly polarized absorption component relative to that of the parallel component. Therefore, polarized infra-red spectra provide an effective means for identifying the molecular motion involved in the transition. *Figure 2* shows the polarized infra-red spectra of the polymer films recorded at selected temperatures. Infra-red spectra were collected for perpendicular and parallel polarizations with respect to the sample stretching direction, but only the perpendicularly polarized spectra are shown here.

The infra-red dichroic ratio is the ratio of peak area for an infra-red band with the two different polarizations, as described previously[21]. The changes in dichroic ratio as a function of temperature for a number of infra-red bands have been tabulated, and these changes are illustrated in *Figure 3*. The trend in the dichroic ratios suggests that the polymer underwent a chain-wagging motion about the ring–ring axis at elevated temperatures, a conclusion consistent with the optical data. First, the changes in the dichroic ratio for all of the bands were relatively smooth from approximately 25 to 310°C. This result is in accord with the optical data, which showed a gradual but rather smooth absorption peak shift in this temperature region. Secondly, the asymmetric methoxy substitution of the phenylene ring introduced a number of methoxy-related vibrational bands. The dichroic ratios for this group of infra-red bands changed markedly from 310 to 370°C, whereas other bands exhibited no or very minor changes over the entire temperature range. For example, there was essentially no change in the dichroic ratios of the ring- or chain skeletal-related modes at 1584, 1418 and 1154 cm^{-1}. In contrast, the changes for vibrations related to the methoxy groups were substantial, starting at 310°C (*Figure 3*).

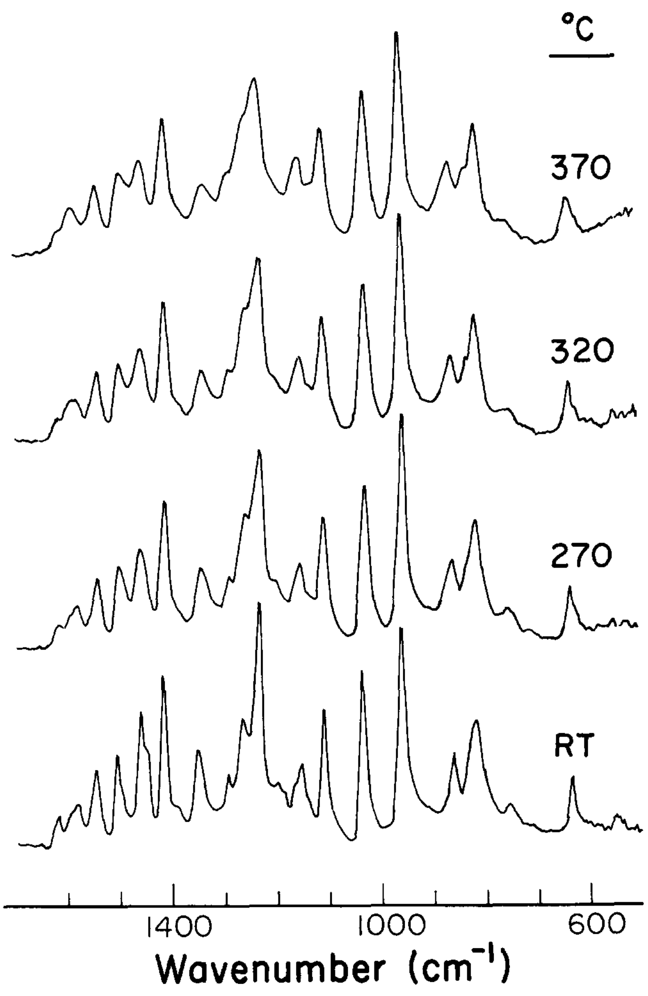

Figure 2 Polarized infra-red spectra of MeO–PPV at selected temperatures. Only the perpendicularly polarized spectra are shown

The i.r. data suggested that the polymer chains undergo wagging and/or rotating motions about the ring–ring axis. Ring-flip motion or 180° ring rotation about the ring axis has been observed in poly(*p*-phenylene)[22] and poly(*p*-phenylene vinylene)[19,20] even at room temperature. Such motion intensifies at elevated temperatures in these polymers[20]. The i.r. data alone cannot differentiate the two types of molecular motions. However, if the i.r. data are compared with the optical results, the gradual changes in i.r. dichroic ratio and optical absorption shift below 310°C are more reasonably assigned to the wagging motions of the polymer chains. The abrupt changes in i.r. dichroic ratio and in optical absorption between 310 and 370°C were attributed to the 180° ring-flip motions. Furthermore, the methoxy groups on the phenylene rings will raise the activation energy of ring-flip motion in MeO–PPV as compared to PPV. We believe that the methoxy groups effectively hinder such ring-flip motion in MeO–PPV at lower temperature. Therefore, the i.r. data corroborated the optical results. A variable-temperature ^2H n.m.r. investigation will differentiate these molecular motions in more detail.

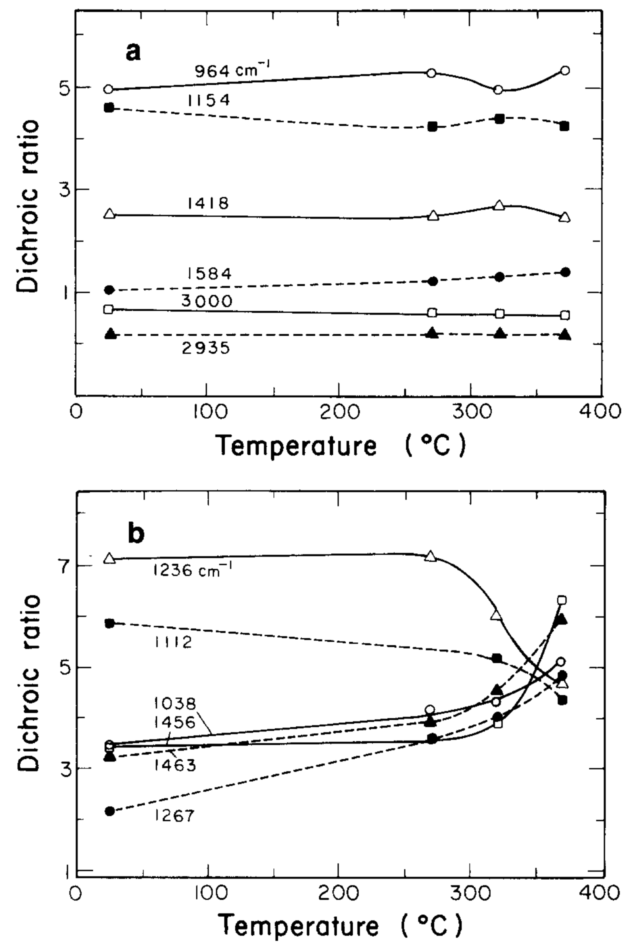

Figure 3 (a) Infra-red dichroic ratios change smoothly with temperature for the skeletal-related vibrations of MeO-PPV. (b) Infra-red dichroic ratios for the methoxy-related vibrations change rapidly with increasing temperature from 310 to 370°C

D.s.c. data and the regions of molecular motion

The d.s.c. data are presented in *Figure 4*. The thermochromic transition occurring between 310 and 370°C described above was accompanied by an endothermic absorption in the d.s.c. thermographs. *Figure 4b* shows the d.s.c. results for a stretched MeO–PPV film sample. Two smaller endothermic peaks were observed at 287 and 305°C prior to the main endothermic absorption at 355°C. These smaller peaks were attributed to the deorientation process of the sample. The corresponding d.s.c. scan of the amorphous MeO–PPV samples (see 'Experimental' section) exhibited only the main endothermic peak at about 350°C (*Figure 4a*).

The heat uptake varied significantly for the two types of samples. The stretch-oriented film sample had a ΔH of $8.3 \mathrm{J\,g^{-1}}$ (cf. $29.5 \mathrm{J\,g^{-1}}$ for the sample with a substantially higher amorphous content). It is known that stretch orientation of a linear polymer increases the crystallinity of the polymer[23]. Thus it is evident that the stretched film sample of MeO–PPV had fewer structural disorders and defects than did the sample obtained by direct precipitation.

Ring-flip motion has been attributed to the amorphous and disordered boundary regions of semicrystalline polymers[24]. Because of the asymmetric monosubstitution on the phenylene rings, MeO–PPV exhibits lower crystallinity and more amorphous defects and paracrystalline disorder than does PPV[17]. Ring-tilting or ring-flipping motions are energetically easier in these regions, and stronger ring-flip motion in these disordered regions is expected. If this is in fact the case, then we should see an increase in heat uptake for samples with a higher content of disordered regions and defects. This increased heat uptake was indeed observed, as shown by the d.s.c. thermogram in *Figure 4*.

CONCLUSIONS

A distinct thermochromic transition was observed in solid films of MeO–PPV, a highly crystalline, conjugated polymer. A possible mechanism of molecular motion is proposed. The chains of MeO–PPV start to wag and tilt about the ring axis as the temperature increases. These motions lead to a gradual decrease in conjugation and thus a blue shift in the optical spectra. As the temperature increases further, the phenylene rings undergo 180° flips about the chain axis, starting at about 310°C. These motions are primarily single-chain conformational changes, which result in a significant decrease in effective conjugation and, therefore, a distinctive colour change. The asymmetric substitution in MeO–PPV introduces a substantially higher content of structural disorders (in paracrystallinity, in particular) in MeO–PPV than in PPV[17]. The ring-flip motion will reduce steric crowding in MeO–PPV and transform the polymer chain into an energetically more stable conformation, such as an all-*trans* arrangement of the methoxy groups. This rearrangement increases the regularity of the chain and

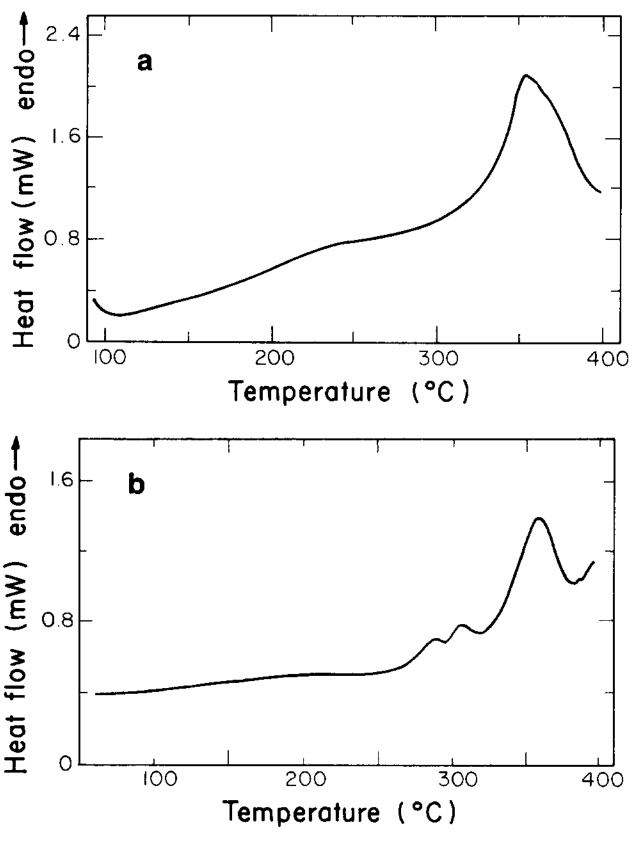

Figure 4 (a) D.s.c. thermogram of an MeO–PPV sample (4.36 mg) obtained by solution precipitation from precursor polyelectrolyte and followed immediately by thermal conversion to MeO–PPV. (b) D.s.c. thermogram of a stretched film sample of MeO–PPV (6.44 mg). Scan rate: 20°C min⁻¹

thus improves the crystallinity of the polymer. This model is consistent with the optical and polarized infra-red data, and is further supported by the X-ray diffraction result, which shows that a heated sample shows higher crystallinity than do unheated films. The d.s.c. data suggest that the polymer chain motions take place primarily in regions with more structural disorder.

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