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FT i.r. investigation of the inclusion compound formed between trans-1,4-polyisoprene and urea

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Several small-molecule hosts form inclusion compounds (ICs) with polymers. In these ICs the guest polymer chains are highly extended and isolated from neighbouring polymer chains by the clathrate wall. Only polymers with extended conformations are narrow enough to reside in the narrow channel. An inclusion compound has been formed between urea and trans-1,4-polyisoprene (TPI) and investigated using *FT*i.r. spectroscopy. Infrared bands observed for this IC indicate that the crystal structure of this IC is most likely different from the usual hexagonal crystal structure. It is also suggested that TPI in the channel adopts a conformation which is similar to bulk TPI with β crystal modification.

(Keywords: trans-1,4-polyisoprene; urea; inclusion compound)

Introduction

The crystallization of trans-1,4-polyisoprene (TPI) from solution and melt have been investigated previously[1–3]. TPI can be crystallized in either, or both, monoclinic (α) or orthorhombic (β) crystal forms. The α form has a monoclinic unit cell with two chains, each containing two repeating units. The β form has an orthorhombic unit cell with two chains, each containing one repeating unit. Crystallization from solution usually yields overgrown α form TPI lamellae. Crystallization from the melt at room temperature yields a β crystal form with hedrite type morphology. It is well known that certain small molecules, such as urea, perhydrotriphenylene (PHTP) and thiourea, can form complexes with homopolymers such as polyethylene (PE), poly(ethylene oxide) (PEO) and polybutadiene[4–6]. This provides an opportunity to study the conformations and motions of polymer chains which are isolated from neighbouring chains and are forced to occupy narrow, cylindrical crystalline channels. D.s.c., *FT*i.r. and solid-state n.m.r. spectroscopy are often applied in the characterization[7,8] of these polymer inclusion compounds (ICs).

The i.r. spectra of α and β TPI have been obtained at room temperature, and the 100% crystalline spectrum obtained by subtraction of a spectrum taken from the melt[9]. Single chain, normal coordinate calculations were carried out for both α and β TPI and correlations between the α and β TPI spectra were made[10]. We have used i.r. spectroscopy to study the conformation of isolated polymer chains in the narrow urea IC channel, the change in urea crystal structure, and the types of interaction involved between host matrix and guest polymer chains[11–13]. In the present work, *FT*i.r. spectroscopy is used to investigate the inclusion compound formed between TPI and urea. Some of the shifts in the vibrations from tetragonal urea that occur in the IC are explained in terms of crystal structure changes during the IC formation.

Experimental

TPI with $MW = 1.7 \times 10^5$ was dissolved in tetrahydrofuran (0.5 g/50 ml) and mixed with 50 ml of urea/methanol saturated solution while continuously warming and stirring. The combined solution was cooled to room temperature. A white precipitate was obtained over a day, and was filtered and dried. Unreacted polymer was removed by washing the sample with warm toluene. Semicrystalline samples with the crystalline component in the α form were obtained by cooling 1% TPI/amyl acetate solution directly to room temperature. Samples with the crystalline component in the β form were obtained from the melt at room temperature.

FT*i.r. spectroscopy.* *FT*i.r. spectra were recorded on powdered TPI–urea(U)–IC samples pressed into KBr pellets on a Nicolet 510P *FT*i.r. spectrometer at frequencies from 4000 to 500 cm^{-1}. All spectra were obtained at a resolution of 2 cm^{-1} via accumulation of 64 scans. Films were used to obtain the i.r. spectra of bulk TPI with α and β crystal forms.

Results and discussion

Figure 1 shows the Fourier transform i.r. spectra of TPI–U–IC, (n-hexadecane) H–U–IC and urea. The comparison of i.r. spectra shows that bands due to urea vibrations observed in TPI–U–IC are shifted from those observed in pure tetragonal urea. The i.r. spectrum of uncomplexed tetragonal urea was studied and band assignments were made[11]. Tetragonal urea has strong absorption bands at 1682 cm^{-1} due to C=O stretching vibration, at 1631 and 1599 cm^{-1} due to N–H bending vibrations, and at 1467 cm^{-1} due to N–C–N stretching

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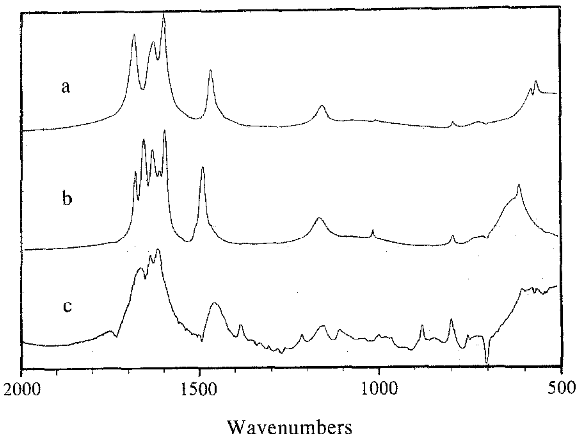

Figure 1 *FT*i.r. spectrum in the region between 2000 and 500 cm^{-1} recorded at room temperature for: (a) tetragonal urea, (b) H–U–IC, and (c) TPI–U–IC

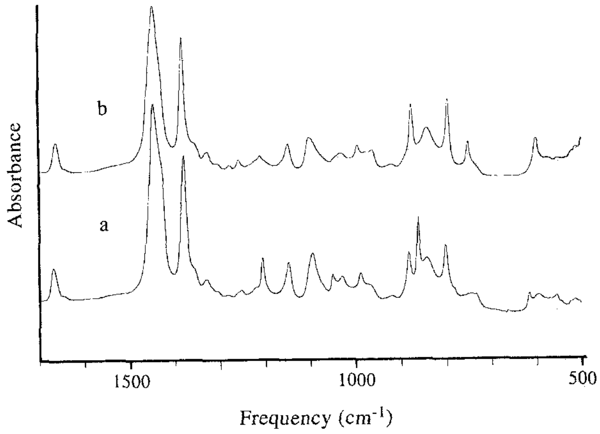

Figure 2 Comparison of *FT*i.r. spectra in the region between 1700 and 500 cm^{-1} recorded for: (a) α TPI and (b) β TPI

vibration. The TPI–U–IC spectrum contains bands characteristic of channel-forming urea and TPI included in the channel. The differences in urea vibrations can be seen in the 1400–1800 cm^{-1} region. In the TPI–U–IC, vibrational bands due to tetragonal urea at 1682, 1631, 1599 and 1467 cm^{-1} are shifted to 1663, 1639, 1617 and 1454 cm^{-1}, respectively. These observed band shifts are different from the band shifts observed for the usual hexagonal U–IC crystal structure. We have investigated a series of inclusion compounds including (n-hexadecane) H–U–IC and [poly(ϵ-caprolactone)] PEC–U–IC using X-ray diffraction and *FT*i.r. spctroscopy[11–13]. It has been inferred that these ICs are isostructural. Two bands at 1658 cm^{-1}, due to C=O stretching, and at 1490 cm^{-1}, due to N–C–N stretching vibrations, were attributed to the hexagonal crystal structure. We see different band shifts for TPI–U–IC, suggesting that the crystal structure of this IC is most likely different from the usual hexagonal crystal structure. Similar *FT*i.r. spectra are also obtained for the inclusion compound made between isotactic polypropylene and urea. It would be useful to determine the crystal structure of these ICs. However, so far we have not been able to obtain single crystals of these materials[14].

In order to determine the conformation of an isolated TPI chain in the narrow urea channel, we have compared the *FT*i.r. spectra of two known crystalline forms of TPI. *FT*i.r. spectra recorded for α and β form containing samples are given in *Figure 2*. A number of differences can be seen between these two spectra. The most notable one is the presence of two bands for the α form at 862 and 882 cm^{-1} instead of one band at 877 cm^{-1} for the β form. These bands were attributed to C–H out-of-plane vibration. The CH_2–CH_2 bond in α or β crystal forms can take only the *trans* conformation, but in amorphous TPI either *trans* or *gauche* conformations are possible. Therefore the band at 877 cm^{-1} was assigned to the $ST\bar{S}$ conformation in the β form and the 862 and 882 cm^{-1} bands assigned to the $CTSCT\bar{S}$ conformation in the α form. In amorphous TPI, a broad band at 842 cm^{-1} with shoulders at 860 and 884 cm^{-1} was attributed to various conformations containing either *gauche* or *trans* CH_2–CH_2 bonds.

Vibrational bands due to the included polymer can be seen in the region between 1400 and 500 cm^{-1} in *Figure 1c*. Based on the characteristic band at 877 cm^{-1}, the TPI chain in the channel presumably assumes the $ST\bar{S}$ conformation, the same conformation obtained when the sample is crystallized from the melt with high super-cooling. As we do not observe any notable band shifts from those observed in bulk β TPI (*Figure 2b*), we conclude that there is no strong interaction between the included TPI chain and channel-forming urea.

The inclusion compound formed between PHTP and TPI has been studied using solid-state n.m.r. spectroscopy by Schilling *et al.*[7]. The chemical shifts and spin lattice relaxation times were obtained for isolated TPI chains in the PHTP channel. These data were compared with chemical shift and spin lattice relaxation times observed for α and β crystal forms of bulk TPI. This suggested that polyisoprene in the channels of the PHTP also adopts the β form crystalline conformation of TPI. Our modelling also suggested that for a channel diameter of <6 Å, TPI can only adopt the $ST\bar{S}$ conformation of the β form and was not able to inter-convert between channel conformers without significant expansion of the channel[15]. Mattice has examined the conformations of TPI in the channels of PHTP using molecular dynamics simulations. He concluded that TPI takes the $ST\bar{S}$ conformation in the channel, interacts strongly with the channel, and tends to distort the matrix[16]. These observations are consistent with the conclusions drawn from our *FT*i.r. investigation.

In conclusion, we have formed the inclusion compound between TPI and urea. Our *FT*i.r. observations indicate that TPI–U–IC takes a crystal structure different from the usual hexagonal crystal structure obtained for H–U–IC, [poly(lactic acid)] PLLA–U–IC[13] and PEC–U–IC[12]. It is also suggested that TPI in the narrow (5.5 Å) channels adopts a conformation similar to bulk TPI with the β crystal modification. Motional behaviour of this isolated TPI chain in the narrow U–IC channel will be investigated in the near future and will be compared with the motional behaviour observed for TPI chains in the PHTP–IC channel by Schilling *et al.*[7].

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