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Formation and characterization of thiourea encapsulated polyethylene oxide

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Abstract

The structure and dynamics of PEO chains encapsulated in thiourea (TU) channels formed in the PEO–TU-inclusion compound (PEO–TU-IC) were studied by XRD, FTIR and solid state NMR spectroscopy. XRD and FTIR observations clearly show PEO–TU-IC adopts a crystal structure different from neat thiourea, and the usual rhombohedral crystal structure of thiourea small molecule ICs. PEO chains in the channel adopt a conformation similar to bulk PEO, as confirmed by solid state NMR spectroscopy. Contact-time array (VCT) NMR profiles shows that PEO chains in the TU channels are considerably more mobile than in bulk PEO. Infrared bands for the PEO shift in the IC, and these were attributed to changes in the secondary forces.

Keywords: Polyethylene oxide; Encapsulation; Thiourea

1. Introduction

Supramolecular chemistry is often pursued to develop new material functions, such as magnetic properties, light responsiveness, catalytic activity, self-healing polymers, and chemical sensors that cannot be obtained from a single molecule [1]. Host–guest chemistry, a class of supramolecular chemistry, describes complexes that are composed of two or more molecules or ions held together by secondary forces, such as hydrogen bonding or by van der Waals forces [2,3]. An inclusion compound is a complex in which one component forms a cavity (host) where a second component (guest = alkanes, cyclic alkanes, and macromolecules, etc.) resides. Urea [4], thiourea [5], and cyclodextrins [6] are known to form inclusion compounds with a variety of organic guest molecules. The dynamics and conformations of polymer guests that have been encapsulated in urea [7] and cyclodextrin [8] hosts were studied extensively by Tonelli and coworkers. Urea forms host clathrate channels with a diameter of 5.5 Å, while thiourea forms larger channels with an approximately 7 Å diameter. Thiourea can accommodate aromatic rings as well as branched aliphatic compounds, while urea can accommodate only linear aliphatic chains. Thiourea channels have prominent bulges (diameter 7.1 Å) and constrictions (diameter 5.8 Å) at different positions along the channel, similar to Zeolites [9]. Therefore thiourea inclusion compounds have attracted a great deal of interest. For the first time PEO was encapsulated in thiourea channels (PEO–TU-IC) and structural details of the IC and the mobility of the guest PEO chains are discussed here.

2. Experimental

A physical mixture of thiourea (1 g) and PEO (0.144 g), which corresponds to 4:1 molar ratio, was prepared. The physical mixture was heated in an oven preset at 80 °C about 1 h. A white powdery sample appeared after 1 h. The product was allowed to cool to room temperature and saved in a desiccator for further analysis.

Wide angle X-ray diffraction of powder samples was obtained using a SCINTAG XGEN-400 at room temperature.

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The Cu Kα radiation was operated at 40 kV and 40 mA. The diffracting intensities were recorded in 0.02° 2θ steps over the range of $5° < 2\theta < 40°$.

FTIR spectra were collected using Nicolet 760 Magna spectrometers at wavenumbers from 4000 to 400 cm^{-1} with resolution 4 cm^{-1}. All spectra were taken using KBr pellets and a DTGS detector. In order to obtain high quality spectra, 64 scans were collected at ambient temperature.

High-resolution solid state ^{13}C NMR experiments were performed on a Varian Unity-Plus-200 spectrometer at Process NMR Associates operating at a ^{13}C resonance frequency of 50.2 MHz. The cross-polarization experiments were performed utilizing the variable amplitude cross-polarization pulse sequence in order to reduce the effects of spin modulation on the quantitative nature of the experiment. Magic angle spinning was employed at a rate of 6 kHz. Variable contact time (VCT) experiment, 15 different contact times from 100 μs to 40 ms were used.

3. Results and discussion

PEO with weight average molecular weight 100,000 g/mol was melt-blended with thiourea at 80 °C. A white powdery sample (PEO–TU-IC) was obtained after 30 min in the oven at 80 °C and was characterized by X-ray diffraction (XRD), FTIR and solid state NMR spectroscopy. Fig. 1 shows XRD patterns of thiourea, PEO, PEO–TU-IC and CB–TU-IC. Major reflections at $2\theta = 17.6$, 19.5, 21.5, and 23.8° were observed for pure PEO. The XRD pattern of PEO–TU-IC is different from pure thiourea or pure PEO, suggesting the formation of a PEO–TU-IC. The XRD pattern of PEO–TU-IC is somewhat similar to pure orthorhombic thiourea, with reflections slightly shifted by $\Delta(2\theta) = 0.1–0.5°$. PEO reflections are absent in the XRD pattern of PEO–TU-IC, indicating that there is no free PEO in our IC sample. FTIR and ^{13}C NMR spectroscopic observations show clear evidence that PEO is encapsulated in the host thiourea channels of PEO–TU-IC. DSC scans observed for PEO/thiourea physical mixture and PEO–TU-IC also provided the absolute confirmation of the formation of PEO–TU-IC. Absence of melting transition of PEO in the DSC scan of PEO–TU-IC eliminates the possibility of having PEO in the surface of thiourea. These inclusion compounds are not held together by conventional covalent bonds; instead they are held together by secondary forces such as van der Waals forces or hydrogen bonding. It is reasonable to argue from the X-ray pattern that the crystal structure of PEO–TU-IC is very close to the orthorhombic crystal structure of pure thiourea, which is different from the crystal structures of thiourea-ICs formed with small molecules, such as cyclohexyl bromide (CB) [5]. CB–TU-IC adopts a rhombohedral crystal structure. The XRD pattern of CB–TU-IC was compared with XRD pattern of PEO–TU-IC and was shown that PEO–TU-IC does not adopt the rhombohedral crystal structure of CB–TU-IC.

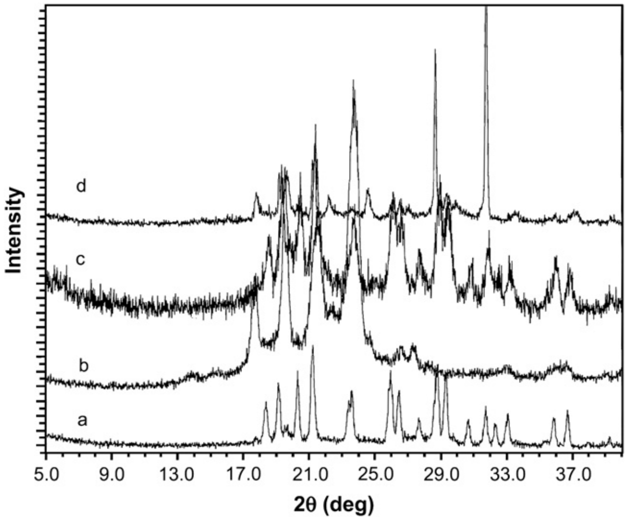


Fig. 1. XRD Patterns of (a) thiourea (b) PEO (c) PEO–TU-IC and (d) CB–TU-IC.

The FTIR spectra obtained for a PEO/thiourea physical mixture and PEO–TU-IC are shown in Fig. 2. FTIR studies were primarily focused on two regions: 3500–3000 cm^{-1} and 1700–600 cm^{-1}. It is clear from the comparison of IR spectra of physical blend and PEO–TU-IC that our PEO–TU-IC is not simply a physical mixture. Pure orthorhombic thiourea shows

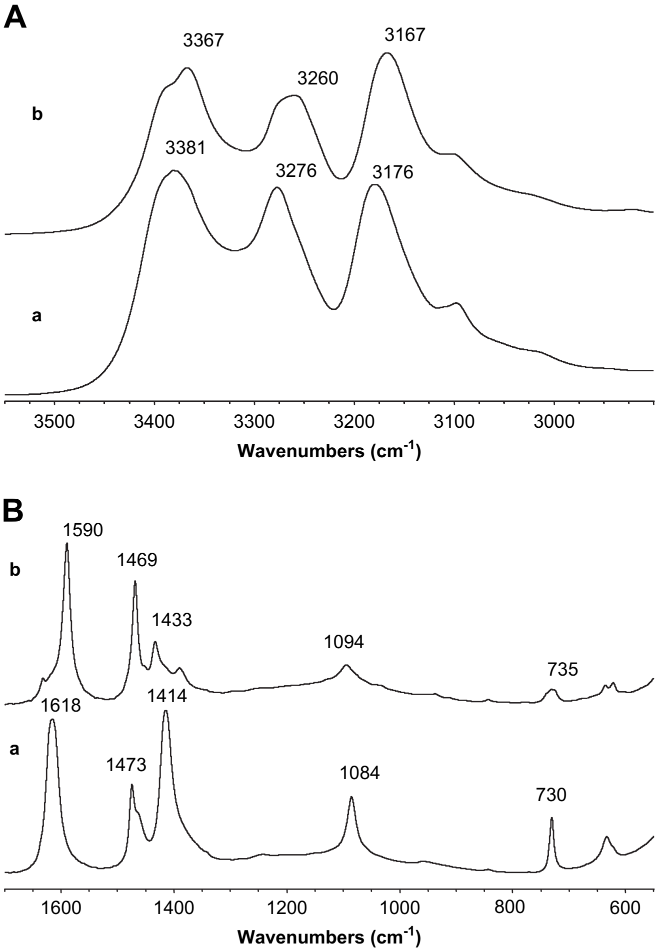


Fig. 2. FTIR spectra of thiourea/PEO physical mixture (a) and PEO–TU-IC (b) in the 3000–3500 cm^{-1} region (A) and 1700–400 cm^{-1} region (B).

strong absorption bands at 3380, 3276, and 3176 cm^{-1} due to the N–H symmetric and asymmetric stretching vibrations, strong absorption bands at 1617 cm^{-1} (N–H bending), 1473 cm^{-1} (N–C–N stretching) and 1414 cm^{-1} (C=S stretching vibrations). PEO shows strong absorption bands at 3000–2800 and 1500–550 cm^{-1} and conformationally sensitive bands occur in the 1400–1000 cm^{-1} region. IR bands associated with N–H stretching in the PEO–TU-IC spectrum are shifted to 3367, 3260, and 3166 cm^{-1}, respectively. The bands due to N–H bending, N–C–N asymmetric stretching, C=S stretching, and N–H rocking appear at 1589, 1468, 1433, and 1094 cm^{-1}, respectively for PEO–TU-IC, and indicate that PEO–TU-IC does not adopt the orthorhombic crystal structure of pure thiourea. A small IR band at 1617 cm^{-1} is apparent in the IR spectrum of PEO–TU-IC and confirms the presence of a small amount of uncomplexed thiourea in our sample. Since the bands associated with N–H stretching and bending are shifted to lower wavenumbers, it is reasonable to assume that PEO–TU-IC has stronger hydrogen bonding than in the orthorhombic crystal structure of pure thiourea. Since our X-ray results indicated that PEO–TU-IC adopts a structure similar to the orthorhombic form of pure thiourea, we attribute these bands to an expanded orthorhombic crystal structure.

It is clear from Fig. 2 that vibrational bands due to PEO in the bulk are broader compared to the PEO–TU-IC spectrum, indicating greater conformational heterogeneity in bulk PEO due to the presence of crystalline and amorphous components. Infrared bands at 1098, 961, and 842 cm^{-1} that are associated with combinations of C–O–C deformation modes, C–O stretching, and CH_2 rocking of PEO are clearly shifted or disappeared. The infrared band at 1098 cm^{-1} in the bulk PEO spectrum is shifted to 1094 cm^{-1} in the PEO–TU-IC spectrum, while the band at 961 cm^{-1} has disappeared. These shifts may be partially attributed to bond weakening due either to the hydrogen bonding between the thiourea N–H groups and the oxygen atoms in the PEO chain or to different conformations of PEO chains in bulk PEO and PEO–TU-IC samples or both. Our NMR observation shows no evidence for the conformational change, so therefore these band shifts are attributed to changes in the secondary bonding forces.

Fig. 3 presents the magic angle spinning dipolar decoupled ^{13}C NMR spectra with cross-polarization (CP/MAS/DD) for PEO, TU, and PEO–TU-IC. Rigid carbons and carbons with no hydrogen can usually be detected using this technique. The NMR spectrum of PEO shows a resonance containing broad and narrow components due to crystalline and amorphous material, respectively, consistent with reported data

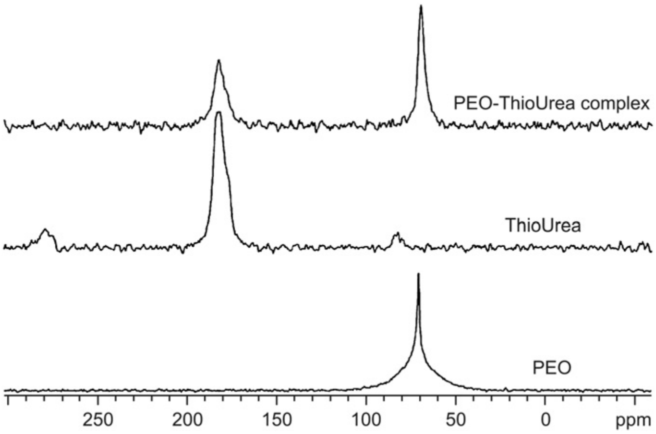


Fig. 3. Solid state ^{13}C NMR spectra with cross-polarization, dipolar decoupling, and magic angle spinning of PEO, thiourea and PEO–TU-IC.

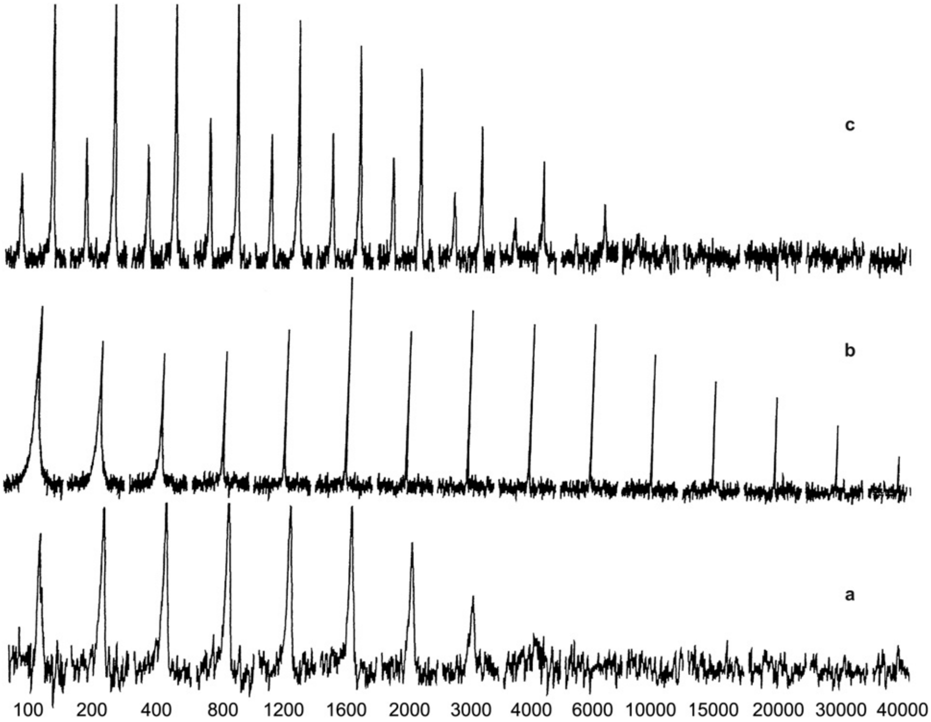


Fig. 4. VCT CP/MAS ^{13}C spectra of (a) thiourea (b) PEO and (c) PEO–TU-IC.

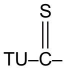
[7], while only a narrow component was observed for PEO in the NMR spectrum of PEO–TU-IC. It can clearly be seen that the width of the  $\mathrm{TU}-\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}-$ resonance in the PEO–TU-IC is reduced compared to that in the pure TU spectrum. Resonance frequencies of both PEO and TU components in PEO–TU-IC are very similar to bulk PEO and pure TU, suggesting that the encapsulated PEO chains adopt a similar conformation to bulk crystalline PEO, i.e., TGT.

Fig. 4a–c show the contact-time array (VCT) ^{13}C NMR spectra for TU, PEO and PEO–TU-IC, respectively. VCT experiment was utilized in order to observe the effect of complexation on the spin dynamics of encapsulated PEO chains in the thiourea channels. It is possible to extract T_{CH} (cross-polarization rate constant) and $T_{1\rho}^{\mathrm{H}}$ (^{1}H spin-locked spin-lattice relaxation time) by curve fitting the signal intensity profiles. Bulk PEO shows a resonance containing narrow and broad components due to the presence of both amorphous and crystalline environments, respectively. The crystalline portion having low mobility leads to shorter T_{CH} values and longer $T_{1\rho}^{\mathrm{H}}$ values, while the amorphous component having higher mobility leads to longer T_{CH} and shorter $T_{1\rho}^{\mathrm{H}}$ values. Therefore, the amorphous component is found in the early part of the plot and the crystalline component is found in the later part of the plot. It can be seen in the VCT relaxation profiles that the PEO contains a broad resonance due to crystalline domains that cross-polarizes rapidly (short T_{CH}) and a narrow resonance from amorphous domains that cross-polarize at a much slower rate and maximize at long contact times. The VCT profile of PEO–TU-IC is completely different from bulk PEO and shows the behavior of a single phase with higher mobility than crystalline PEO. It should be noted that PEO chains are separated within the narrow channels of thiourea. Mobility of PEO chain is higher in the IC due to the absence of cooperative chain interaction.

4. Conclusions

In conclusion, encapsulation of PEO chains in thiourea channels by formation of the PEO–TU-IC was confirmed by XRD, FTIR and solid state NMR. XRD and FTIR observations clearly show the crystal structure of PEO–TU-IC is different from the crystal structure of neat thiourea and the usual rhombohedral crystal structure of thiourea small molecule ICs. The conformation of PEO chains in the TU channels are similar to bulk crystalline PEO, as confirmed by NMR. VCT NMR profiles show that PEO chains in the TU channels are considerably more mobile than in bulk crystalline PEO.

Acknowledgement

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References

[1] Farina M. Inclusion polymerization. In: Atwood JL, Davies JED, McNicol DD, editors. Inclusion compounds, vol. 3. Academic Press; 1984.

[2] Lehn JM, Atwood JL, Davies JED, McNicol DD, Vogtle F, editors. Comprehensive supramolecular chemistry. Oxford: Pergamon Press; 1996.

[3] Vögtle F. Angew Chem Int Ed Engl 1985;24:728.

[4] (a) Angla BCR. Aca Sci 1947;224:420;
(b) Redlich O, Gable CM, Beason LR, Miller RW. J Am Chem Soc 1950;72:4161;
(c) Brown ME, Hollingsworth MD. Nature 1995;376:323.

[5] (a) Mahdyafar A, Harris KDM. J Chem Soc Chem Commun 1993:51;
(b) Li Q, Mak TCM. J Inclusion Phenom 1997;28:151;
(c) Dobado JA, Molina J, Portal D. J Phys Chem 1998;A102:778.

[6] (a) Lu L, Guo QX. J Inclusion Phenom 2002;42:1;
(b) Harada A. Carbohydr Polym 1997;34:183;
(c) Harada A. Acc Chem Res 2001;34:456;
(d) Ceccato M, Lo P, Nostro P, Baglioni P. Langmuir 1997;13:2436.

[7] (a) Tonelli AE. Polymer 1994;35:573;
(b) Vasanthan N, Shin ID, Tonelli AE. Macromolecules 1994;27:6515;
(c) Vasanthan N, Shin ID, Tonelli AE. Macromolecules 1996;29:263;
(d) Vasanthan N, Shin ID, Tonelli AE. J Polym Sci Part B Polym Phys 1995;33:1358.

[8] (a) Rusa CC, Rusa M, Gomez MMA, Shin ID, Fox JD, Tonelli AE. Macromolecules 2004;37:7992;
(b) Porbeni FE, Edeki EM, Shin ID, Tonelli AE. Polymer 2001;42:6907;
(c) Uyar T, El-Shafei A, Hacaloglu J, Tonelli AE. J Inclusion Phenom Macrocyclic Chem 2006;55:109.

[9] (a) Harris KDM. Chem Soc Rev 1997;26:279;
(b) Harris KDM. Supramol Chem 2007;19:47.