Inclusion Compound Formed between Poly(ϵ-caprolactone) and Urea

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Received June 15, 1992
Revised Manuscript Received November 5, 1992

Introduction

Crystalline inclusion compounds (IC's) formed between polymers and small-molecule, host clathrates provide a unique environment for observing the solid-state behavior of isolated polymer chains. In their IC's with small-molecule, host clathrates, such as urea (U)[1] and perhydrotriphenylene (PHTP),[2] the included polymer chains are confined to occupy narrow channels (ca. 5.5 Å in diameter) where they are extended and separated from neighboring chains by the channel walls, which are composed exclusively of the host clathrate, crystalline matrix (see Figure 1). We have been studying the behavior of isolated, extended polymer chains included in their IC's with U and PHTP by a combination of molecular modeling[3-9] and experimental observations (principally solid-state NMR)[10-14] in an effort to determine their conformations and mobilities in these well-defined, constraining environments.

Molecular modeling of aliphatic polyesters and polyamides suggested[5] that both classes of polymers may be capable of forming these IC's. For example, it was suggested[5] that poly(ϵ-caprolactone) (PEC) chains in either the all-trans or kink ($g^{\pm}tg^{\mp}$) conformations are slim enough to fit in these narrow IC channels (D = 5.5 Å). Here we report the successful formation of the IC between PEC and U, and our preliminary studies of its stability, stoichiometry, and structure, both the three-dimensional, solid-state structure of the PEC-U-IC and the conformation adopted by the included PEC chains.

Experimental Section

PEC-U-IC was formed by adding a 200-mL solution of 0.8 g of PEC (Aldrich; average molecular weight by GPC 72 000) in acetone to a 200-mL methanol solution saturated with urea (ca. 26 g). The PEC solution was gradually added to the saturated urea solution while continuously warming and stirring. The combined solution was then sealed and allowed to cool to room temperature, and finally stirring was discontinued. A fine white precipitate was gradually formed over 2 days and was isolated by filtration. The precipitate was air-dried overnight and weighed ca. 2.5 g.

A Perkin-Elmer DSC-4 was employed in the calorimetric observations of pure PEC and urea samples together with the observations of PEC-U-IC performed over several heating and cooling cycles. A Rigaku diffractometer was used to record X-ray diffractograms in the reflection geometry at 1° (2θ/min) under Ni-filtered Cu Kα radiation. In addition to the diffractograms recorded for PEC-U-IC between 20 and 150 °C, pure PEC and urea, the urea-IC formed with polyethylene (PE) (PE-U-IC, obtained from P. Sozzani), and pure PE were examined in powder form by X-ray diffraction.

Results and Discussion

In Figure 2 the first (a) and second (b) heating DSC scans of PEC-U-IC recorded at a heating rate of 10 °C/min are presented. Note that our as-prepared PEC-U-IC samples contain small portions of uncomplexed PEC and free crystalline urea, as indicated by the small melting endotherms at T = 55 and 134 °C, respectively. Bulk samples of pure PEC and pure urea showed melting temperatures of 57 and 135 °C associated with endotherms of 19.8 and 49.4 cal/g, respectively. On the basis of the reported[15] enthalpy of melting observed and extrapolated to 100% crystalline PEC (32.4 cal/g), our bulk PEC sample is (19.8/32.4) × 100 = 61% crystalline. In addition, the small endotherms at T = 55 and 134 °C correspond to ca. 17 wt % of uncomplexed PEC and free urea in our as-prepared PE-U-IC sample.

The large melting endotherm at T = 142 °C corresponds to the PEC-U-IC. After calculating the weight of PEC-U-IC in our sample, which was obtained by subtracting from the total sample weight the amounts of uncomplexed PEC and free urea corresponding to the small endotherms at 55 and 134 °C, the heat of fusion of PEC-U-IC was

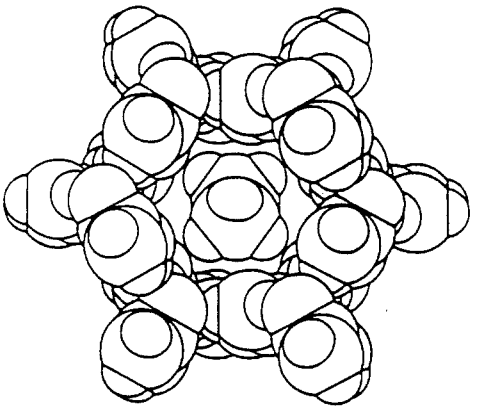

Figure 1. Space-filling drawing of a channel in the urea-*n*-hexadecane clathrate.[1]

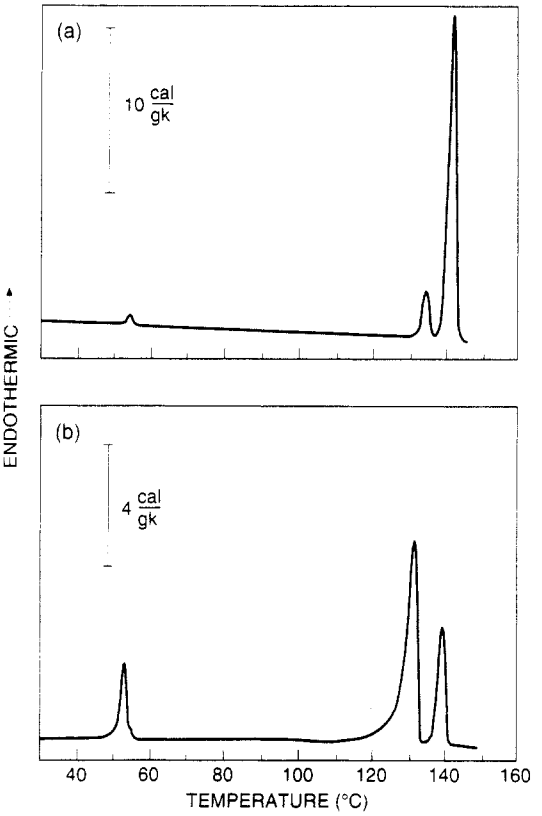

Figure 2. (a) First heating (10 °C/min) DSC scan of PEC-U-IC. (b) Second heating (10 °C/min) DSC scan of PEC-U-IC that had previously melted (a).

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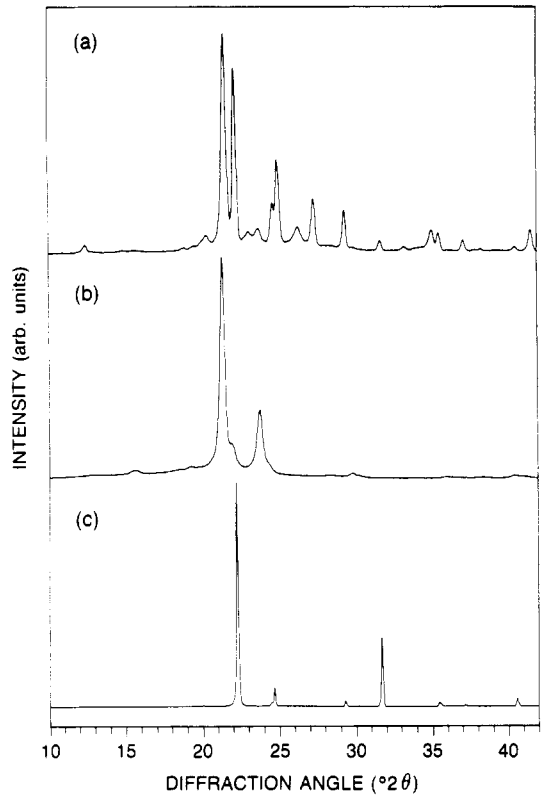

Figure 3. Comparison of the X-ray diffractograms recorded for (a) PEC-U-IC, (b) PEC, and (c) urea all observed at room temperature.

determined to be 54 cal/g. It was assumed that uncomplexed PEC and free urea in our PEC-U-IC have the same melting enthalpy per gram as that observed in their pure bulk samples.

In part b of Figure 2, which shows the second heating of our PEC-U-IC sample, note the large increases in the amounts of uncomplexed PEC and free urea that are created after melting and cooling to re-form the PEC-U-IC. Comparing the calculated amounts of uncomplexed PEC, free urea, and PEC-U-IC present before and after the initial heating, as obtained from the observed melting endotherms, we find that the U-PEC repeat unit stoichiometry of the PEC-U-IC is 2.1 (g/g) or 4.0 (mol/mol).

If we assume the PEC chains in the urea-IC adopt the nearly all-trans, planar zigzag conformation with a fiber repeat of ca. 8 Å/repeat unit found[16] in its bulk crystals, then one repeat unit of PEC in its urea-IC would occupy 8 Å of the narrow channel. If the crystalline structure of the urea clathrate matrix is the same in PEC-U-IC as that determined by X-ray diffraction[17] on single crystals of PE-U-IC, then each urea molecule constitutes 1.83 Å of the channel (see below).[18] Consequently 8/1.83 = 4.4 urea molecules/PEC repeat unit would correspond to the stoichiometry of the PEC-U-IC, in reasonable agreement with the stoichiometry (4) obtained from our DSC analysis.

Figure 3 presents the X-ray diffractograms recorded at room temperature for (a) PEC-U-IC, (b) pure PEC, and (c) pure urea powders. Their comparison reveals that several prominent peaks in the PEC-U-IC diffractogram are unique and are not present in either of the diffractograms recorded for pure PEC or pure urea. This comparison constitutes direct evidence that the PEC-U-IC has indeed been formed.

In Figure 4 the X-ray diffractograms recorded for PEC-U-IC at room temperature (a) and 130 °C (b) are compared to the room temperature diffractogram (c) recorded for PE-U-IC. Notice that the high-temperature diffractogram of PEC-U-IC (b) contains noticeably fewer peaks than the room temperature diffractogram (a), presumably because the peaks contributed by the crystals of uncomplexed PEC and free urea to the latter diffractogram are eliminated at 130 °C, where both uncomplexed PEC and free urea are molten and amorphous.

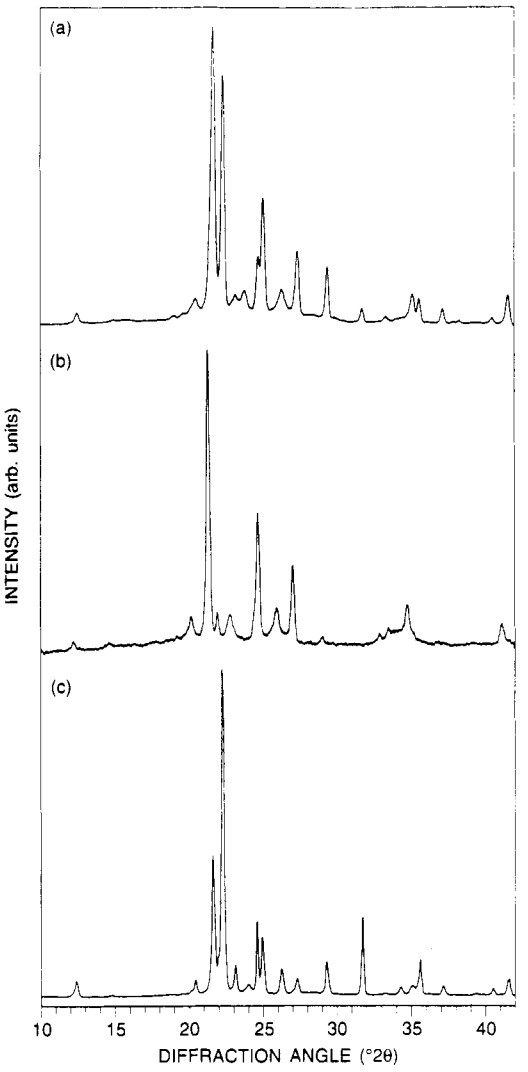

Figure 4. X-ray diffractograms of (a) PEC-U-IC at 25 °C, (b) PEC-U-IC at 130 °C, (c) PE-U-IC at 25 °C.

The PE-U-IC sample seen in part c of Figure 4 contains excess free urea but no uncomplexed PE. When the peaks appearing at $2\theta = 22.2, 24.7$, and 31.7° due to free tetragonal urea crystal (see Figure 3a) are discounted, we observe a close correspondence between the X-ray diffractograms of PEC-U-IC (Figure 4b) and PE-U-IC (Figure 4c) powders. Clearly the overall three-dimensional structures of PEC-U and PE-U IC's are very similar,[17,18] confirming the assumption made in our comparison of the DSC-derived stoichiometry of PEC-U-IC with that obtained by analogy to the known structure of PE-U-IC.

With the results from direct observations performed on PEC-U-IC and by comparison to observations made on PE-U-IC, whose three-dimensional structure is known from single-crystal X-ray diffraction,[17,18] we are confident that the structure of PEC-U-IC is quite similar. We are currently beginning high-resolution, solid-state CPMAS/DD ^{13}C NMR and vibrational spectroscopic measurements on PEC-U-IC, so that we might compare the conformations and mobilities of PEC chains when confined by the neighboring chains in their bulk crystals to those observed for the isolated PEC chains residing in the narrow channels of their IC with urea.

References and Notes

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