

Structural investigations of the poly(ϵ -caprolactam)–urea inclusion compound

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Abstract

An interesting inclusion compound (IC) between guest poly(ϵ -caprolactam) (P ϵ CL) and host urea was successfully obtained, for the first time, by co-crystallization from their common solution. X-ray diffraction, infrared spectroscopy and differential scanning calorimetry have been utilized for a detailed structural investigation of P ϵ CL–urea IC (U IC) crystals. The results were compared with those obtained for well-known structures of the hexagonal polyethylene–U IC, the trigonal polyethylene oxide–U IC and the 'large tetragonal' poly(propylene)–U IC. The structure of P ϵ CL–U IC reconfirms that the urea host molecules may crystallize, even in the presence of a rather slim polymer guest, into an IC with a lattice channel diameter of more than 5.25 Å. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Through crystallization of urea (U) host molecules from a common solution with an appropriate guest molecule, inclusion compounds (ICs) having various crystal structures may be obtained. The guest molecules might be either small organic molecules (such as sufficiently long *n*-alkanes) or different types of polymers (such as polyethylene (PE) [1,2], polyethylene oxide (PEO) [3], poly(propylene) (PP) [4], poly(ϵ -caprolactone) (PCL) [5,6], etc.) or block copolymers [7].

The importance of urea inclusion compound (U IC) formation consists in the isolation of polymer chains in the narrow, cylindrical IC channels. In this isolated environment, it is possible to study the conformational and motional behaviour of a single segregated polymer chain, which usually exists in a highly extended state [8].

Urea host molecules can form ICs crystals only in the presence of a suitable guest polymer with a certain cross-sectional area. Usually, the urea crystallizes into a matrix composed of a hexagonal crystal structure. Perturbations in U IC crystals have also resulted in urea matrices with trigonal and orthorhombic crystal structures, but the diameter of the channel is still approximately 5.5 Å. A

'large tetragonal' crystal structure with a larger diameter has also been reported for the PP–U IC [4].

X-ray diffraction, differential scanning calorimetry (DSC) and infrared spectroscopy have been used to characterize the poly(ϵ -caprolactam) (P ϵ CL)–U IC. By comparison to the results of structural investigations obtained for different U IC structures, we found that the P ϵ CL–U IC does not adopt a hexagonal or trigonal crystal structure, but instead a large tetragonal structure.

2. Experimental

The P ϵ CL–U IC formation by a co-crystallization method has raised several difficulties, because of differences between the solubilities of the two components. After many experimental attempts, we found that the mixture of *m*-cresol and methanol (70:30, v:v) represents a very good solvent for both urea and P ϵ CL.

2.1. Materials

Urea (Aldrich Co.) was recrystallized from pure methanol. P ϵ CL was purified by extraction in a Soxhlet apparatus with methanol, and dried at 50 °C and 50 Pa for 24 h. Viscometric analysis, in 85% formic acid, as solvent, at 25 ± 0.05 °C, has indicated a viscosity-average molecular

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weight of 22,500. All the solvents have been purified by standard procedures.

2.2. Preparation of samples

The urea solution was obtained by dissolving 2 g of urea in a mixture of 25 ml of *m*-cresol and 10 ml of methanol, at 50 °C. 0.15 g of P ϵ CL was added to the urea solution while continuously heating and stirring. After 2 h, the solution containing both urea and P ϵ CL was allowed to slowly cool down while stirring. A white precipitate was obtained over a period of several days, and was filtered and washed with warm xylene to remove any excess *m*-cresol adhering to the external surfaces of the crystals. The resulting precipitate was a fine white crystalline powder, which was finally air-dried.

2.3. Sample characterization

Melting points were determined on a Mettler DSC 12E TA instrument with a heating rate of 10 °C/min. An indium standard was used for calibration. Temperatures at maximum peak heights were consistently taken as the melting temperatures.

Absorbance Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 510p FTIR spectrometer with OMNIC software at frequencies from 400 to 4000 cm⁻¹, gain = 1, and scans = 128.

A Siemens type-F X-ray diffractometer with a nickel filtered Cu K α radiation source (wavelength = 1.54 Å) and voltage and current set to 30 kV and 20 mA, respectively, was operated at a scan rate of ($2\theta = 1^\circ$) per minute, between a 2θ value of 5 and 40°, to obtain the powder diffractograms.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 presents the X-ray diffractograms recorded at room temperature for (a) urea, (b) P ϵ CL, and (c) P ϵ CL–U IC. The diffraction pattern of the IC was similar to that of pure tetragonal urea, but notable are the absence of diffraction peaks attributable to the pure, semicrystalline phases of P ϵ CL ($2\theta = 20$ and 24°). Since the FTIR investigation shows clear evidence for the presence of P ϵ CL, we must conclude that P ϵ CL is not present in phase-separated, bulk form, but rather included in the channels of its IC formed with urea. (To eliminate the possibility that the U IC formed has included *m*-cresol rather than P ϵ CL, the U IC was washed with cold water, which is a good solvent for urea, but is a non-solvent for P ϵ CL. This resulted in dissolution of urea and precipitation of P ϵ CL, and so our U IC must have included P ϵ CL and not *m*-cresol.)

The scattering angles (2θ) and distances (d -spacing) between scattering planes for components (urea and

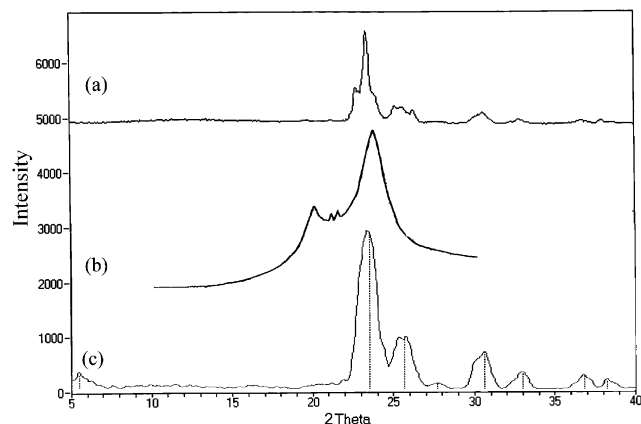


Fig. 1. Comparison of the X-ray diffractograms recorded for (a) urea, (b) poly(ϵ -caprolactam), and (c) P ϵ CL–U IC.

P ϵ CL), P ϵ CL–U IC, and PP–U IC are compared in Table 1. Clearly, the overall diffraction peaks of P ϵ CL–U IC and PP–U IC are very similar, confirming the fact that the P ϵ CL–U IC adopts a large tetragonal crystal structure as did the latter PP–U IC.

Molecular modelling of polyamides (nylon-6) found that this chain might adopt five different extended conformations that are able to fit in a channel with a diameter of 5.25 Å [9]. Nevertheless, we may conclude [12] that P ϵ CL guest chains can adopt many conformations in the large tetragonal structure identified for P ϵ CL–U IC ($D > 7$ Å), in addition to those (*trans* and *kink*) determined by molecular modelling of nylon-6 [9] to fit in the narrower hexagonal crystal structure channels.

The presence of free urea in our P ϵ CL–U IC sample makes the separation of the pure tetragonal urea and IC diffraction peaks difficult. Since, a single crystal of P ϵ CL–U IC has not been successfully grown, accurate data concerning unit cell characteristics cannot be reported here. Further analyses of the structure and stoichiometry of P ϵ CL–U IC are in progress.

Table 1
Crystallographic data of the pure components, P ϵ CL–U IC, and PP–U IC

| Urea | | P ϵ CL | P ϵ CL–U IC | | PP–U IC |
|---------------|------------------|-----------------|----------------------|------------------|---------------|
| 2θ (°) | d -spacing (Å) | 2θ (°) | 2θ (°) | d -spacing (Å) | 2θ (°) |
| 22.63 | 3.9257 | 20.2 | 11.55 | 7.6558 | |
| 24.94 | 3.5665 | 23.9 | 16.07 | 5.5095 | |
| 29.63 | 3.0125 | | 18.26 | 4.8530 | 18.2 |
| 32.03 | 2.7918 | | 22.57 | 3.9366 | 22.5 |
| 35.79 | 2.5069 | | 24.95 | 3.5664 | 24.7 |
| 37.44 | 2.4000 | | 26.35 | 3.3798 | 26.3 |
| 40.69 | 2.2150 | | 29.57 | 3.0184 | 29.5 |
| 44.68 | 2.0263 | | 32.03 | 2.7918 | 31.8 |
| | | | 35.84 | 2.5017 | 35.6 |
| | | | 37.37 | 2.4043 | 37.3 |
| | | | 40.79 | 2.2099 | 40.8 |
| | | | 41.87 | 2.1555 | 41.6 |

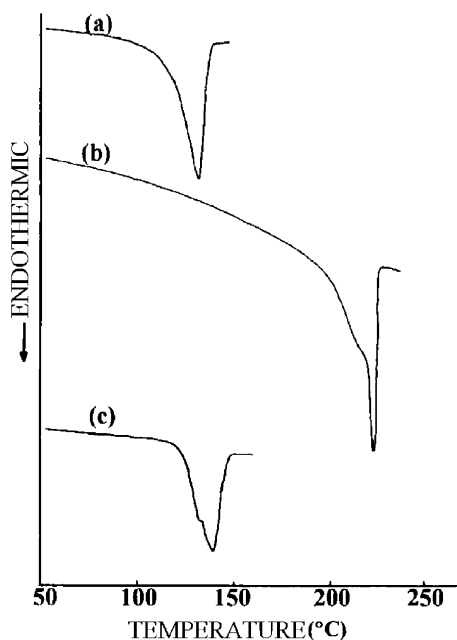


Fig. 2. DSC thermograms of (a) urea, (b) poly(ϵ -caprolactam), and (c) P ϵ CL-U IC.

3.2. DSC measurements

DSC was used in order to determine the thermal properties and stability of the pure components and P ϵ CL-U IC crystals. The thermograms of the pure urea (a), of the P ϵ CL (b) and the P ϵ CL-U IC (c) are shown in Fig. 2. The thermogram of the P ϵ CL-U IC shows one major endotherm peak at 139 °C, corresponding to IC fusion, which is 6 °C higher than the melting point of pure urea. Also, a shoulder at 133 °C is apparent in this thermogram. This endothermic peak corresponds to the melting of free urea in our P ϵ CL-U IC sample. An increase in the melting point of the host urea containing trapped polymer molecules is thought to be due to favourable van der Waals forces between host urea molecules and the included guest polymer chains. Therefore, the increase in the melting point of the urea lattice provided the first tentative evidence that an IC has been formed [10]. The melting points of the pure components are very well separated, with the melting point of P ϵ CL (228 °C) being greater than the degradation temperature of urea. Since degradation of urea occurs at 160 °C, evaluation of polymer endotherms in the presence of urea cannot be accomplished for those polymers that melt above 160 °C. As a

consequence, an estimate of IC stoichiometry, as determined by comparison of the changes in the amount of uncomplexed urea and polymer as the IC is melted and converted to pure components, could not be achieved by calorimetry [11].

3.3. FTIR spectroscopy

By comparison to the U ICs formed with poly(ethylene glycol) (PEG; $M_w = 400$) [10], polypropylene (PP) [4], PE [2] and PEO [3], it can be suggested that P ϵ CL-U IC has a large tetragonal crystal structure similar to the first two ICs. All of these ICs have been investigated using FTIR, DSC, X-ray diffraction, and solid-state NMR spectroscopy. Table 2 contains the vibrational band assignments and crystal structures for the complexes enumerated earlier.

It is clear that the urea lattice in P ϵ CL-U IC is distinct from the hexagonal PE-U IC and trigonal PEO-U IC structures. Previous studies performed by Tonelli and Suehiro, respectively, suggest the possibility that the P ϵ CL-U IC structure is similar to the 'expanded tetragonal' i-PP-U IC and PEG-U IC structures [4,10].

Though the FTIR spectra are not shown, the vibrational band frequencies observed for the P ϵ CL-U IC are very close to those of i-PP-U IC, with only very slight differences in the position of some peaks. In both IC spectra, the U C=O stretching vibration occurs at 1663 cm^{-1} . In the i-PP-U IC spectrum, the N-C-N vibration is at 1454 cm^{-1} (1458 cm^{-1} for P ϵ CL-U IC), and the NH bending vibrations are at 1638 and 1614 cm^{-1} (1637 and 1612 cm^{-1} , respectively, for the P ϵ CL-U IC). Considering the 2 cm^{-1} resolution of our instrument, it is possible to say that IR spectroscopy strongly indicates that the P ϵ CL-U IC structure appears similar to the large tetragonal structure observed for PEG-U IC and i-P-U IC. (As further support for the formation of P ϵ CL-U IC, we mention that in its FTIR spectrum bands at $\sim 2900 \text{ cm}^{-1}$, which originate from the P ϵ CL -CH₂- groups ($\nu \rightarrow$ C-H stretches) and are not characteristic for urea, are evident.)

We remain puzzled by our observation that, unlike the closely related aliphatic polyester PCL, which forms a hexagonal U IC with narrow inclusion channels [5,6,11], P ϵ CL complexes with urea to form a large tetragonal P ϵ CL-U IC structure with roomier inclusion channels. Despite similar results obtained [9] in the search for PCL and P ϵ CL conformations narrow enough to be included in U ICs, P ϵ CL and PCL chains do and do not, respectively, require the roomier

Table 2
The characteristic IR frequencies of urea in its different IC crystal structures

| Vib. freq. for bulk urea (cm^{-1}) | PEG ₄₀₀ -U IC (cm^{-1}) | i-PP-U IC (cm^{-1}) | PE-U IC (cm^{-1}) | PEO-U IC (cm^{-1}) | P ϵ CL-U IC (cm^{-1}) | Assignment |
|---|---|--------------------------------|------------------------------|-------------------------------|---|----------------------|
| 1685 | 1665 | 1663 | 1695, 1660 | 1694, 1659 | 1663 | ν_{CO} |
| 1630 | 1631 | 1638 | 1640 | 1639 | 1637 | δ_{NH} |
| 1600 | 1617 | 1614 | 1605 | 1577 | 1612 | δ_{NH} |
| 1470 | 1454 | 1454 | 1500 | 1457 | 1458 | $\nu_{\text{N-C-N}}$ |
| Tetragonal | Large tetragonal | Large tetragonal | Hexagonal | Trigonal | Large tetragonal | |

channels found in the large tetragonal U ICs [4,10] formed by PEG and i-PP. The only explanation we can currently offer is that the hydrogen-bonding capability of P ϵ CL leads to the large tetragonal U IC structure, so that hydrogen-bonding between the amide groups and urea can be facilitated compared to that permitted by the narrower hexagonal U IC channels found sufficient for complexing the non-hydrogen-bonding polyester PCL.

4. Conclusions

In summary, we report that urea host molecules can include guest polymers to give ICs having an unusual expanded tetragonal crystal structure, which also appears to be the case for the P ϵ CL–U IC studied here. Consolidation, via coalescence, of the segregated and extended P ϵ CL chains included in the channels of its U IC might lead to a non-entangled, chain-extended morphology that confers better mechanical properties. U IC crystals with large inclusion channels could have many uses, including the study of bulky polymers with rings in their backbone,

because the traditional hexagonal U ICs have a channel diameter that is too small for many types of polymers [13].

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