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Separation of Polymers by Molecular Weight through Inclusion Compound Formation with Urea and α-Cyclodextrin Hosts

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ABSTRACT: α-Cyclodextrin (α-CD) and urea (U) hosts were used in order to separate a mixture of poly(ethylene glycols) (PEGs) with two different molecular weights ($M_w = 600$ [PEG_{600}] and $M_w = 20\,000$ [PEG_{20000}]) by forming the respective inclusion compounds (ICs). Differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, and wide-angle X-ray diffraction (WAXD) have been used to verify the formation and successfully characterize all inclusion compounds. The high melting point of the urea inclusion compound (PEG*-U IC) formed from the solution containing both polymers was the first evidence that urea preferentially included poly(ethylene glycol) with the higher molecular weight. The PEG*-U IC and PEG_{20000}-U IC X-ray diffraction patterns and FTIR spectra were very similar to each other, confirming that urea preferentially complexes PEG_{20000} in their mutual solution. Since the above-mentioned techniques were not as useful in the case of α-CD ICs, viscosity measurements were made in order to demonstrate the molecular weight selectivity of α-CD host. The efflux time of PEG*-α-CD IC solution was much closer to that of a PEG_{20000}-α-CD IC solution, which suggested that α-CD also included poly(ethylene glycol) having a high molecular weight rather than the low molecular weight PEG_{600}. The efflux time of PEG*-U IC solution is almost identical with that of the PEG_{20000}-U IC solution indicating that urea has better molecular weight selective properties than α-CD.

Introduction

The ability of inclusion compounds to isolate polymer chains into their narrow cylindrical, crystalline channels is well-known. The most widely known inclusion compound (IC) hosts are urea (U), thiourea (TU), perhydrotriphenylene (PHTP), and cyclodextrins (CD), and their cavity-forming matrices are stable only when a guest is present. Guests can be either small molecules or polymers (such as: polyethylene (PE),[1,2] poly(ethylene oxide) (PEO),[3,14,15] poly(tetrahydrofuran) (PTHF),[4] poly(ε-caprolactone) (PEC),[5,6] poly(ε-caprolactam),[7,8] poly(L-lactic acid) (PLLA),[9] polypropylene (PP),[10] etc.).

Unlike U, TU, and PHTP, whose inclusion compounds can only exist in the solid state and in which guest molecules are included in channels (diameter of ca. 5.5 Å) provided by the crystalline structure of the host (Figure 1), CDs can also form inclusion compounds which are soluble and stable in solution.

Cyclodextrins are cyclic molecules consisting of six, seven, and eight glucose units joined by α-1,4-glycosidic linkages and are named α-, β-, and γ-CD, respectively. Figure 2 presents the chemical structure for α-CD. Packing of the CD molecules within the crystal lattice occurs in one of two modes, described as cage and channel structures (see Figure 3). In general, polymer−CD ICs have a channel structure as a result of a polymer's long chain nature.

A polymer chain in the narrow IC channels usually exits in an extended state and is isolated from the effects of other polymer chains. In this isolated environment, it is possible to study the conformational and motional behavior of a single polymer chain in the solid state.

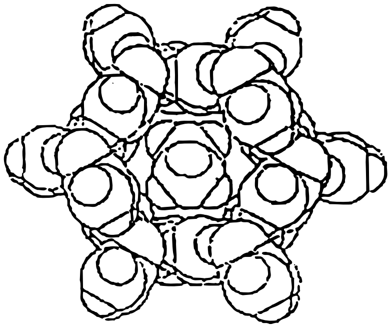

Figure 1. Schematic representation of urea−*n*-hexadecane clathrate as determined by X-ray diffraction.[22]

ICs have also been used as an environment in which to polymerize stereoregular polymers.[11]

In more practical applications, isolation of molecules through inclusion have led to the purification of materials based on branching, pendant groups, and even specific configurations, like separation of isomers, enantiomers, and isotopes. However, there are no reports, to our knowledge, on the separation of polymers by molecular weight based on inclusion compound formation. Here, we choose urea and α-cyclodextrin as the host small molecules in order to isolate poly(ethylene glycol) with a specific molecular weight from their common solution.

Both urea and α-CD can form ICs with PEG of various molecular weights. Inclusion compounds formed between U and polyethers ($[-O(CH_2)_m-]_n$, $m = 2-4, 6, 8-10$) were characterized by Suehiro et al.[12,13] There it was found that U IC with low molecular weight PEG apparently adopts a tetragonal crystal structure while PEG with $M_w > 1000$ has a trigonal crystal structure. In addition, Suehiro has found that the melting points of PEG-U ICs increased with an increase in the molecular weight of PEG.

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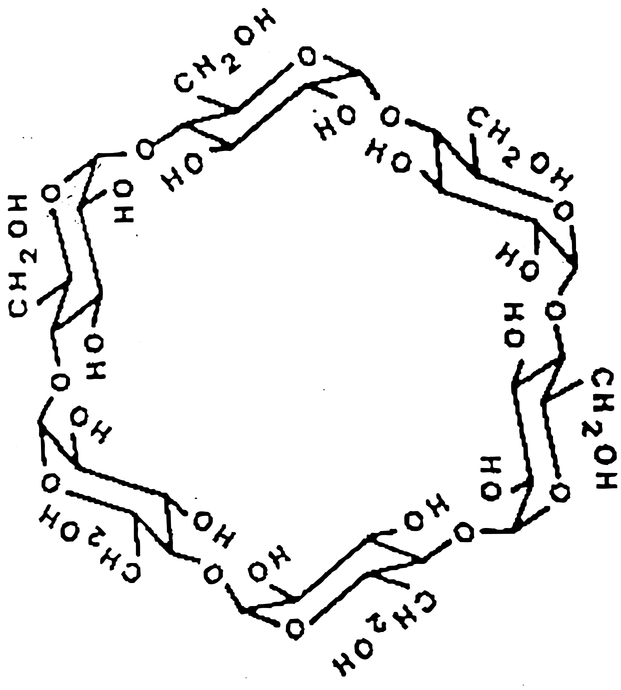

Figure 2. Chemical structure for α-cyclodextrin.

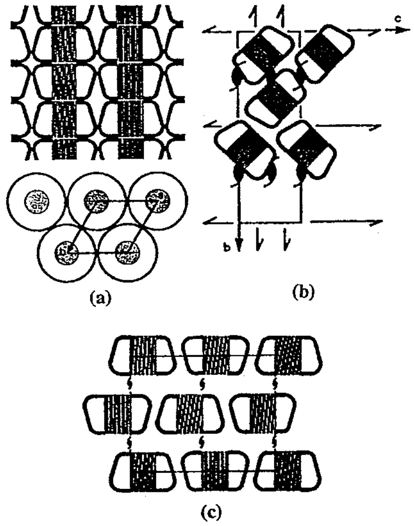

Figure 3. Schematic description of (a) channels type, (b) cage herringbone type, and (c) cage brick type crystal structures formed by crystalline cyclodextrin inclusion compounds.

Harada et al. have found that α-CD forms complexes with PEG of various molecular weights to give stoichiometric complexes in high yields in a crystalline state.[14,15] The rate of the complex formation depends on the molecular weight of PEG. PEG of molecular weight 1000 forms complexes most rapidly. The complex formation of α-CD with PEG was studied quantitatively. The stoichiometry of the ICs is 2:1 (two ethylene glycol units to one α-CD) and was further confirmed by the ^{1}H NMR spectrum of their solution. X-ray powder patterns of the PEG-α-CD complex show that guest polymer chains reside in the channels provided by the orderly stacked α-cyclodextrin molecules.

This paper describe the preparation and properties of the inclusion compounds of PEG (M_w = 600 and 20000) with urea and α-CD, and the modes of PEG separation by molecular weight are discussed.

Experimental Section

Samples. Poly(ethylene glycol) samples with average molecular weights 600 and 20000 were obtained from Sigma Chemical Co. Since PEGs are obtained by anionic living polymerization, their molecular weight distributions are narrow, namely 1.1 for PEG_{600} and 1.34 for PEG_{20000}. α-Cyclodextrin and urea were purchased from Cerestar Co. and Aldrich Chemical Co., respectively.

PEG-U ICs and PEG-α-CD ICs were prepared via a cocrystallization method. Two grams of PEG (M_w = 600 and 20000, respectively) was dissolved together (1:1, w:w) and separately in 100 mL of methanol saturated with urea while the solution was continuously warmed (65 °C) and stirred. The solution was then cooled to room temperature, and a white precipitate was observed to form after 2 days.

PEG-α-CD ICs were prepared by slowly adding 2.5 mL of a heated (ca. 60 °C) solution of 0.375 g of PEG (M_w = 600 and 20000, respectively) in water to 25 mL of an aqueous solution saturated with α-CD (3.625 g of α-CD), also held at 60 °C. After 2 h of stirring at 60 °C, the covered flask was removed from the hot plate and left undisturbed overnight. A white precipitate was collected by filtration, and the crystals were washed and dried. The same procedure was applied in the case of a PEG* mixture, when 5 mL of PEG* aqueous solution (0.3282 g for each, M_w = 600 and 20000) was dripped into 50 mL of aqueous solution saturated with α-CD (7.25 g of α-CD) to form an IC. According to Harada's studies the above-mentioned quantities represent the stoichiometric ratio (2:1) between the two components (ethylene glycol unit:α-CD).[15]

To obtain a better understanding about viscosity measurements of different α-CD IC solutions, we have prepared PEG*-α-CD ICs using excess (3:1 and 4:1) amounts of PEGs. Thus, 5 mL of PEG solutions (0.3282 g of PEG_{600} + 0.6564 g of PEG_{20000}, 0.6564 g of PEG_{600} + 0.3282 g of PEG_{20000}, and 0.6564 g of PEG_{600} + 0.6564 g of PEG_{20000}, respectively) in water were added to 50 mL of aqueous solution saturated with α-CD (7.25 g). The powder collected by filtration was washed with water to remove uncomplexed α-CD and free PEG and then dried at 80−90 °C for 12 h.

DSC Measurements. To obtain melting temperatures, differential scanning calorimetric scans were conducted on 3−10 mg samples with a Perkin-Elmer DSC-7. A heating rate of 10 °C/min and a calibration with indium were employed for all samples. The melting points were consistently taken as the maximum endothermal peak height.

FTIR Spectroscopy. Infrared spectra between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} were recorded on a Nicolet 510P FTIR spectrometer. The samples were thoroughly mixed with KBr and pressed into pellet form. Because of the hygroscopic behavior of KBr, the sample cell was purged with desiccated air.

Wide-Angle X-ray Diffraction. X-ray diffraction data were collected from powdered samples on a Siemens type-F X-ray diffractometer in a wide-angle setup. The X-ray radiation used was Ni-filtered Cu Kα with a wavelength of 1.54 Å. The voltage was set at 30 kV, and the current was set at 20 mA. Samples were mounted on a solid circular sample holder with Scotch brand tape, and the proportional counter detector was set to collect data at a rate of 2θ = 5°/min over the range 2θ = 5−40°.

Viscosity Determinations. A Cannon-Ubbelohde dilution viscometer was used to measure the efflux times for different solutions of PEG-α-CD ICs and PEG-U ICs. The viscometer constant is 0.00835 cSt/s. All determinations of efflux times were carried out at either 25 or 30 °C and repeated five times for each solution. The maximum difference between two efflux times of the same solution was 0.1 s. To maintain a constant temperature, a Fisher water bath was used.

Results and Discussion

To determine whether inclusion compound formation represents a good means for separation of PEG mixtures, three analytical techniques were used. DSC, FTIR and XRD were employed to characterize PEG-U ICs and

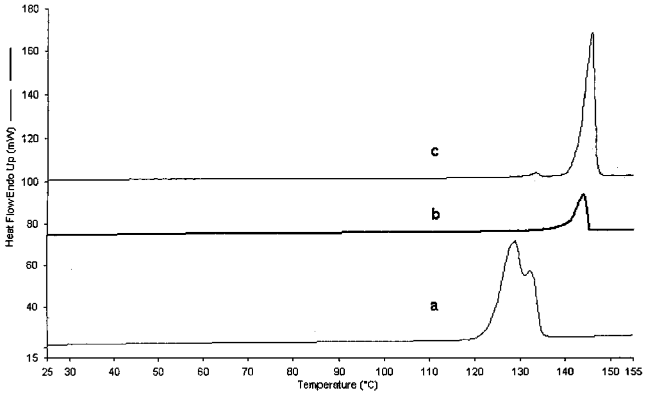

Figure 4. DSC thermograms of (a) PEG_{600}-U IC, (b) PEG_{20000}-U IC, and (c) PEG*-U IC recorded at a rate of 10 °C/min.

PEG-α-CD ICs and to compare the results to those of inclusion compounds prepared with a mixture of PEGs (PEG*). However, these techniques are more useful in the case of urea inclusion compounds since PEG_{600}-U IC and PEG_{20000}-U IC adopt different crystal structures. Because we did not note any differences among the data recorded for PEG-α-CD ICs, we resorted to viscosity measurements to measure the efflux times of the PEG-α-CD IC solutions.

DSC Measurements. To determine whether a urea inclusion compound preferentially included PEG chains with a certain molecular weight, DSC thermograms for PEG_{600}-U IC, PEG_{20000}-U IC, and PEG*-U IC were recorded (see Figure 4). We noted that the melting points of PEG-U ICs increase with the molecular weight of the included PEG. The thermogram of PEG_{600}-U IC (Figure 4a) shows a large endothermic peak at 129 °C with a well-defined shoulder at 132 °C. According to Suehiro's work, these two peaks correspond to the melting points of forms II and I, respectively, which represent the two crystalline forms of PEG_{600}-U IC.[12] A solid−solid transition from form II crystals (tetragonal unit cell) to form I complex (trigonal unit cell) occurs when the PEG_{600}-U IC is heated to a temperature between the two peaks and then cooled to room temperature. This monotropic transition is available only for urea inclusion compounds formed with PEGs having molecular weight between 400 and 1000.

The thermogram of PEG*-U IC (Figure 4c) exhibits one major endothermic peak at 145 °C, corresponding to IC fusion and a very small endotherm at 132 °C, associated with a very small amount of uncomplexed urea. Since the melting points of PEG_{20000}-U IC (144 °C, see Figure 4b) and PEG*-U IC are very close, we concluded that urea forms the inclusion compound only with the polymeric guest of higher molecular weight. This may imply that urea tends to build its IC with a better thermal stability conferred by a larger number of hydrogen bonds between host and guest. The lack of endothermic peaks corresponding to pure PEG_{600} (24 °C), PEG_{20000} (65 °C), and urea (132 °C) from DSC curves of PEG_{600}-U IC and PEG_{20000}-U IC indicates that we obtained pure adducts.

Since cyclodextrins and their ICs decompose while melting, we tested them below their decomposition temperature in order to observe whether the IC samples contain free polymers. As can be seen from Figure 5, the α-CD ICs are free from uncomplexed PEG.

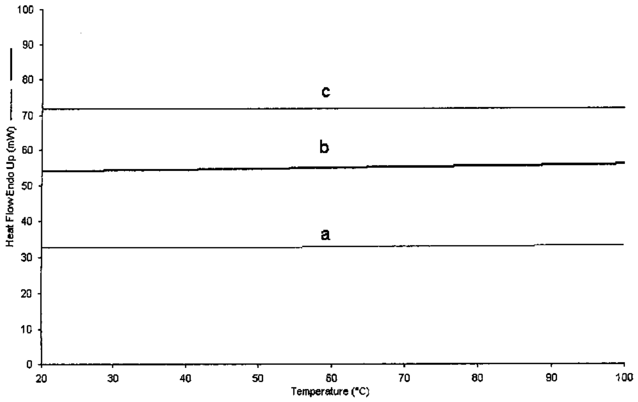

Figure 5. DSC thermograms of (a) PEG_{600}-α-CD IC, (b) PEG_{20000}-α-CD IC, and (c) PEG*-α-CD IC recorded between 20 and 100 °C.

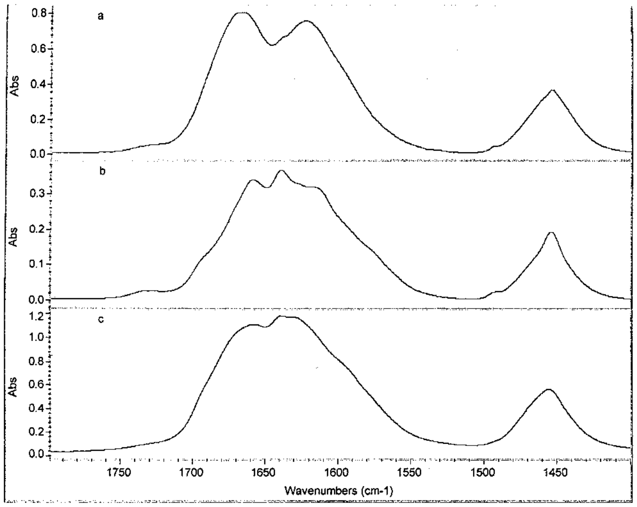

Figure 6. Comparison of infrared spectra in the region between 1400 and 1800 cm^{-1}: (a) PEG_{600}-U IC, (b) PEG_{20000}-U IC, and (c) PEG*-U IC.

FTIR Spectroscopy. It has been demonstrated that FTIR is sensitive to the change in hydrogen bonding that occurs when urea converts from bulk tetragonal to the hexagonal, trigonal or large tetragonal IC crystal forms.[16] Figure 6 shows a comparison of PEG_{600}-U IC (a), PEG_{20000}-U IC (b), and PEG*-U IC (c).

The most noticeable shifts occurs in the 1400−1800 cm^{-1} range. These U IC vibrational frequencies are summarized in Table 1 in order to compare one to another as well as with those of well-known U ICs, namely PP-U IC (large tetragonal unit cell) and PEO-U IC (trigonal unit cell). The urea C═O stretching vibration has shifted from 1681 cm^{-1} (bulk tetragonal urea) to 1728 and 1666 cm^{-1} (for PEG_{600}-U IC) and to 1729 and 1659 cm^{-1} (for PEG_{20000}-U IC). The two different vibration frequencies observed for C═O stretching were attributed to the two different types of urea in the complex.[17] Two-thirds of the urea molecules form the walls of the channels and one-third of the molecules reside in the IC channels. The extra urea molecules within the channels are hydrogen bonded to the poly(ethylene oxide) chain as well as to the channel-forming urea molecules. The NH bending vibrations for pure urea at 1626 and 1605 cm^{-1} have shifted to 1631 and 1622 cm^{-1} (for PEG_{600}-U IC) and to 1638 and 1616 cm^{-1} (for PEG_{20000}-U IC). In both U IC spectra the N−C−N vibrational stretching occurs at 1453 cm^{-1}, while in bulk urea one strong absorption band appears at 1464 cm^{-1}. In fact, wide-angle X-ray diffraction studies of both PEG-U ICs were previously reported in the litera-

Table 1. Comparison of the Important Vibrational Frequencies of Tetragonal Bulk Urea and Its Different IC Crystal Structures

		tetragonal structure		trigonal structure		
band assignt	bulk urea (cm^{-1})	PEG_{600}-U IC (cm^{-1})	PP-U IC (cm^{-1})	PEG_{20000}-U IC (cm^{-1})	PEO-U IC (cm^{-1})	PEG*-U IC (cm^{-1})
C=O str	1681	1728 (sh)		1729 (sh)	1694	
		1666	1663	1659	1659	1657
NH bend	1626	1631 (sh)	1638	1638	1639	1638
NH bend	1605	1622	1614	1616	1577	1629
NCN asym str	1464	1453	1454	1453	1457	1454

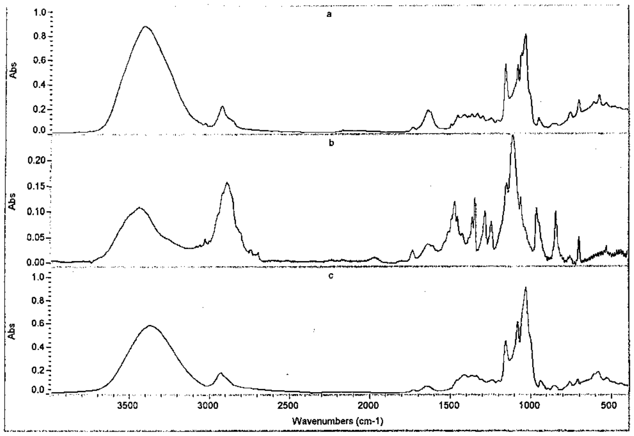

Figure 7. Fourier transform infrared spectra of (a) PEG_{600}-α-CD IC, (b) PEG, and (c) α-CD.

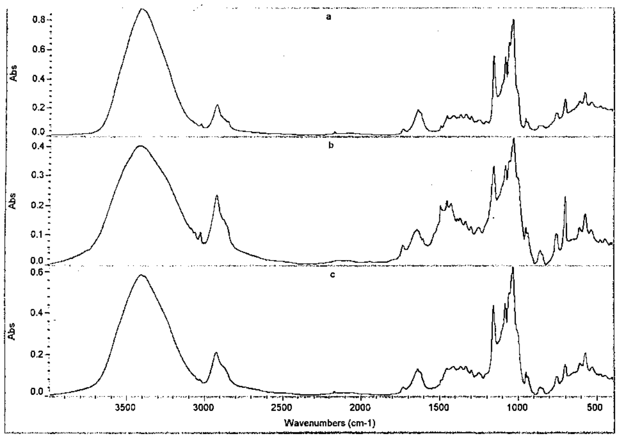

Figure 8. Fourier transform infrared spectra of (a) PEG_{600}-α-CD IC, (b) PEG_{20000}-α-CD IC, and (c) PEG*-α-CD IC from 400 to 4000 cm^{-1}.

ture;[12,16] therefore, all vibrations of PEG_{600}-U IC can be attributed to large tetragonal urea vibrations, while the vibrations mentioned for PEG_{20000}-U IC can be assigned to trigonal urea vibrations. The same conclusion can be arrived at by comparing the PEG_{600}-U IC vibrations with PP-U IC vibrations. The latter has been reported to have a large tetragonal crystalline structure.[10] The PEG_{20000}-U IC vibrations are compared to those of PEO_{100000}-U IC, whose structure was found to be trigonal. The shifts in the vibrational bands of PEG*-U IC are very similar to those seen in PEG_{20000}-U IC, though there are slight differences in the positions of some peaks, owing possibly to the instrumental resolution. Consequently, this suggests that urea has included preferentially in its IC channels PEG of higher molecular weight from a mixture of PEGs with different molecular weights.

In the case of PEG-α-CD IC, the FTIR spectroscopy was used only to get a qualitative confirmation concerning IC formation, because there is no difference among the crystalline structures of these compounds.

The FTIR spectra of PEG_{600}-α-CD IC (a), PEG (b), and α-CD (c) in the region from 400 to 4000 cm^{-1} are presented in Figure 7. The α-CD spectrum shows bands at 3371 cm^{-1} due to the symmetric and antisymmetric O−H stretching modes, at 2931 cm^{-1} due to C−H stretching mode, and several peaks in the 1500−1200 cm^{-1} region, which are assigned to C−H, CH_2 and O−H bending modes.[18] Positions and relative intensities of a few bands due to both α-CD and PEG are affected by the formation of the inclusion compound. Thus, the broad band at 3371 cm^{-1} is shifted to higher frequency at 3407 cm^{-1}, most probably due to hydrogen bond formation between the CD O−H groups and the oxygen atoms in the included PEG chain. New bands appearing in the 2800−3100 cm^{-1} region of the PEG_{600}-α-CD IC spectrum are contributed by the C−H antisymmetric stretching modes (3026 cm^{-1}) and the C−H symmetric stretching mode (2865 cm^{-1}, as a broad shoulder) of the PEG segments in their IC sample. According to DSC, the samples do not contain any free crystalline PEG, so the observation of these bands also confirm that the PEG polymer chains are included inside the channels provided by the cyclodextrins. Since there is a low concentration of polymer in the IC sample, the absorption bands contributed by the polymer are very weak.

Among the bands in the 1500−400 cm^{-1} region of the IC spectrum, some are due to the included PEG chain, as well. In this region, many bands of α-CD and PEG chain are shifted or altered in terms of relative intensity. Thus, the most important bands owing to included polymer appear at 1297, 1057, 950, and 699 cm^{-1}. The change in relative intensities of the 1731, 1644, 1492, and 1452 cm^{-1} bands were also observed in the PEG_{600}-α-CD IC spectrum. These changes may be accounted for by the overlapping between the absorbances of the two IC components.

Figure 8 shows a comparison of the FTIR spectra for PEG_{600}-α-CD IC(a), PEG_{20000}-α-CD IC (b), and PEG*-α-CD IC (c). These spectra are very similar, which means that all three inclusion compounds were formed.

X-ray Diffraction. Figure 9 is a comparison of wide-angle X-ray diffraction patterns recorded for PEG_{600}-U IC (a), PEG_{20000}-U IC (b), and PEG*-U IC (c) at room temperature from $2\theta = 0$ to 40°. Both PEG_{600}-U IC and PEG_{20000}-U IC were previously obtained and investigated using X-ray diffraction. It was mentioned that the structure of urea inclusion compounds with PEG of low molecular weights ($M_w < 1000$) is different from that with PEG having a molecular weight higher than 1000.[12]

All the reflections in the PEG_{600}-U IC diffractogram were indexed by Suehiro et al. with a large tetragonal unit cell with dimensions of $a = b = 9.30$ Å and $c = 19.51$ Å.[12] However, there is no report, to our knowledge,

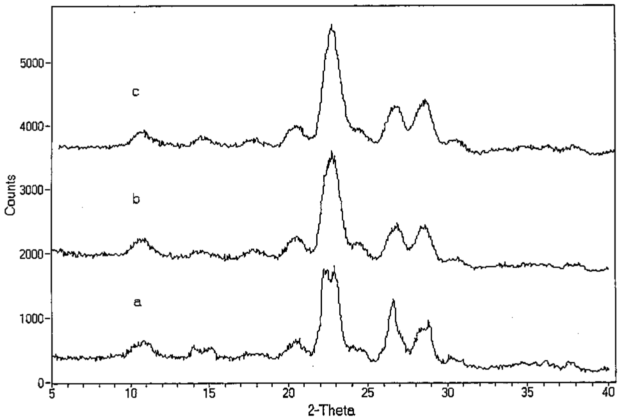

Figure 9. Comparison of X-ray diffractograms recorded at room temperature for (a) PEG_{600}-U IC, (b) PEG_{20000}-U IC, and (c) PEG*-U IC.

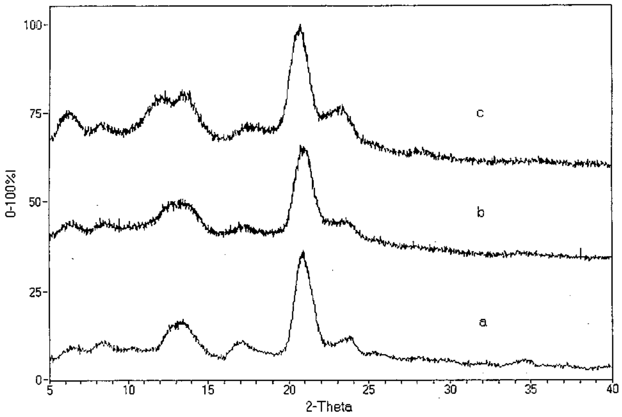

Figure 10. X-ray diffraction patterns for (a) PEG_{600}-α-CD IC, (b) PEG_{20000}-α-CD IC, and (c) PEG*-α-CD IC.

on the structure of PEG_{600}-U IC single crystals. Structural determination of recently obtained single crystals of PEG_{600}-U IC is in progress and will be published later in order to completely elucidate its structure.[19] The stoichiometry of this inclusion compound was found to be 1:1 from the unit cell parameters, the observed density, and the molecular composition.

In the case of urea inclusion compounds with PEG having $M_w > 1000$, a trigonal unit cell with dimensions of $a = b = 10.43$ Å and $c = 9.12$ Å was found.[12] A urea IC single-crystal having PEO of high molecular weight as guest was prepared and the three-dimensional structure analysis was established by Brisse and coworkers.[17] Also, this complex takes a trigonal crystal structure, and the stoichiometry of the adduct is $(-CH_2CH_2O-)_4 \cdot (urea)_9$.

By comparing X-ray diffraction patterns of these two above-mentioned different structures with the PEG*-U IC pattern, we observe that the last one resembles rather more closely the pattern of PEG_{20000}-U IC than that of PEG_{600}-U IC. This is further evidence that urea has a preference to complex with the higher molecular weight polymer, forming an IC with a trigonal structure.

Unfortunately, we are not able to perform the analogous analysis in the case of PEG-α-CD ICs, because these complexes exhibit identical crystal structures, as can be seen from the close similarity of their diffractograms as presented in Figure 10.

Yet, by comparing PEG-α-CD IC patterns with the X-ray diffraction of valeric acid−α-CD IC and propionic acid−α-CD IC, whose structures are already known as channel type and cage type, respectively,[20,21] we may say that our PEG-α-CD ICs are obtained and have a channel type structure and diffraction pattern very similar to valeric acid−α-CD IC (see Figure 11).

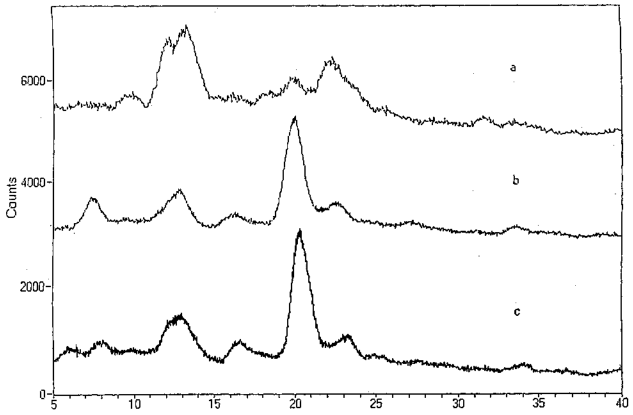

Figure 11. Wide-angle X-ray diffraction of (a) propionic acid−α-CD IC, (b) valeric acid−α-CD IC, and (c) PEG-α-CD IC.

Table 2. Efflux Time (s) of Different PEG-U IC Solutions

t_1 methanol	t_2 PEG600−U IC	t_3 PEG20000−U IC	t_4 PEG*−U IC
78.80	96.00	108.76	108.46

As stated earlier, a strong peak at approximately 20.0° corresponds to a polymer−α-CD IC channel structure. This peak also appears in all X-ray diffraction patterns of PEG-α-CD IC.

Viscosity Measurements. In Table 2 efflux times of urea IC/methanol solutions, as well as of pure methanol, are listed. All determinations were recorded at 30 °C for a concentration of urea IC solutions of 0.15 g of IC/10 mL methanol. Since values of t_3 and t_4 are almost equal, we may conclude once again that only PEG having higher molecular weight resides in the urea IC channels formed in the presence of the PEG mixture. This is strong evidence for the preference of the host urea to include the polymer of high molecular weight, since the IC formed is more thermodynamically stable. There is the possibility that during the IC formation process urea included both polymers, and since there is a sufficient stoichiometric amount of PEG_{20000} in solution, an interchange process between PEG_{600} chains residing in the IC channels and PEG_{20000} in solution took place. The interchange theory was reported, for the first time, by Monobe and Yokoyama for PE-U IC formation.[1]

Table 3 presents the efflux times of different solutions of PEG_{600}-α-CD IC, PEG_{20000}-α-CD IC, and PEG*-α-CD IC. Because the PEG-α-CD ICs are not soluble in water we have prepared the IC solutions (0.1 g/10 mL of water) by adding a very small amount of urea (0.025 g; which did not lead to a precipitation process due to U IC formation) and heating. The addition of urea, which is thought to affect the hydrogen-bonding network, results in solubilization of the complexes.

To understand whether α-CD has molecular weight selective inclusion properties, different molar ratios of α-CD and PEG were used, starting from 1:2 (7.25 g of α-CD:0.6564 g of PEG), which represents the stoichiometric ratio of the complex. By comparing the efflux times of PEG*-α-CD IC to those of PEG_{600}-α-CD IC and PEG_{20000}-α-CD IC, we can see that α-CD does not exclusively include only PEG_{20000} chains as urea does. However, the high values of IC_2 and IC_4 efflux times

Table 3. Comparison of Efflux Times Measured for PEG_{600}-α-CD IC, PEG_{20000}-α-CD IC, and PEG*-α-CD IC Solutions

			amount of included polymers		
α-CD:PEG molar ratio		efflux time of IC solution (s)	PEG_{600} (wt %)	PEG_{20000} (wt %)	yield[a] (%)
1:2	α-CD(7.25 g) + PEG_{600}(0.3282 g) + PEG_{20000} (0.3282 g) → IC_1	113.08	69	31	65.13
1:3	α-CD(7.25 g) +PEG_{600}(0.3282 g) + PEG_{20000}(0.6564 g) → IC_2	114.35	26	74	76.21
1:3	α-CD(7.25 g) +PEG_{600}(0.6564 g) + PEG_{20000}(0.3282 g) → IC_3	112.96	73	27	69.28
1:4	α-CD(7.25 g) + PEG_{600}(0.6564 g) + PEG_{20000}(0.6564 g) → IC_4	114.58	19	81	79.00
	PEG_{600}-α-CD IC	112.14	100		68.68
	PEG_{20000}-α-CD IC	115.14		100	68.27

[a] The yields are based on the starting amount of α-CD.

(114.35 and 114.58 s, respectively) which are closest to the efflux time of PEG_{20000}-α-CD IC solution (115.14 s), shows that there is a much larger quantity of PEG_{20000} than PEG_{600} inside of the α-CD IC channels. To find the ratio between the two included polymers we must take into account the efflux times of PEG_{600}-α-CD IC and PEG_{20000}-α-CD IC and the relation

$$x t_{\mathrm{PEG600-\alpha-CD\ IC}} + (100 - x) t_{\mathrm{PEG20000-\alpha-CD\ IC}} = t_{\mathrm{PEG^*-\alpha-CD\ IC}}$$

where

x = the amount of PEG_{600} (wt %)

t = the efflux time of the α-CD IC solution

The calculated amounts of PEG_{600} and PEG_{20000} in the PEG*-α-CD IC channels are listed in Table 3.

Harada and co-workers have found that the rates of the complex formation depend on the molecular weight of PEG.[15] The variation curve of the rate of the complex precipitation vs molecular weight of PEG shows a maximum for PEG_{1000}, and then the rate decreases as the molecular weight increases. On the basis of these determinations there is the possibility that immediately after mixing of host–guest solutions, α-CD includes a larger quantity of PEG_{600}, and then an interchange process between PEG_{600} in the IC channels and PEG_{20000} in the solution takes place.

As we can see from Table 3, a larger initial amount of PEG_{20000} leads to a final ratio between the two included polymers favorable to PEG_{20000}. When equal initial amounts of PEG_{600} and PEG_{20000} were used (IC_1 and IC_4), a sharp contrast between final weight ratios of included polymers was obtained. This can be attributed to the fact that in the IC_1 case just half the stoichiometric amount of PEG_{20000} was used and that the yield of forming PEG_{20000}-α-CD IC is ca. 68%.

In the IC_2 and IC_4 cases, where the amount of PEG_{20000} is sufficient in order to obtain a 100% yield of IC, a very small quantity of PEG_{600} resides in the channels of α-CD IC irrespective of the initial ratio of polymers used. These results indicate that the interchange process is reversible and shifted toward obtaining PEG_{20000}-U IC.

Though not exclusive as in the case of the urea host, α-CD still strongly prefers the inclusion of the higher molecular weight PEG.

Conclusion

In summary, we report, for the first time, that both urea and α-CD exhibit molecular weight selective polymer inclusion in the complexation process. Unlike α-CD, the urea host exclusively complexes the polymer (PEG_{20000}) having the higher molecular weight in order to form more thermodynamically stable IC, while α-CD exhibits a similar, though not exclusive, preference for the high molecular weight PEG. Thus, IC formation with urea and cyclodextrins could be a useful tool in the separation process of certain polymer types, which cannot be fractionated by other conventional methods.

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