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Study of the inclusion compounds formed between α-cyclodextrin and high molecular weight poly(ethylene oxide) and poly(ε-caprolactone)

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We report the formation of high molecular weight polymer inclusion compounds (ICs) between α-cyclodextrin and poly(ethylene oxide) (PEO) ($M_n = 100$ kg mol^{-1}), and poly(ε-caprolactone) (PCL) ($M_n = 40$ kg mol^{-1}). Both high molecular weight polymer ICs were successfully made by ultrasonic and heating techniques. Dsc, tga, X-ray diffraction, *FT* i.r. and solid state ^{13}C n.m.r. were utilized to observe the PCL and PEO polymer chains included inside the channels formed by α-cyclodextrin. Dsc and tga scans showed that the high temperature stable polymer-CD-IC samples contain no free crystalline polymer. The much higher decomposition temperatures observed for these polymer-CD-ICs may imply that polymer chains included inside the polymer CD-IC channels can greatly improve cyclodextrin's stability. The polymer-CD-IC's X-ray diffraction patterns were very similar to that of valeric acid-CD-IC, which is confirmed to be a channel crystal structure, and the strong peak for both polymer-CD-ICs at approximately 20.0° (2θ) may confirm their IC formation. New bands appeared at 1729 cm^{-1} for PEO-CD-IC and at 1739 cm^{-1} for PCL-CD-IC in their *FT* i.r. spectra. Both bands were absent from the α-cyclodextrin spectrum. In CP/MAS/DD ^{13}C n.m.r. spectra, single resonances for PEO-CD-IC, which compared with the multiple resonances observed for each carbon type in α-cyclodextrin, may indicate that α-cyclodextrin adopts a more symmetrical cyclic conformation in the PEO-CD-IC sample, while pure α-cyclodextrin assumes a less symmetrical conformation in the crystal when it does not include a guest polymer PEO inside its cavity. A one-pulse ^{13}C n.m.r. spectrum was observed to identify the resonance peak for PEO inside the PEO-CD-IC.

(Keywords: polymer inclusion compounds; X-ray diffraction; Ftir)

INTRODUCTION

It has been known for many years that certain small molecules such as urea (U), thiourea (TU) and perhydrotriphenylene (PHTP) can form crystalline inclusion compounds (ICs) with semicrystalline polymers via a co-crystallization process[1]. Some polymers may be prepared directly in the channels of their inclusion compounds by irradiation of the inclusion compounds formed by their monomers[2]. Some linear polymers which were examined in ICs are poly(ethylene) (PE), poly(ethylene oxide) (PEO), and polyester, etc.[1,3,4]. The biodegradability and nontoxicity of aliphatic polyesters, such as poly(ε-caprolactone) (PCL), has caused them to be widely studied for biomedical applications such as controlled release of drugs from polymer devices[5]. The behaviour of isolated PCL chains confined to the narrow channels of their crystalline IC with urea has also been studied[4].

Cyclodextrins (CDs) are carbohydrates which can form inclusion complexes with a wide range of guest compounds. *Figure 1* presents the chemical structure for α-cyclodextrin. Since the discovery of cyclodextrins (CDs), a large number of inclusion compounds of CDs with various low molecular weight compounds were prepared and characterized. However, there are few reports on the inclusion compounds formed between cyclodextrins and polymers[6]. Unlike U, TU and PHTP whose inclusion compounds can only exist in the solid state and in which guest molecules are included in cavities or cages provided by the crystalline structure of the host, CDs can also form inclusion compounds which are soluble and stable in solution. In solution, a single cyclodextrin molecule can provide the cavity in which a guest molecule is bound.

Cyclodextrin ICs formed with low molecular weight guests can either have channel or cage structures. *Figure 2*

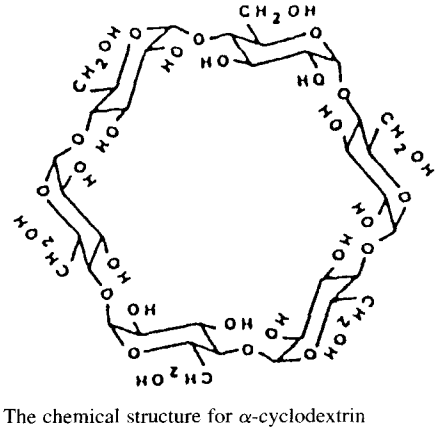

Figure 1 The chemical structure for α-cyclodextrin

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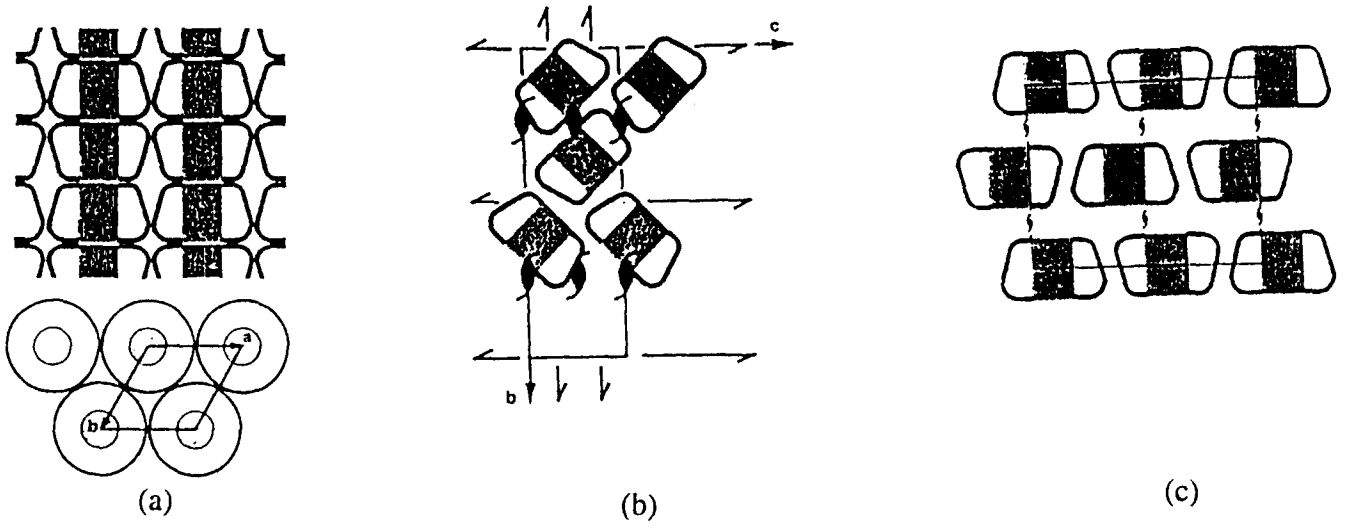

Figure 2 Schematic description of: (a) channel type, (b) cage herringbone type, and (c) cage brick type crystal structures formed by crystalline cyclodextrin inclusion complexes

presents schematic descriptions of channel type, cage herringbone type and cage brick type cyclodextrin IC crystal structures[7]. Normally the channel structures can be assigned to polymer-CD-IC samples caused by the polymer's long chain nature. Mole ratios of host cyclodextrin and guest polymer will depend on the length of the polymer's repeat unit and on the extent to which the CD channels are filled.

Recently, Harada *et al.*[8,9], reported that α-cyclodextrin can form inclusion complexes with various low molecular weight poly-(ethylene glycol)s (PEG) to give stoichiometric compounds in a crystalline state. When aqueous solutions of PEG were added to a saturated aqueous solution of α-CD at room temperature, the solution became turbid and the complexes were obtained as precipitates when the average molecular weight of PEG was between 400 and 10^4. The PEG of molecular weight 10^3 forms the complex most rapidly, and the rate of complexation decreases as the molecular weight increases beyond 10^3 [9].

Inclusion compounds have many uses, such as separating isomers, preparing highly stereoregular polymers and obtaining monodispersed fractions from unfractionated polymer samples[10]. Since each polymer chain included in the cyclodextrin IC channels is highly extended and stretched and is also separated from neighboring polymer chains by the host matrix channel walls, polymer-CD-ICs can be studied as models for ordered, bulk polymer phases. For example, we can measure the contributions made by the intrinsic nature of a confined polymer chain and the pervasive, cooperative, interchain interactions, which can complicate the behaviour of bulk samples, by comparing the behaviour of those isolated, stretched polymer chains in their crystalline ICs with ordered, bulk samples of the same polymers. Thus, we should enhance our understanding of the behaviour of polymer chains in their ordered, bulk phases as found in crystalline, liquid-crystalline, and oriented samples[1].

In the work presented herein, PEO-CD-IC and PCL-CD-IC are prepared via ultrasonic and heating techniques. Tga, dsc, wide angle X-ray diffraction, and FTIR and ^{13}C n.m.r. spectroscopies are used to characterize the ICs and the PEO and PCL polymer chains isolated in the narrow CD-IC channels.

EXPERIMENTAL

Materials

Poly(ethylene oxide) (PEO) and poly(ϵ-caprolactone) (PCL) samples with weight average molecular weight 100 kg mol^{-1} and 40 kg mol^{-1} (provided by the vendor), respectively, were obtained from Aldrich Chemical Company, α-cyclodextrin was obtained from AMAIZO Company and was used after drying in a vacuum oven at 70°C for 12 hours.

Preparation of the physical mixtures

The physical mixture of PEO and α-CD was prepared by mixing both PEO and α-CD powders together at room temperature in 2:1 (monomer unit:CD) molar ratio, which was indicated by model studies.

The PCL pellets were ground into a granular powder with a Wiley mill. The physical mixture of PCL and α-CD was made by mixing both PCl and α-CD powders together at room temperature in 1:1 (monomer unit:CD) molar ratio, which was indicated by model studies.

Preparation of IC samples by solution technique

Ultrasonic Technique. Polymer-CD-IC was successfully made by an ultrasonic technique:

(1) PEO-CD-IC: 1.5 g of PEO was dissolved in 10 ml of distilled water, then added slowly to 100 ml of saturated α-CD aqueous solution at room temperature with ultrasonic treatment for 15 min. After storing quiescently for 10 hours, the white precipitate was filtered and dried. The yield is 74%.

(2) PCL-CD-IC: 0.2 grams of PCL was dissolved in 50 ml of acetone and 7.25 grams of α-cyclodextrin was dissolved in 50 ml of distilled water; both solutions were stirred on a warm hot plate at 70°C, and then the PCL solution was added slowly to the α-CD aqueous solution using an addition funnel and accompanied by sonication. The mixture was kept at 70°C and sonicated for a total of 17 min. After storing quiescently for 10 hours, the white precipitate was filtered and dried. The yield is 47%.

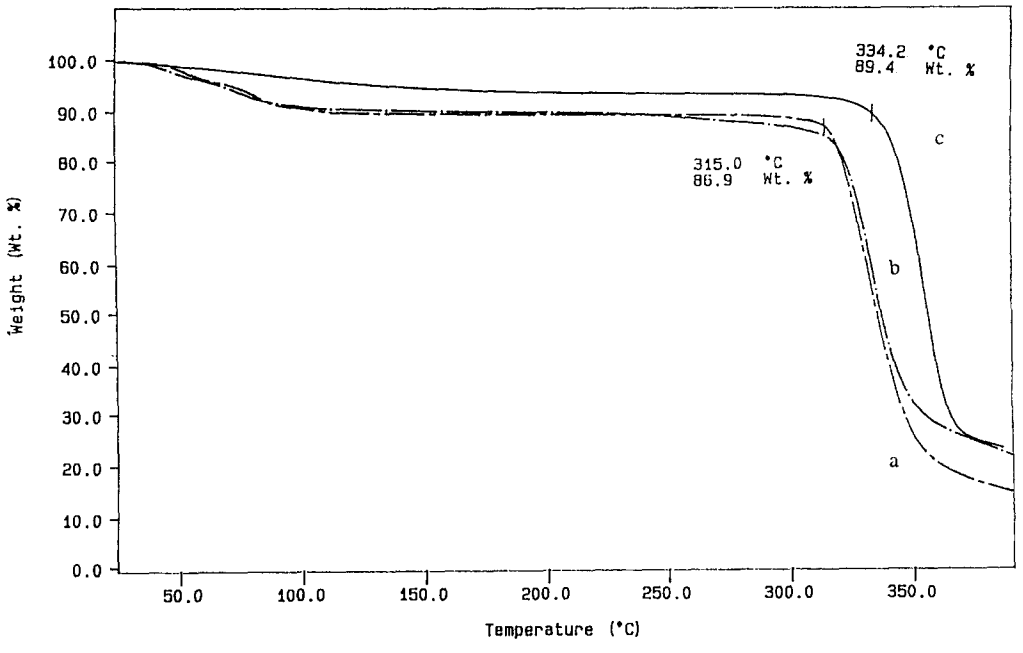

Figure 3 TGA scans of: (a) α-CD, (b) α-CD and PEO physical mixture, and (c) PEO-CD-IC (10°C min^{-1})

Heating Technique. The heating procedure for making cyclodextrin and polymer solutions is similar to the ultrasonic technique. However, instead of sonication for 15–17 min, the mixed solutions of polymer and cyclodextrin were kept on a hot plate for 3 hours at 70°C, then cooled to room temperature while stirring for another 6 hours. After storing quiescently for 10 hours, the white precipitate was filtered and dried. The yields are approximately the same as reported earlier.

CHARACTERIZATION

Thermal property analysis

Thermal characteristics of samples were determined with a Perkin–Elmer Model 7 series/UNIX different scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). Samples of 5–10 mg were used in both tests. In dsc, the samples were sealed in aluminum pans designed for volatile materials and scanned from 25 to 190°C at a heating rate of 10°C min^{-1}; in tga, the samples were put inside the platinum pans which were hanging in the heating furnace. The weight percentage of remaining material was recorded while the furnace was heating from 25 to 400°C. Both instruments used nitrogen as the purge gas, and a heating rate of 10°C min^{-1} was employed.

X-ray diffraction

Wide angle X-ray diffraction patterns of powder samples were obtained at ambient conditions on a Siemens type-F X-ray diffractometer with a nickel filtered CuKα radiation source (wavelength = 1.54 Å). The supplied voltage and current were set to 30 kV and 20 mA, respectively. Samples were mounted on a sample holder with Scotch tape and exposed at a scan rate of $2\theta = 1°$ min^{-1} between $2\theta = 5$ and 40°.

Infrared spectroscopy

Absorbance Fourier transform infrared spectra were recorded on a Nicolet 510 p *FT*i.r. spectrometer with OMNIC software at frequencies from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}, gain = 1, and scans = 128. Samples were thoroughly mixed with KBr and pressed into pellet form.

n.m.r. measurements

High resolution solid state ^{13}C n.m.r. spectroscopy was carried out at 50.14 MHz on a Chemagnetics CMC 200S n.m.r. spectrometer. The cross polarized (CP), magic angle spinning (MAS) and one pulse spectra were observed with probes using Zirconia rotors at spinning rates of 3 to 4 KHz. High power dipolar decoupling (DD) was applied at about 47 KHz during acquisition. The spectral width was 15 KHz stored in a memory that was zero filled to 8 k before Fourier transformation.

RESULTS AND DISCUSSION

Thermal property analysis

Figure 3 shows the TGA for α-cyclodextrin and the PEO, and the PEO-CD-IC formed by the ultrasonic technique up to 400°C, respectively. From *Figure 3*, we can see that α-cyclodextrin and a physical mixture of α-cyclodextrin and PEO both started to decompose at 315°C. However, the pure α-cyclodextrin reached a lower weight percentage of remaining material which was 20% at 360°C, while the physical mixture had 30% weight remaining. The reason that pure α-cyclodextrin had a greater weight loss while decomposing compared with the physical mixture of CD and PEO is probably because the PEO in the physical mixture was just in the molten state and did not decompose to cause weight loss. The most striking feature for the PEO-CD-IC is that it showed a much higher decomposition temperature (334°C) than pure α-CDs (315°C).

In *Figure 4*, it is seen that both α-cyclodextrin and the physical mixture with PCL started to decompose at 315°C, which was the same decomposition behaviour observed in *Figure 3*. The physical mixture of α-cyclodextrin and PCL had a higher weight percentage remaining (44%) compared

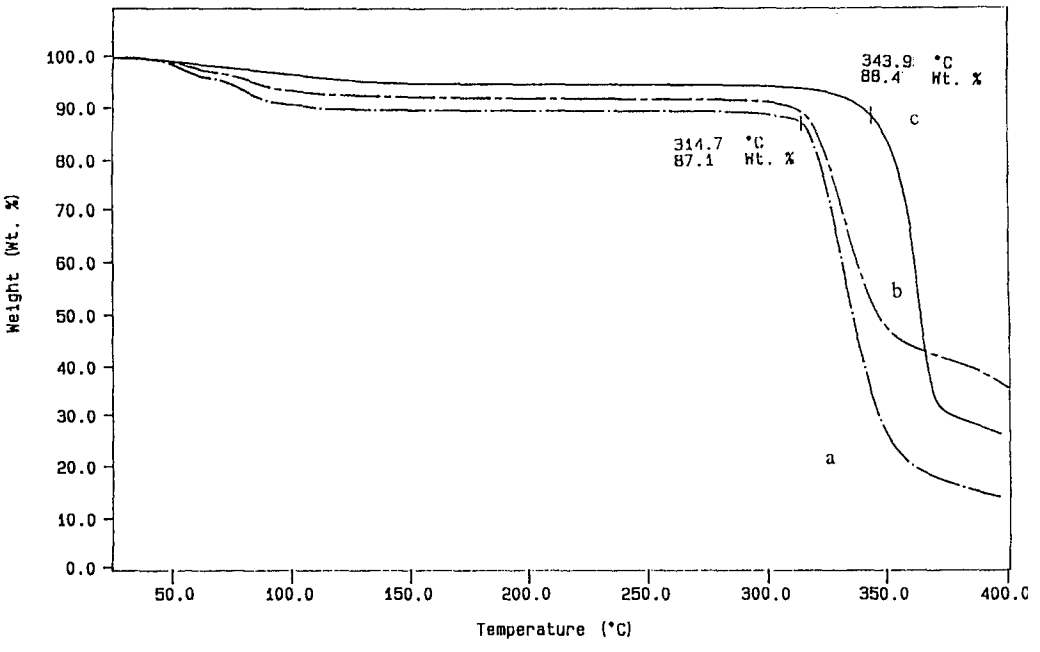

Figure 4 TGA scans of: (a) α-CD, (b) α-CD and PCL physical mixture, and (c) PCL-CD-IC (10°C min^{-1})

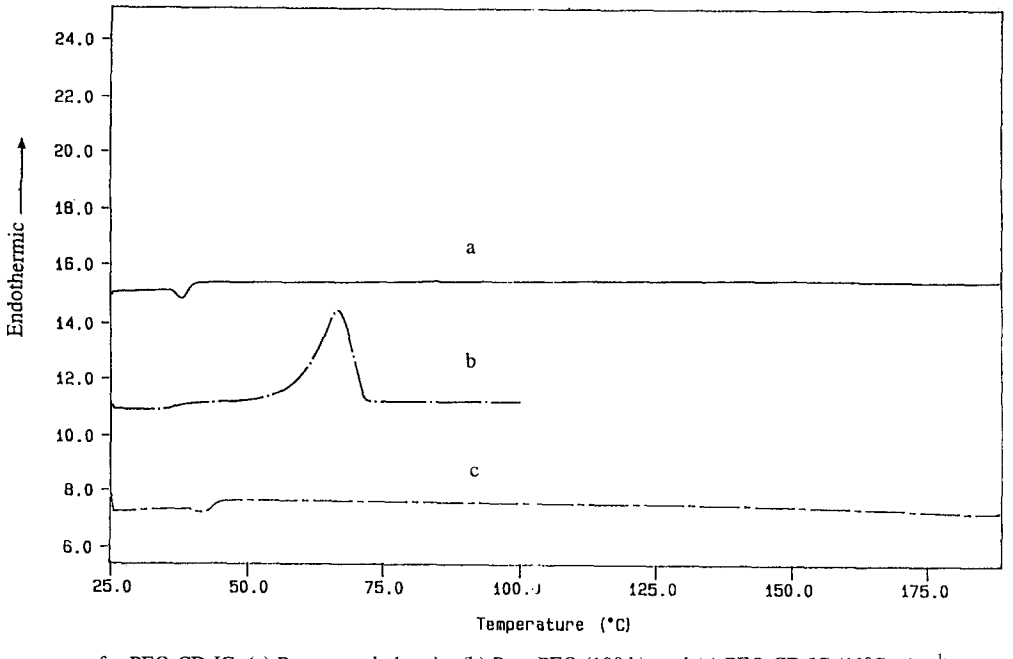

Figure 5 DSC thermograms for PEO-CD-IC: (a) Pure α-cyclodextrin, (b) Pure PEO (100 k), and (c) PEO-CD-IC (10°C min^{-1})

with the pure α-cyclodextrin (20%), while the PCL-CD-IC also showed a much higher decomposition temperature (344°C) than pure α-CDs (315°C). This phenomenon of a much higher decomposition temperature in polymer-CD-ICs may imply that the polymer chains included inside the polymer CD-IC channels can greatly improve cyclodextrin's thermal stability. This might provide a great potential benefit for studying these rather high temperature stable polymer-CD-ICs in several areas, such as using polymer ICs in the fabrication of polymer–polymer molecular composites. Normally other kinds of polymer ICs, like those formed with urea, thiourea, and PHTP as hosts, are not stable in IC structures at temperatures above 150–180°C.

The polymer-CD-IC samples made by the heating technique showed the same tga and dsc results (which are not shown here) as the samples made by the ultrasonic technique. They are also identical in the following tests, so we discuss the following results without separating them.

Since cyclodextrins and their ICs will decompose while melting, we only tested them below their melting temperatures in DSC. *Figures 5 and 6* show DSC curves for α-cyclodextrin, a physical mixture of α-cyclodextrin and PEO or PCL, and polymer-CD-IC from 25.0 to 190°C, respectively. We can see the pure bulk PEO melts at 61°C and PCL melts at 58°C. The absence of these two polymer peaks in polymer-CD-IC scans may indicate that there is no free crystalline polymer in the polymer-CD-ICs. So we expect that most of the polymer chains may be included inside the channels which are provided by orderly stacked α-cyclodextrin molecules, and form the channel type

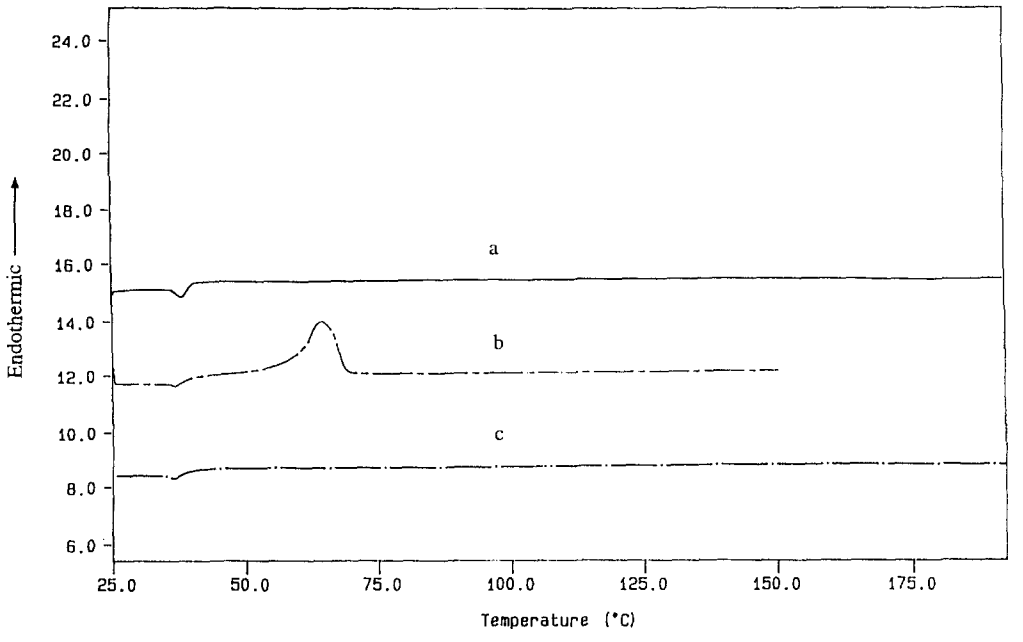

Figure 6 DSC thermograms for PCL-CD-IC: (a) Pure α-cyclodextrin, (b) Pure PCL (40 k), and (c) PCL-CD-IC (10°C min^{-1})

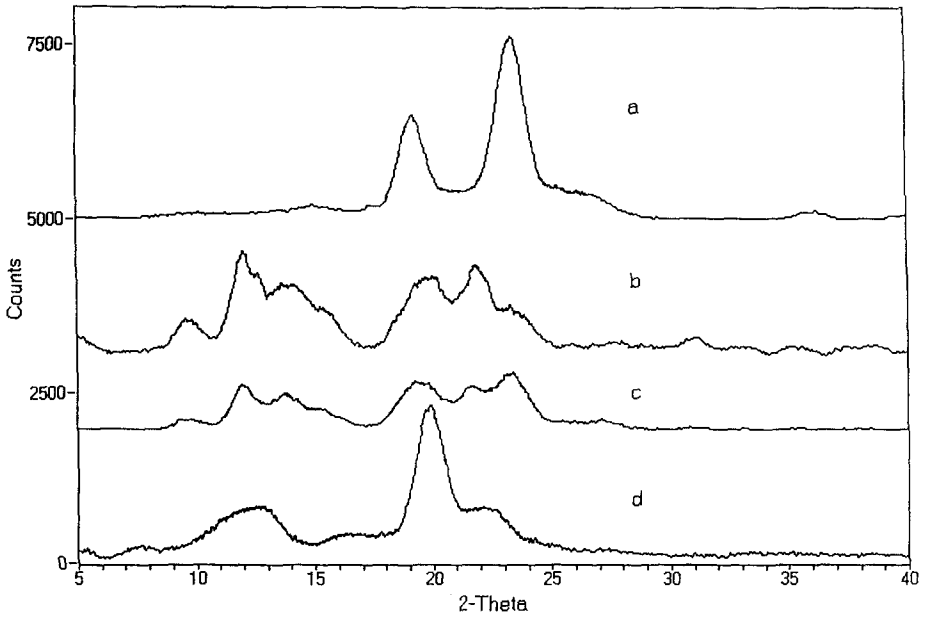

Figure 7 Wide Angle X-ray Diffraction of: (a) PEO, (b) α-CD, (c) α-CD and PEO mixture, and (d) PEO-CD-IC

crystalline IC samples, just like the picture shown in *Figure 2a*.

X-ray diffraction

Figure 7 is the comparison of wide angle X-ray diffraction patterns observed for PEO, α-CD, α-CD and PEO mixture, and PEO-CD-IC at room temperature from $2\theta = 5$ to 40°. Major peaks at 9.6°, 12.03°, 19.5°, and 21.8° were observed for pure α-cyclodextrin. PEO showed two strong reflections at $2\theta = 19.3°$ and 23.5°. The diffraction patterns of the physical mixture is simply the superposition of each crystalline component, while the diffractogram of PEO-CD-IC showed a diffraction pattern quite different from the diffractograms of PEO and α-cyclodextrin, and this constitutes primary evidence that a different crystal type was formed. We suggest that the strong peak for PEO-CD-IC at approximately 20.0° (2θ) may indicate that the inclusion compound formed with PEO included formed with PEO included inside the CD channels.

Figure 8 is the comparison of wide angle X-ray diffraction patterns observed for PCL, α-CD, α-CD and PCL mixture, and PCL-CD-IC at room temperature from $2\theta = 5$ to 40°. PCL showed two strong reflections at $2\theta = 22.0$ and 23.8°. Like PEO-CD-IC, the diffractogram of PCL-CD-IC also showed quite a different diffraction pattern from those of PCL and α-cyclodextrin, which constitutes primary evidence that a different crystal type was formed. The strong peak for PCL-CD-IC at approximately 20.0° (2θ) may also indicate that the inclusion compound formed with PCL included inside the CD channels.

By comparing PEO-CD-IC and PCL-CD-IC with the X-ray diffraction of valeric acid-CD-IC and propionic

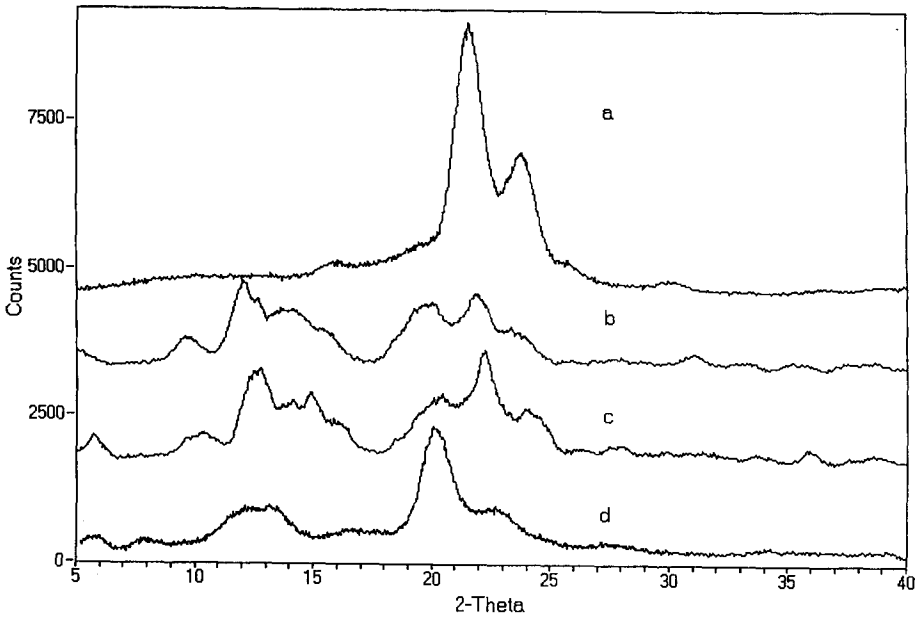

Figure 8 Wide Angle X-ray Diffraction of: (a) PCL, (b) α-CD and PCl mixture, and (d) PCL-CD-IC

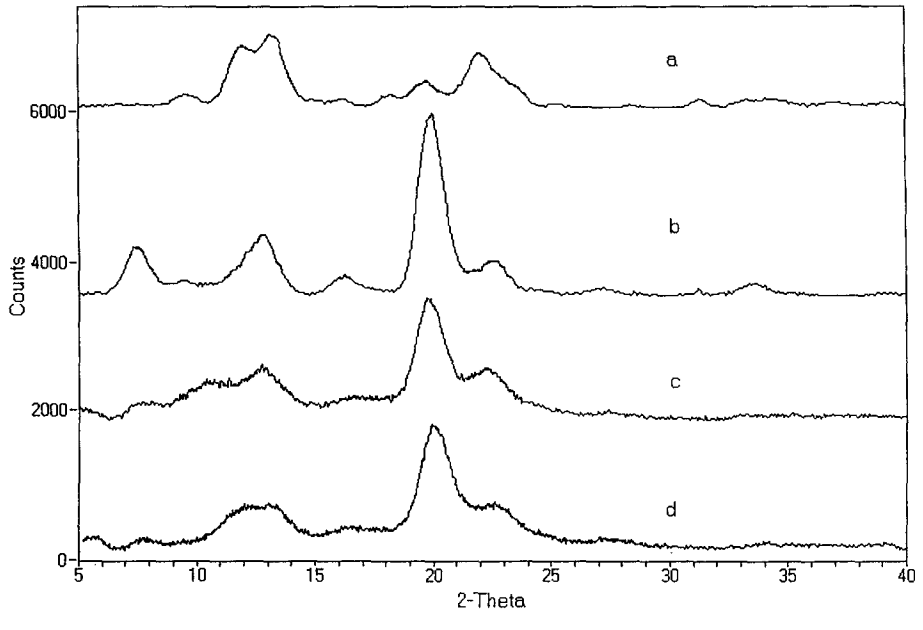

Figure 9 Wide Angle X-ray diffraction of: (a) propionic acid-CD-IC, (b) valeric acid-CD-IC, (c) PEO-CD-IC, and (d) PCL-CD-IC

acid-CD-IC, whose inclusion structures are already known as channel type and cage type, respectively[11,12], we observe both PEO-CD-IC diffraction patterns are much more similar to that of valeric acid-CD-IC (See *Figure 9*). This is very strong evidence for the proposed channel type polymer-CD-IC structure mentioned earlier. More interesting is that the X-ray diffraction patterns of PEO-CD-IC and PCL-CD-IC are very similar to each other, and they both have a strong peak at approximately 20.0°. From this we further suggest that this peak is probably contributed to by the polymer-CD-IC's channel structure.

Although PEO-U-IC single crystals were prepared and the three dimensional structure analysis was established by Brisse *et al.*[13], a similar X-ray structural determination for PEO-CD-IC and PCL-CD-IC single crystals has not been performed. From the similarity of both PEO-CD-IC and PCL-CD-IC wide angle X-ray diffractograms, we may say that these two polymer IC crystal structures are quite similar.

FTi.r. spectroscopy

Figure 10 shows the *FT*i.r. spectra in the region from 400 to 4000 cm^{-1} obtained for α-cyclodextrin, PEO and PEO-CD-IC. The bands in the 4000-3000 cm^{-1} region are normally assigned to the symmetric and antisymmetric O–H stretching modes, and are extremely broad. The centre of this band shifted to higher frequency for the PEO-CD-IC (3446 cm^{-1}) compared with α-cyclodextrin which was at 3386 cm^{-1}. This shift may be accounted for in terms of O–H stretching modes associated with a α-cyclodextrin bridged systems[14]. There is also a shoulder appearing on the low frequency side which may be the result of hydrogen bonding between α-cyclodextrin bridged hydroxyl groups and the PEO polymer chains.

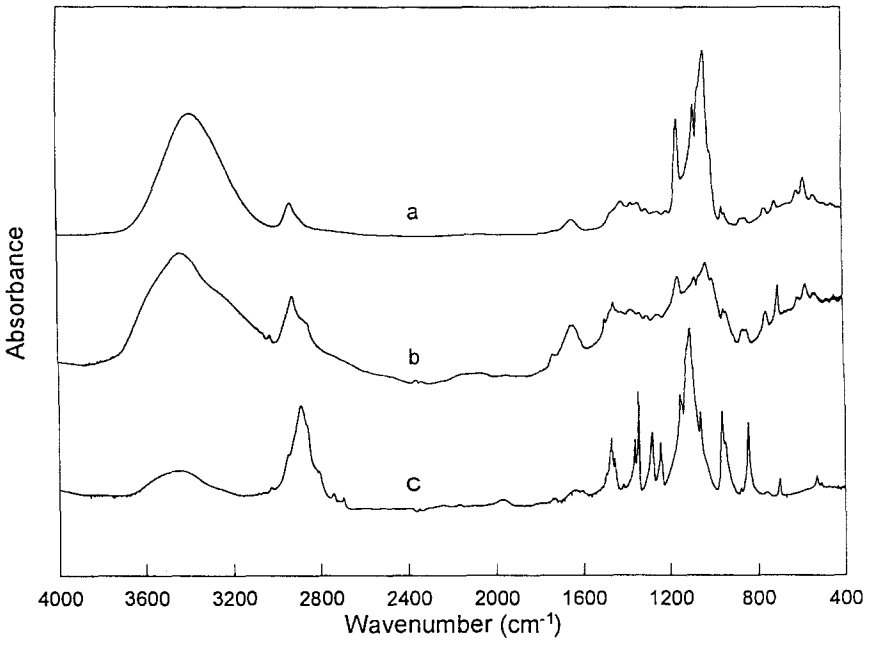

Figure 10 Fourier transform infrared spectra in the region between 400 and 4000 cm^{-1}: (a) α-cyclodextrin, (b) PEO-CD-IC, and (c) PEO (100 k)

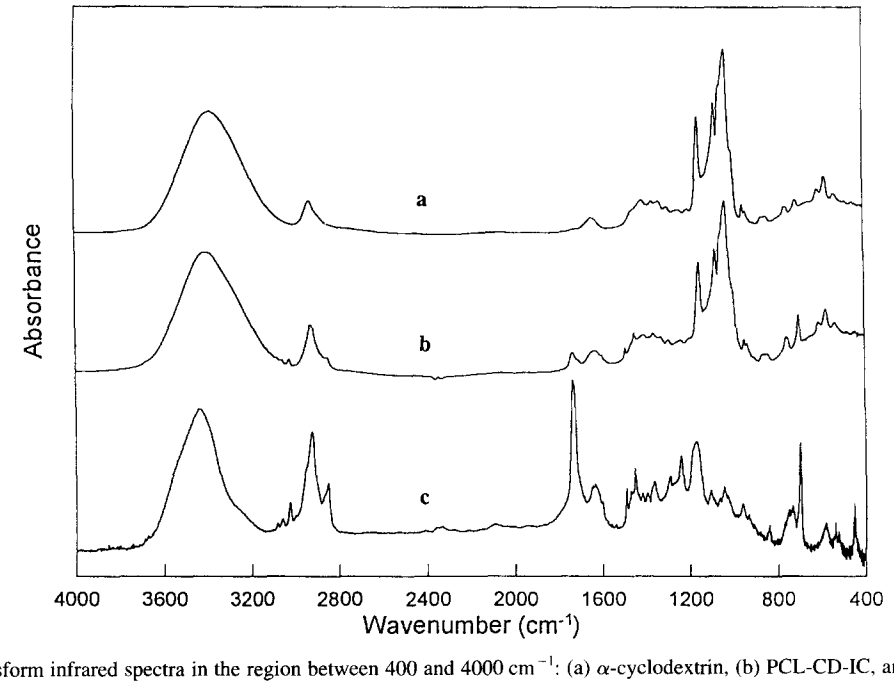

Figure 11 Fourier transform infrared spectra in the region between 400 and 4000 cm^{-1}: (a) α-cyclodextrin, (b) PCL-CD-IC, and (c) PCL (40 k)

The bands observed in the 3000–2000 cm^{-1} region for pure α-CD (*Figure 10*a) and PEO-CD-IC (*Figure 10*b) spectra are different. Poly(ethylene glycol) (PEG, which has the same repeat unit as PEO), was reported[15] to have several bands caused by the C–H stretching mode at 2940-2925 cm^{-1} (the C–H antisymmetric stretching mode) and at 2880–2865 cm^{-1} (the C–H symmetric stretching mode). At slightly lower frequency, the multiple bands at around 2922 cm^{-1} and a broad shoulder (around 2851 cm^{-1}) appeared in the PEO-CD-IC spectrum, which were different from the α-cyclodextrin spectrum and were most probably contributed to by the included PEO segments in their IC sample. Combined with the previous dsc result, which showed there was not any free crystalline PEO in the PEO-CD-IC sample, these bands also confirm that the PEO polymer chains are included inside the channels provided by the cyclodextrins.

The bands in the 1500–1200 cm^{-1} region of the α-CD spectrum are assigned to C–H, CH_2 and O–H bending modes[16]. Changes in relative intensity of the 1472 cm^{-1} and 1421 cm^{-1} bands were also observed in the PEO-CD-IC sample.

Bands in the 1200–800 cm^{-1} region were very similar for both α-cyclodextrin and PEO-CD-IC. These bands are referred to as stretching modes of the glycosidic group coupled with C–C and C–O stretching modes[16].

Figure 11 shows the *FT*i.r. spectra in the region from 400 to 4000 cm^{-1} obtained for α-cyclodextrin, PCL and PCL-CD-IC, with the latter being very similar to the PEO-CD-IC spectrum. The centre of the symmetric and antisymmetric

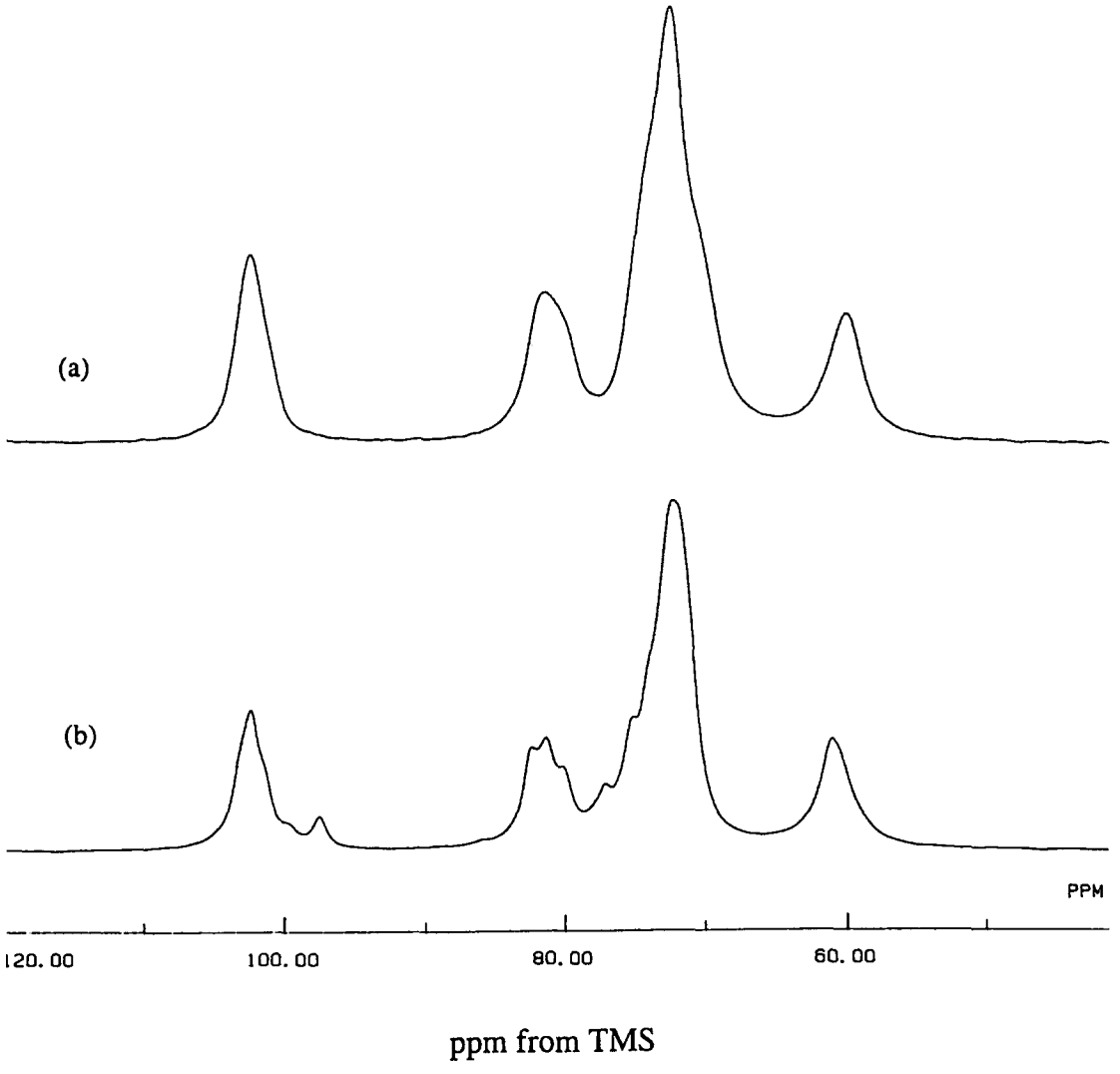

Figure 12 ^{13}C NMR spectra with cross polarization for: (a) PEO-CD-IC and (b) α-cyclodextrin

O–H stretching modes band shifted to higher frequency for the PCL-CD-IC (3410 cm^{-1}) compared with α-cyclodextrin which was at 3386 cm^{-1}. Just as for PEO-CD-IC, this shift may be also be accounted for in terms of O–H stretching modes associated with the α-cyclodextrin bridged systems[14].

A new band appeared at 1739 cm^{-1} in the PCL-CD-IC spectrum which was absent from the α-cyclodextrin spectrum, and this is the C = O stretching band for amorphous bulk phases of PCL[17]. This is consistent with the previous dsc result which showed no free crystalline PCL in the PCL-CD-IC sample. The appearance of this band confirms that these PCL polymer chains are included inside the channels provided by α-cyclodextrins.

The changes in relative intensity of the 1493 cm^{-1} and 1453 cm^{-1} bands were also observed in the PCL-CD-IC sample.

n.m.r. spectroscopy

The CP/MAS/DD ^{13}C n.m.r. spectra of α-cyclodextrin and PEO-CD-IC are shown in *Figure 12*. The resonance frequencies were very similar for α-cyclodextrin and PEO-CD-IC, except that the multiple resonances observed for each carbon type in α-cyclodextrin become single resonances for PEO-CD-IC. This may indicate that α-cyclodextrin adopts a symmetrical cyclic conformation in the PEO-CD-IC sample, while α-cyclodextrin assumes a less symmetrical conformation in its own pure crystal where a guest polymer PEO chain is not included.

Since it was difficult to observe the PEO peak in the PEO-CD-IC sample by using CP solid state n.m.r. spectroscopy, we recorded the one pulse spectrum of PEO-CD-IC sample without cross polarization with a 30 s delay time between signal accumulations. *Figure 13* shows a comparison of the one pulse n.m.r. spectra of PEO-CD-IC with the cross-polarized n.m.r. spectra of α-cyclodexrin. There the peak at 69.61 ppm which is referred to the PEO polymer can be clearly seen. This implies that PEO chains were included inside the PEO-CD-IC channels. When this result is combined with previous evidence, the formation of PEO-CD-IC is confirmed.

In summary, we have confirmed that high molecular weight PEO-CD-IC and PCL-CD-ICs were formed via ultrasonic and heating techniques. These two polymer-CD-ICs have much different crystal structures and thermal behaviour compared to their bulk polymers. The long polymer chains were included inside the channels which are provided by the orderly stacked α-cyclodextrin molecules. Both ICs' structures are quite similar according to WAXD. Further analyses of the structures, stoichiometries, and stabilities of these polymer-CD-ICs are in progress. The CP/MAS/DD ^{13}C n.m.r. observation of PCL-CD-IC and more

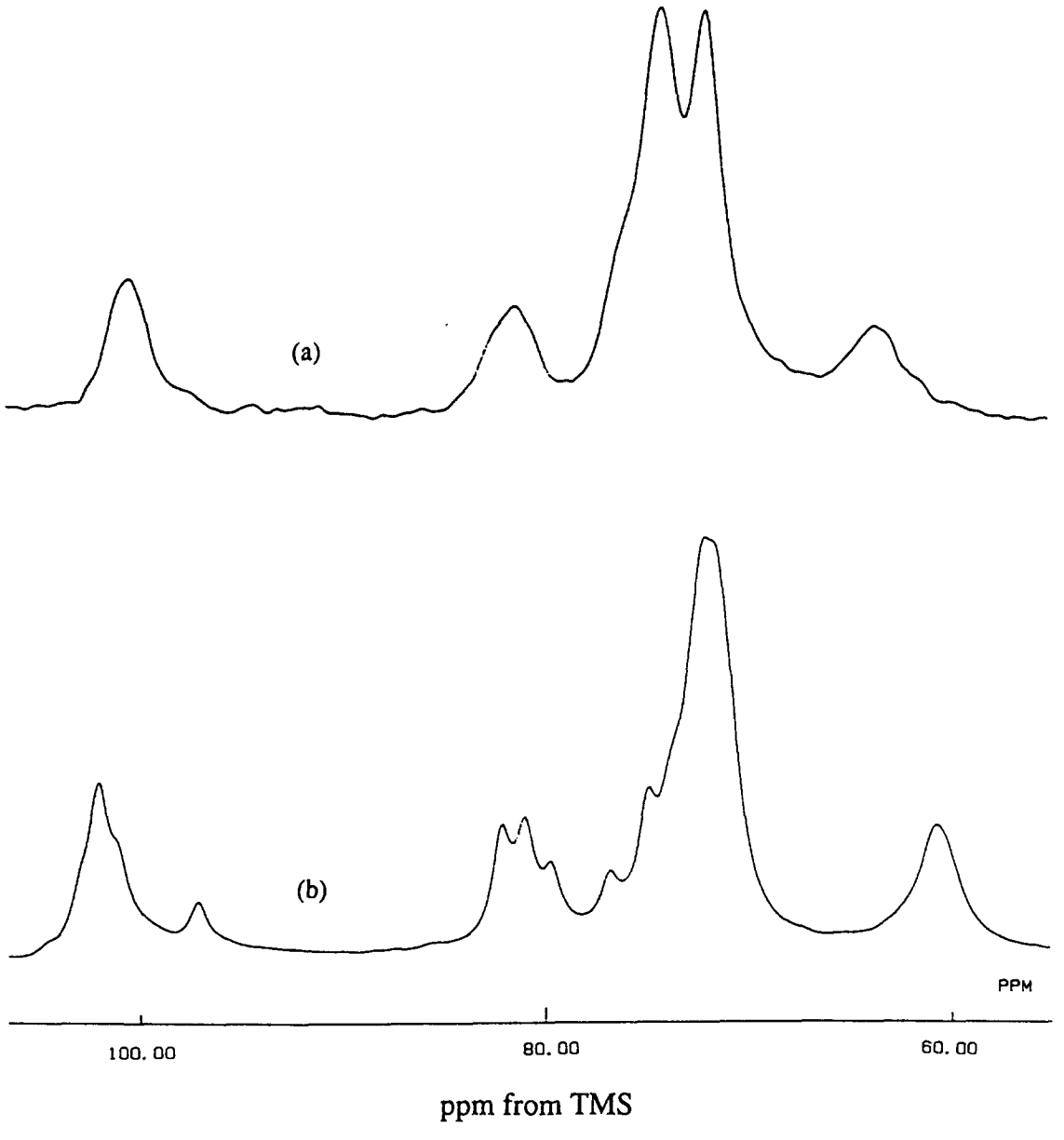

Figure 13 ^{13}C NMR spectra for: (a) PEO-CD-IC with one pulse and (b) α-cyclodextrin with CP

detailed studies of the behaviour of the included polymer chain conformations and mobilities are also underway.

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