

Formation and characterization of the inclusion compounds between poly(ϵ -caprolactone)-poly(ethylene oxide)-poly(ϵ -caprolactone) triblock copolymer and α - and γ -cyclodextrin

Jin Lu^a, I.D. Shin^b, S. Nojima^c, A.E. Tonelli^{a,*}

^aFiber and Polymer Science Program, North Carolina State University, Campus Box 8301, Raleigh, NC 27695-8301, USA

^bDepartment of Chemistry, Fayetteville State University, Fayetteville, NC, USA

^cSchool of Material Science, Japan Advanced Institute of Science and Technology (JAIST), Tatsunokuchi, Ishikawa 923-12, Japan

Received 19 July 1999; received in revised form 12 October 1999; accepted 15 October 1999

Abstract

We report the formation of crystalline inclusion compounds (ICs) between poly(ϵ -caprolactone)-poly(ethylene oxide)-poly(ϵ -caprolactone) triblock copolymer guest and the small-molecule hosts α -cyclodextrin (α -CD), and γ -cyclodextrin (γ -CD). The triblock copolymer-CDs-ICs are formed by cocrystallization from saturated solutions of CDs, and each of them was observed with TGA, DSC, X-ray diffraction, and FTIR and ¹³C NMR spectroscopies. It was found that the ICs have higher temperature stability than the pure CDs. The absence of a melting peak for the crystalline PCL blocks in the heating scan of triblock-CDs-ICs indicates that there is no free crystalline block copolymer. The X-ray powder diffraction patterns of triblock- α CD-IC and triblock- γ CD-IC were similar to that of valeric acid- α CD-IC and 1-propanol- γ CD-IC, which were confirmed to be a channel crystal structures by single crystal X-ray diffraction. In FTIR studies, new bands appeared at 1737 cm⁻¹ for triblock- α CD-IC and 1730 cm⁻¹ for triblock- γ CD-IC compared with the pure cyclodextrins, which confirms the formation of IC. CP/MAS/DD ¹³C NMR spectra of triblock-CDs-ICs indicate that CDs adopt a more symmetrical conformation in the triblock-CDs-ICs, while pure CDs assume a less symmetrical conformation in the crystal when they do not include a guest block copolymer inside their cavities. One pulse ¹³C NMR spectra were observed to confirm that crystalline triblock-CDs-ICs have channel structures, with CDs forming the crystal frame of the inclusion compound. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Inclusion compounds; Cyclodextrins; Channel structures

1. Introduction

The physical properties of all bulk polymer systems are determined by two distinct types of interactions: firstly, the inherent or intrinsic characteristics (conformations and mobility) of individual polymer chains, which depend solely on intramolecular or intrachain interactions. Secondly, the effect of cooperative interactions between polymer chains. Polymers in dilute solution at the θ temperature [1], where the chains are free from excluded volume and cooperative chain interactions, are often used to understand the properties of bulk amorphous polymers. However, we do not have a dilute solution analog to help understand the behavior of ordered polymer chains in liquid-crystalline and crystalline polymer samples. We believe that the study of crystalline inclusion compounds (ICs) provides a means to decouple these two factors so that the behavior of single chains can be

observed in isolated, well-defined environments. Certain small molecules, such as urea, perhydrotriphenylene and cyclodextrin (CD) are able to form crystalline ICs with polymers via a cocrystallization process. The guest polymer chains in the ICs are included in and confined to occupy narrow channels provided by the crystalline matrix formed by the small-molecule host. The study of the conformations and mobilities of isolated polymer chains can lead to an assessment of the inherent single-chain behavior of ordered, bulk polymer solids, while comparison with the behavior of bulk ordered polymers could provide some measure of the nature of cooperative, interchain interactions occurring in ordered solid polymers.

Cyclodextrins (CDs) are cyclic molecules consisting of six to eight glucose units joined by α -1,4-glycosidic linkages. The α -cyclodextrin (α -CD) and the γ -cyclodextrin (γ -CD) are composed of six and eight glucose units, respectively. Since the discovery of cyclodextrins, a large number of inclusion compounds of host CDs with various low molecular weight guest compounds have been prepared

* Corresponding author. Tel.: +1-919-515-6635; fax: +1-919-515-6532.

E-mail address: alan_tonelli@nesu.edu (A.E. Tonelli).

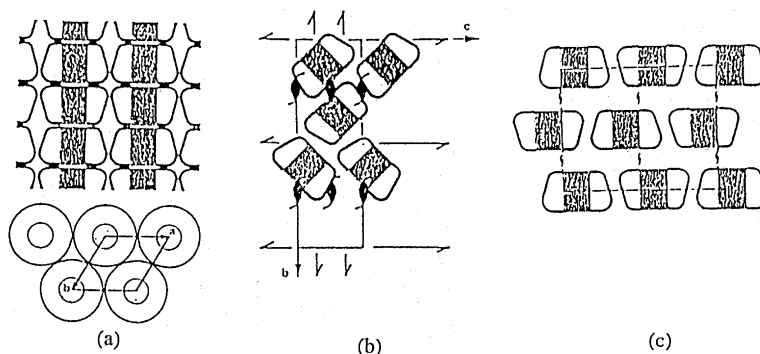


Fig. 1. Schematic description of: (a) channel type; (b) cage herringbone type; and (c) cage brick type, crystal structures formed by crystalline cyclodextrin inclusion complexes.

and characterized [2,3]. However, not until 1990, did Harada et al. [4] first observe that cyclodextrin forms crystalline inclusion complexes with polymers. Since then, many papers have reported the formation of CDs with different kinds of polymers, such as hydrophilic polymers poly(ethylene glycol) [4,5], poly(propyleneglycol) [6], and hydrophobic polymers polyisobutylene [7], poly(ϵ -caprolactone) [8,9]. However, there are few reports on the inclusion compounds formed between cyclodextrins and block copolymers [10–12].

The inclusion compounds formed between CDs and low molecular weight guests can either have channel or cage structures. Fig. 1 shows the schematic descriptions of channel type, cage herringbone type and cage brick type crystal structures of crystalline CD inclusion complexes [13]. The average diameters of cyclodextrin “doughnut-shape” cavities are 4.7–5.3 Å for α -CD, and 7.5–8.3 Å for γ -CD, respectively. The height of the CD torus is 7.9 Å for both [14]. In channel structure ICs, the cyclodextrin rings are stacked on top of each other to produce cylindrical central cavities; in cage structures, the cavity of one CD molecule is closed on both sides by adjacent molecules. Due to the long chain nature of polymers, normally the crystal structure of polymer-CD-IC is channel type, which provides the possibility to study the behavior of single chains squeezed inside the CD channels. Mole ratios of host cyclodextrin to guest polymer depend on the length of the polymer’s repeat unit and the number of chains which can occupy the CD channels.

Harada et al. [5] reported that α -CD can form inclusion compounds with poly(ethylene glycol)(PEG) of various low molecular weights (from 400 to 10^4), to give stoichiometric compounds in a crystalline state. The rate of the complex formation depends on the molecular weight of PEG. PEG of molecular weight 1000 form complexes most rapidly. The stoichiometry of the complex is 2:1 (two ethylene glycol units to one α -CD). The high molecular weight polyethylene oxides (PEO) were also found to form a channel type crystalline IC with α -CD [8]. Harada et al. [15] also reported the formation of γ -CD-ICs with PEG derivatives. It is interesting that four ethylene glycol units were found to

be included in a single γ -CD cavity, which suggest that γ -CD cavities include two chains of PEG. Poly(ϵ -caprolactone) (PCL) can also form inclusion compounds with α -CD [8,9] and γ -CD [16] to give channel type crystalline compounds. The PCL- α CD-IC are stoichiometric one-to-one(cyclodextrin:monomer unit) compounds. So we expected that PCL-PEO-PCL triblock copolymer can form channel type structure with both α -CD and γ -CD.

Earlier our group [17] reported the formation of the crystalline inclusion compound between PCL-PEO-PCL triblock copolymer and urea. Although both PEO and PCL homopolymers can form U-ICs, only the PCL blocks are found to be included in the triblock-U-IC crystals. A motional study of the triblock copolymer chains in their U-ICs was also conducted and compared with similar observations made on the bulk and constituent homopolymer-U-IC samples. It will be interesting to observe the crystal structure of triblock-CD-ICs and thus compare the molecular motion of block copolymer chains in different IC environments.

In this paper, we describe the preparation of PCL-PEO-PCL- α CD-IC and PCL-PEO-PCL- γ CD-IC via a heating technique. The complex structures were characterized by TGA, DSC, wide angle X-ray diffraction, FTIR and ^{13}C NMR spectroscopies. Both triblock- α CD-IC and triblock- γ CD-IC were found to have channel type crystalline structures.

2. Experimental

2.1. Materials

PCL-PEO-PCL triblock copolymer with $M_w = 14140$ is characterized by PCL, PEO block lengths of 35, 140 repeat units [17]. Cyclodextrins were obtained from Cerestar Company and used after drying in a vacuum at 60°C for 24 h. The PCL-PEO-PCL-CDs-ICs were formed by adding a 50 ml solution of 0.25 g of triblock copolymer in acetone to 50 ml aqueous solution saturated with CDs(7.25 g α CD, 11.6 g γ CD). The PCL-PEO-PCL solution was

gradually added to the CD solutions while continuously warming at 60°C and stirring for 3 h, then cooling to room temperature, and finally stirring was discontinued. A white precipitate was obtained overnight and was filtered and dried.

2.2. Thermal property analysis

Thermal characteristics of samples were determined with a Perkin–Elmer Model 7 differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). Samples of 3–7 mg were used in both tests. A heating rate of 10°C/min was employed, and the temperature range was from 0 to 250°C for DSC and 25 to 400°C for TGA. Both instruments used nitrogen as the purge gas.

2.3. FTIR spectroscopy

Absorbance spectra were recorded on powdered samples pressed into KBr pellets on a Nicolet 510P FTIR spectrometer at the frequencies from 4000 to 400 cm⁻¹, under the following conditions: resolution = 2 cm⁻¹, gain = 1, scans = 32. Owing to the hygroscopic nature of KBr, the sample cell was purged with dry air.

2.4. Wide angle X-ray diffraction

X-ray diffraction was recorded on powdered samples in a wide-angle set-up using a Siemens type-F X-ray diffractometer. The radiation source used was Ni-filtered, CuK α radiation with a wavelength of 1.54 Å. The voltage was set to 30 kV and the current was set to 20 mA. Samples were mounted on a circular sample holder with scotch tape, and the proportional counter detector collected data at a rate of $2\theta = 5^\circ \text{ min}^{-1}$ over the range $2\theta = 5\text{--}40^\circ$.

2.5. NMR spectroscopy

High resolution solid state NMR spectra were recorded using a Chemagnetics 200S spectrometer at 50.1 MHz, under cross-polarization (CP), magic-angle spinning (MAS) and high-power ¹H dipolar decoupling (DD). The optimum Hartmann-Hahn and magic angle conditions were calibrated using *p*-di-tert-butylbenzene (PDTBB, 31.0 ppm versus tetramethylsilane (TMS)). Zirconia rotors were used and the sample spinning speed ranged from 3.5 to 4.1 kHz. High power dipolar decoupling (DD) was applied at about 47 kHz during acquisition. The spectral width was 15 kHz stored in 2K memory that was zero filled to 8K before Fourier transformation.

3. Results and discussion

3.1. Thermal property analysis

The TGA thermograms of pure α -cyclodextrin and

PCL-PEO-PCL- α CD-IC recorded at a heating rate of 10°C/min between 25 and 400°C are presented in Fig. 2. They show that the inclusion compound started to decompose at 328°C, which is higher than the decomposition temperature of pure α -CD (298°C). This may imply that the copolymer chains included inside the α -cyclodextrin channels can improve α -cyclodextrin thermal stability. Fig. 3 presents the TGA thermograms of pure γ -CD and PCL-PEO-PCL- γ CD-IC. The triblock- γ CD-IC sample started to decompose at a temperature similar to γ -CD, which indicates that there is some free γ -CD, then showed a higher decomposition temperature. This may also indicate that the copolymer chains included inside the γ -CD can improve the γ -CD thermal stability. This phenomenon is similar to the observation of homopolymer-CD-ICs [8].

Since cyclodextrins and their ICs will decompose while melting, we only tested them below their melting temperatures in DSC. Fig. 4 presents the DSC thermograms for pure bulk PCL-PEO-PCL triblock copolymer from 0 to 250°C. In the first heating scan an endothermic peak appears at about 67°C, corresponding to the melt of the crystalline block. As discussed below, X-ray diffraction indicates no bulk crystalline PEO in the bulk copolymer sample, so we attribute the endotherm at 67°C to the melting of bulk crystalline PCL block. After quenching to 0°C at 100°C/min and holding at 0°C for 1 min, two poorly resolved peaks at melting temperature 55.4 and 59.14°C are observed, which may be attributed to the melting of PCL blocks in different crystal sizes. As is seen from Figs. 5 and 6, the DSC thermograms of triblock- α CD-IC and triblock- γ CD-IC contain no peaks corresponding to the melting of PCL blocks. This fact indicates that there is no free bulk triblock copolymer in the triblock-CDs-ICs samples. Since the pure PCL and PEO homopolymer can form inclusion compounds with α -CD and γ -CD, we expect the entire triblock copolymer to be included in the channels of the host cyclodextrin lattice. The single sharp peak for PCL-PEO-PCL- α CD-IC and a broad peak for PCL-PEO-PCL- γ CD-IC in the region from 140 to 200°C, which appear in the first heating scan and disappear in the second heating scan, maybe due to the dehydration of the complexes [12].

3.2. X-ray diffraction

The X-ray diffractograms of α -cyclodextrin, bulk PCL-PEO-PCL, and PCL-PEO-PCL- α CD-IC are presented in Fig. 7, where their comparison clearly reveals that our sample of PCL-PEO-PCL- α CD-IC is not simply a mixture of free cyclodextrin and free triblock copolymer, but that a crystalline IC has been formed between the two. Major peaks at 10.2, 12.8, 14.7, 20.4 and 22.5° were observed for pure α -cyclodextrin. The only diffraction peaks attributable to crystalline PCL blocks [18] at 21.6 and 23.8° are evident in the bulk triblock copolymer, so the PEO blocks apparently do not crystallize in the bulk

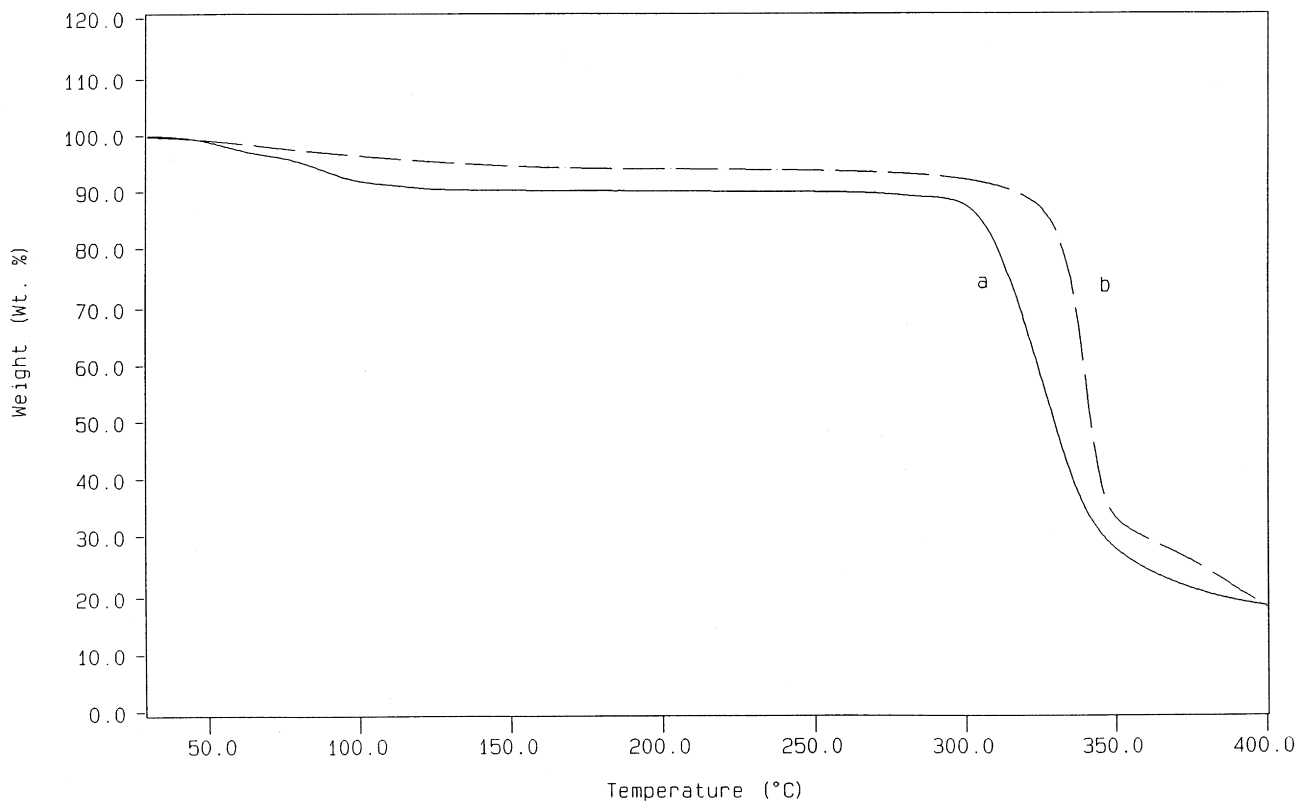


Fig. 2. TGA scans observed for: (a) α -cyclodextrin; and (b) PCL-PEO-PCL- α -CD-IC, at a heating rate of 10°C.

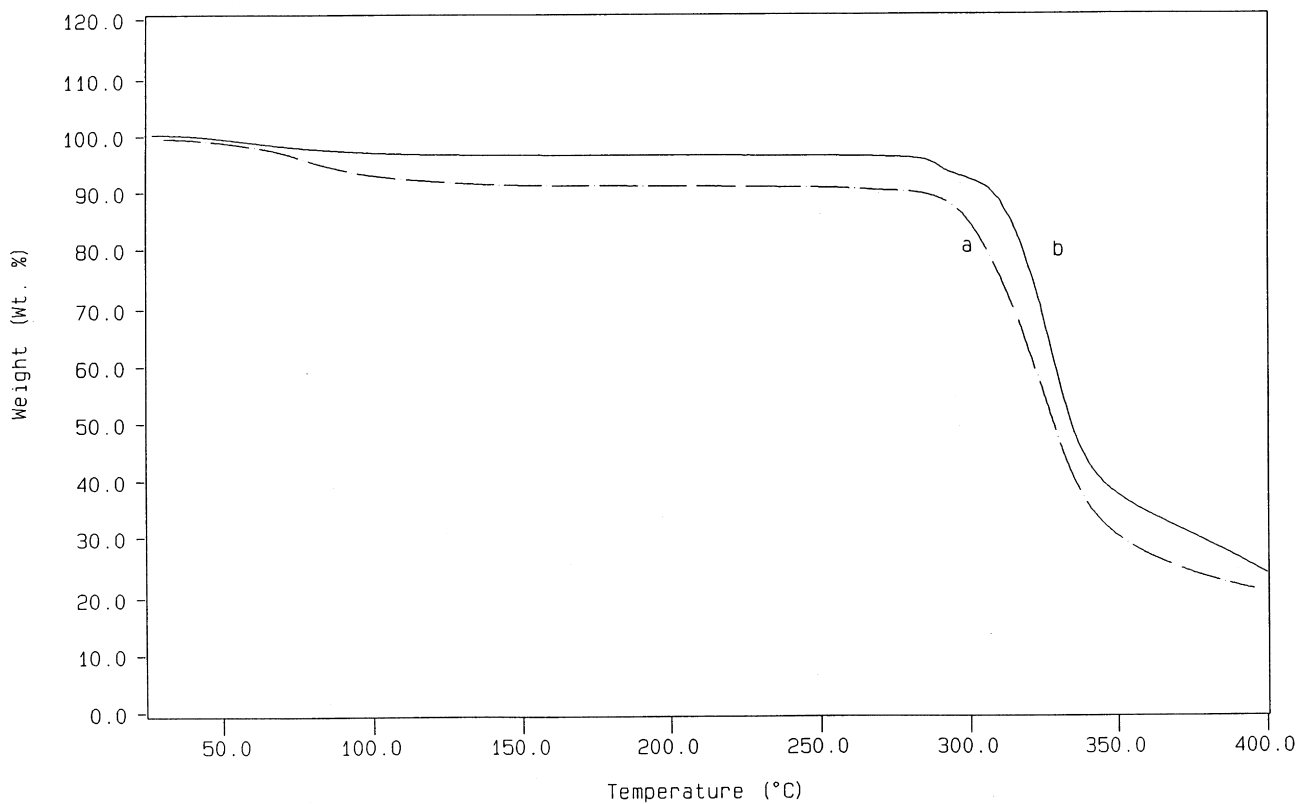


Fig. 3. TGA scans observed for: (a) γ -cyclodextrin; and (b) PCL-PEO-PCL- γ -CD-IC, at a heating rate of 10°C.

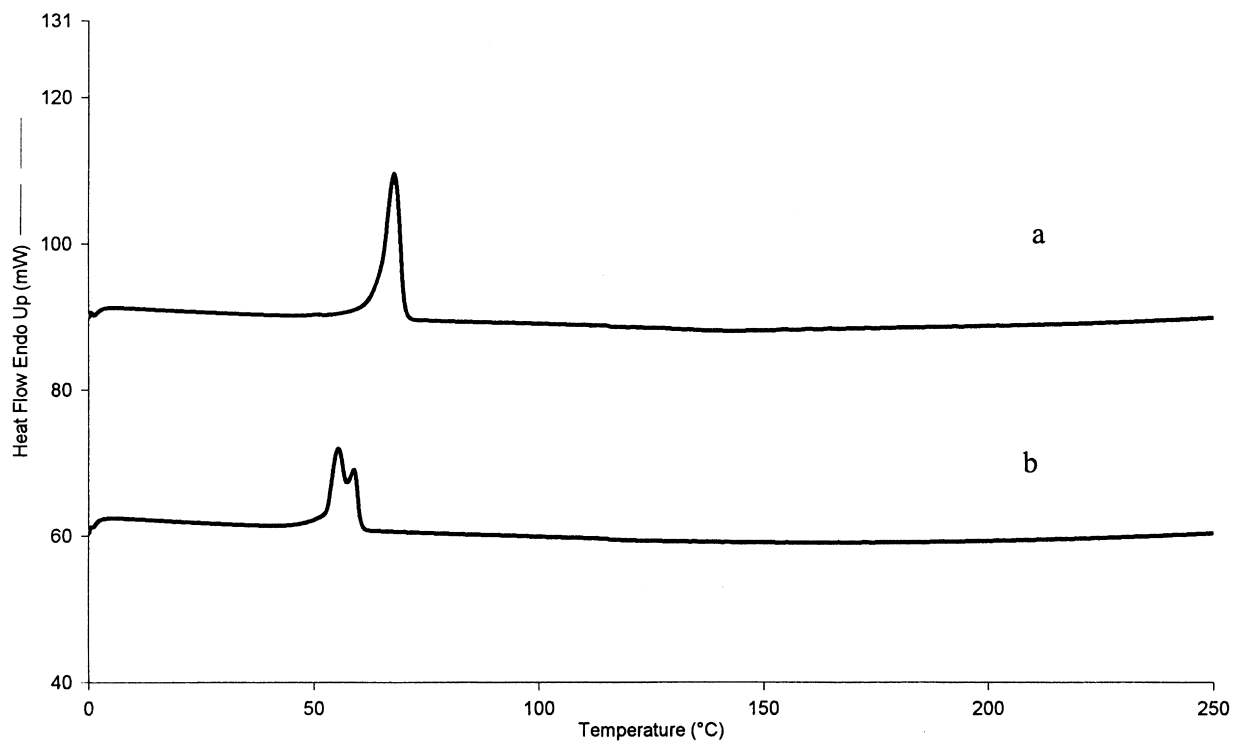


Fig. 4. DSC scans observed for PCL-PEO-PCL during the first (a), and second (b), heating at a rate of 10°C.

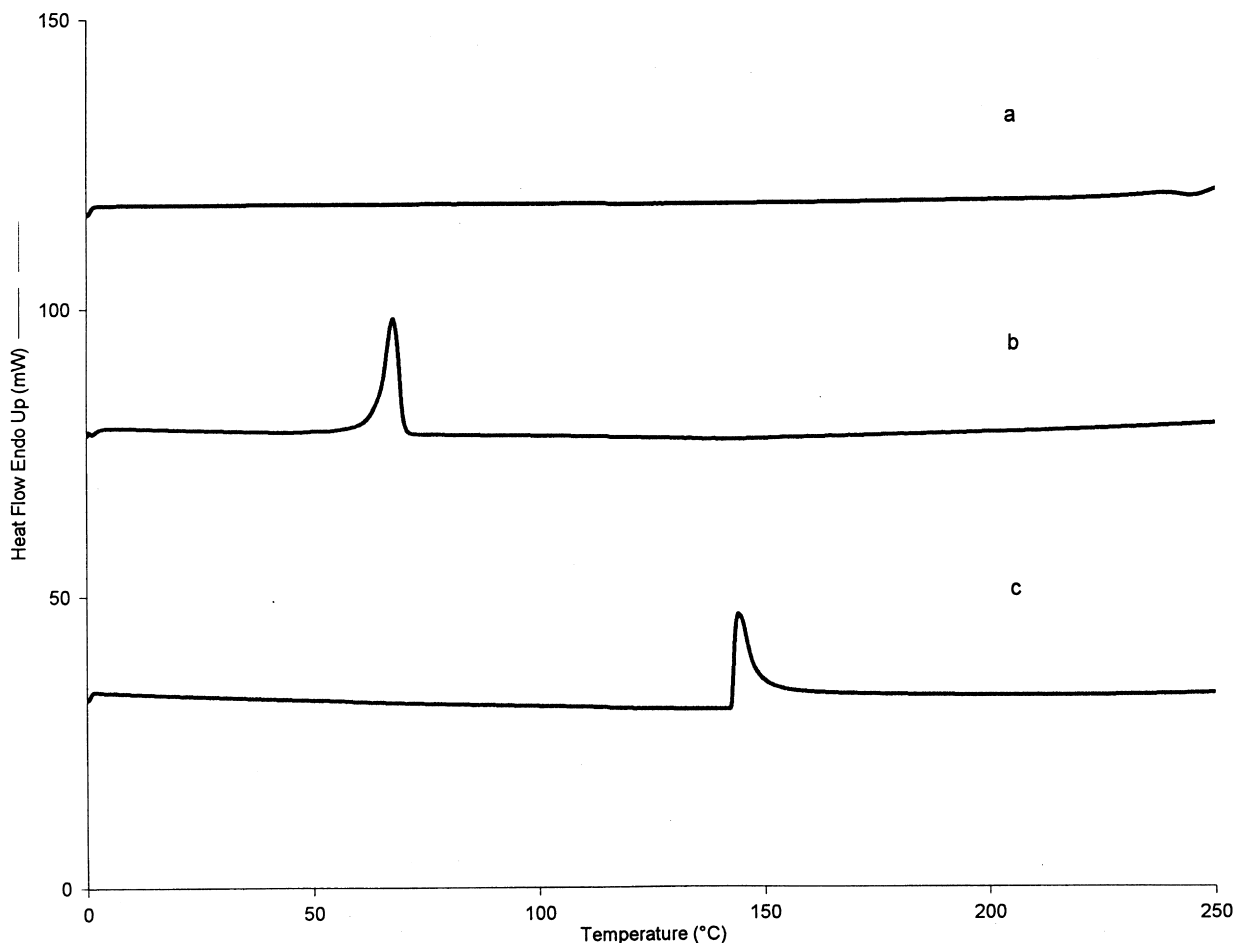


Fig. 5. DSC scans observed for: (a) α -cyclodextrin; (b) PCL-PEO-PCL; and (c) PCL-PEO-PCL- α CD-IC, at a heating rate of 10°C.

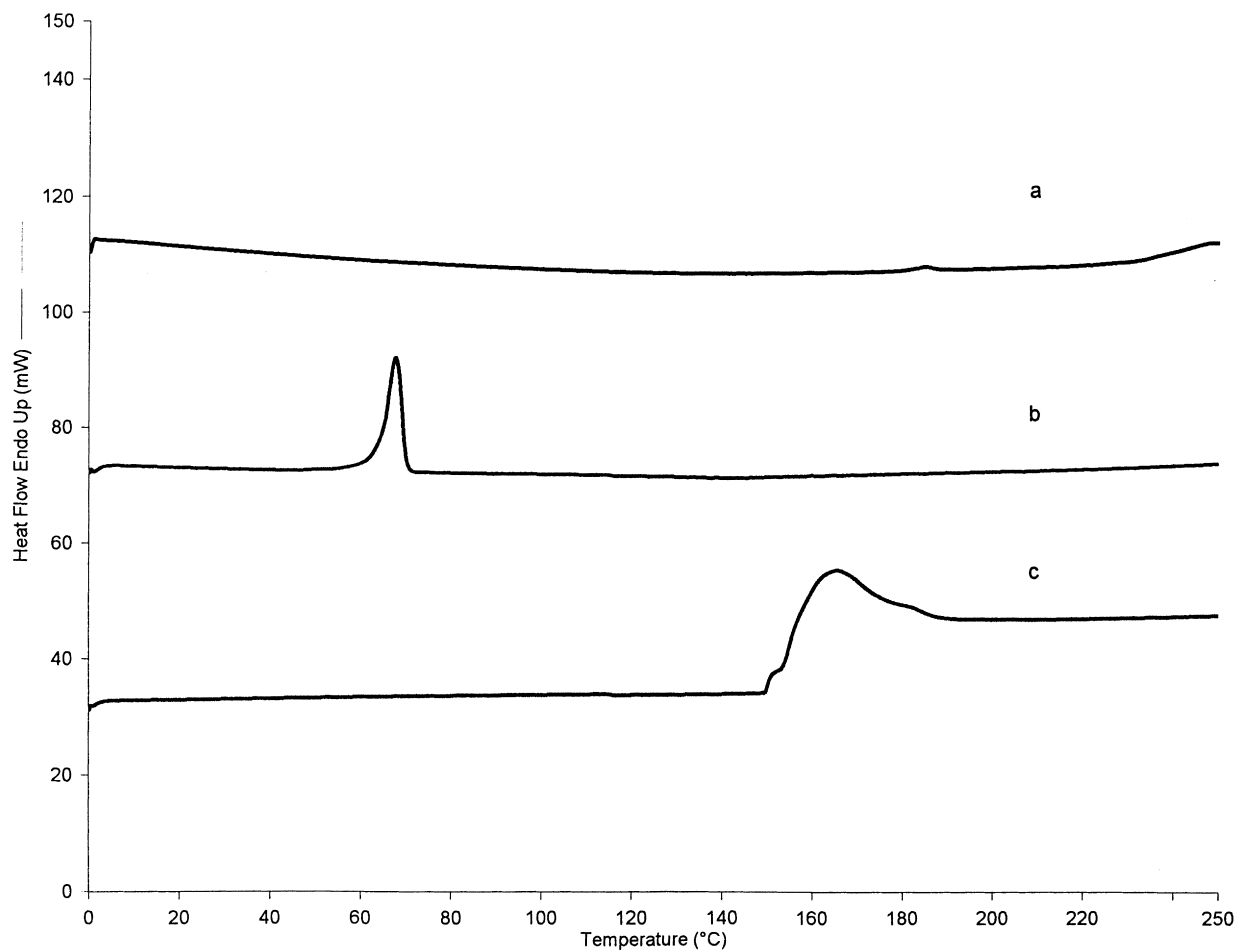


Fig. 6. DSC scans observed for: (a) γ -cyclodextrin; (b) PCL-PEO-PCL; and (c) PCL-PEO-PCL- γ -CD-IC, at a heating rate of 10°C.

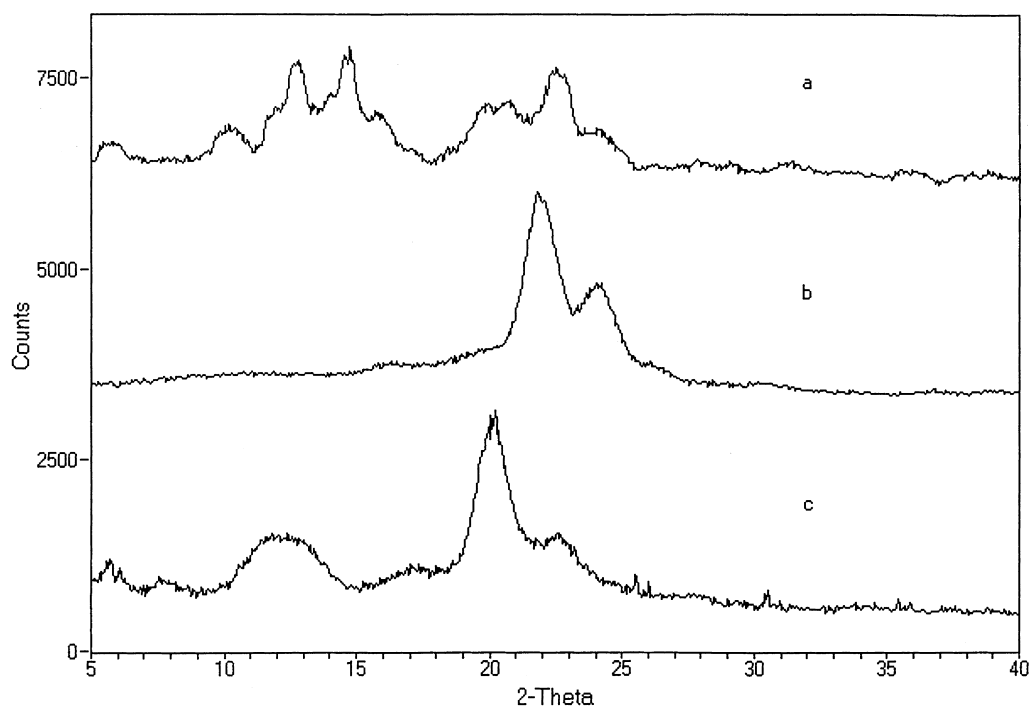


Fig. 7. X-ray diffractograms of: (a) α -cyclodextrin; (b) PCL-PEO-PCL; and (c) PCL-PEO-PCL- α -CD-IC.

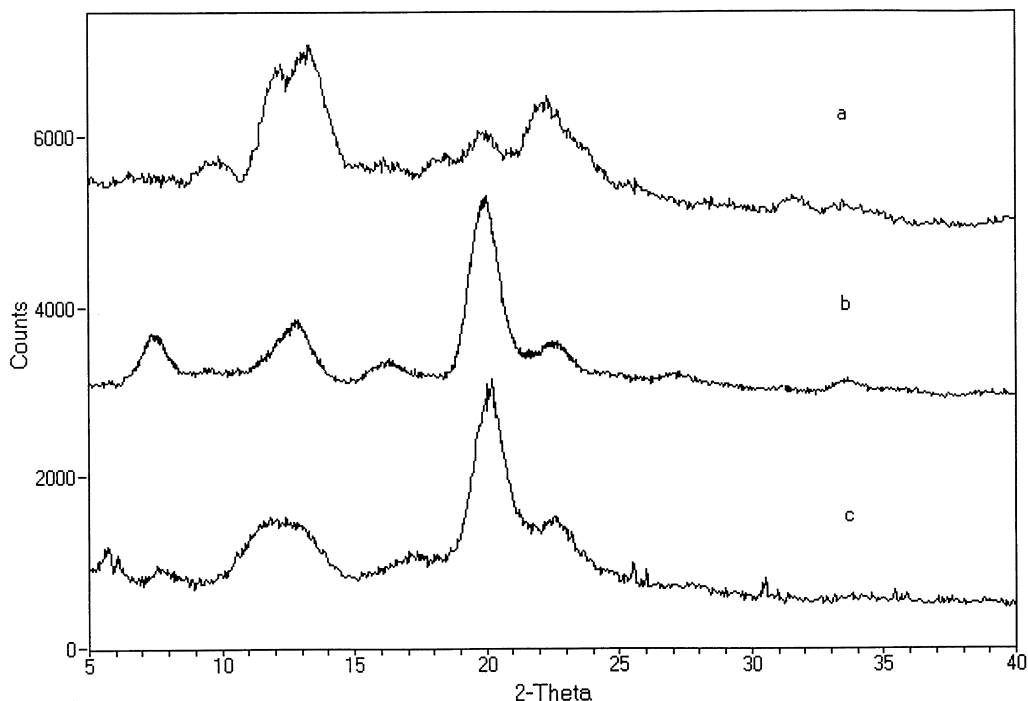


Fig. 8. X-ray diffractograms of: (a) propionic acid- α CD-IC; (b) valeric acid- α CD-IC; and (c) PCL-PEO-PCL- α CD-IC.

triblock copolymer samples. The strong peak at about 20° for PCL-PEO-PCL- α CD-IC may indicate that at least one block of the triblock copolymer is included inside the α -cyclodextrin channels. By comparing the triblock- α CD-IC with the X-ray diffractograms of propionic acid- α CD-IC and valeric acid- α CD-IC (see Fig. 8), we can observe that

the X-ray pattern of triblock- α CD-IC is similar to that of the IC between valeric acid and α -CD, which has been reported to have a channel type structure [19], and is different from that of the IC between propionic acid and α -CD, which has been reported to have a cage type structure [20]. This gives strong evidence that triblock- α CD-IC has a channel

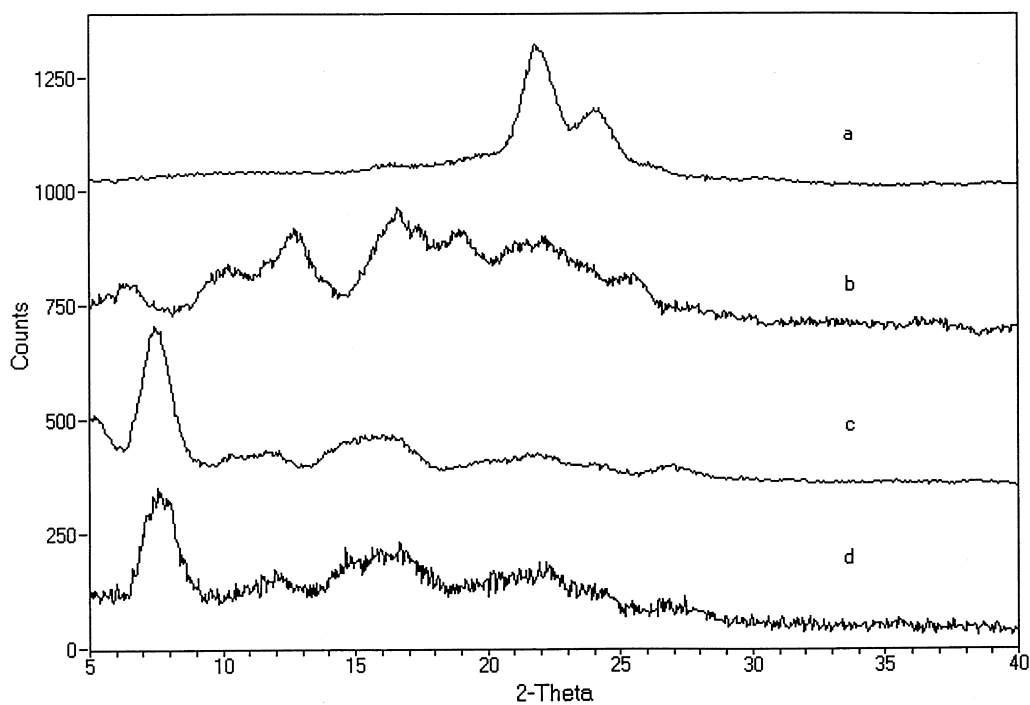


Fig. 9. X-ray diffractograms of: (a) PCL-PEO-PCL; (b) γ -cyclodextrin; (c) 1-propanol- γ CD-IC; and (d) PCL-PEO-PCL- γ CD-IC.

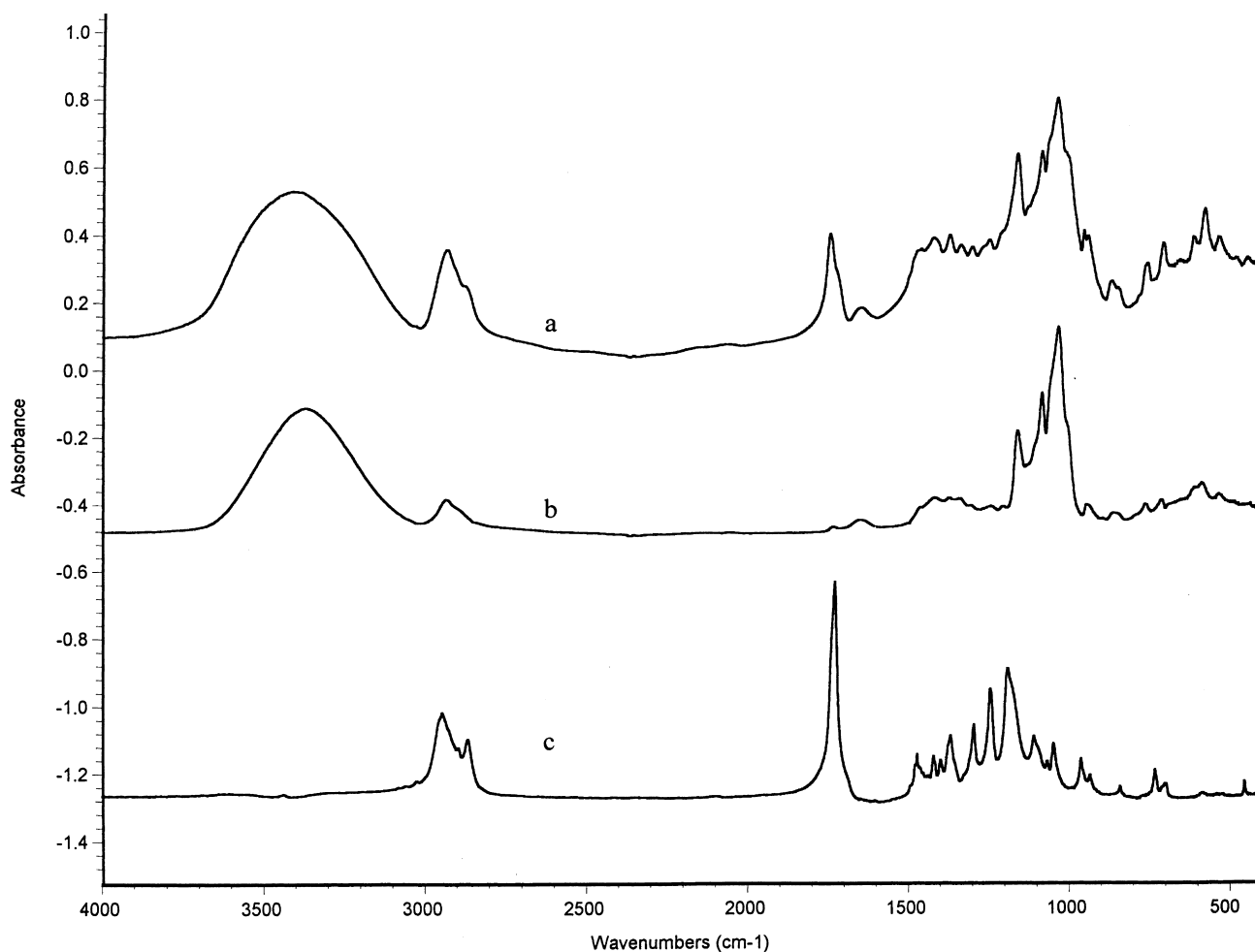


Fig. 10. FTIR spectra of: (a) PCL-PEO-PCL- α CD-IC; (b) α -cyclodextrin; (c) PCL-PEO-PCL.

structure. More interesting is that all the X-ray diffraction patterns of PCL-PEO-PCL- α CD-IC, PCL- α CD-IC and PEO- α CD-IC are similar with strong peaks at about $2\theta = 20^\circ$ [8]. Since both PCL- α CD-IC and PEO- α CD-IC have the channel structure, we expect that both the PCL and PEO blocks of the triblock copolymer are included inside the α -CD channel.

Fig. 9 presents the X-ray diffractograms of bulk PCL-PEO-PCL copolymer, γ -cyclodextrin, 1-propanol- γ CD-IC and PCL-PEO-PCL- γ CD-IC. The diffractogram of triblock- γ CD-IC shows quite a different pattern from bulk triblock copolymer and γ -CD, which provides the primary evidence that a different crystal type was formed. However, it shows a pattern similar to the complex between 1-propanol and γ -CD, which has been proved to have a channel structure by the X-ray study of a single crystal of this inclusion compound [21]. The characteristic peak at about 7.6°C can be observed for the IC of γ -CD with triblock copolymer and with 1-propanol, although the pure γ -CD does not show this peak. These results indicate that in the PCL-PEO-PCL- γ CD-IC, the CD exhibits a different packing form from that in free γ -CD, which has the cage type structure,

and instead has the channel structure as in the 1-propanol- γ CD-IC.

3.3. FTIR spectroscopy

The FTIR spectra of PCL-PEO-PCL- α CD-IC, α -CD and PCL-PEO-PCL in the region from 400 to 4000 cm^{-1} are presented in the Fig. 10. The peak between 3000 and 4000 cm^{-1} is normally assigned to symmetric and antisymmetric O-H stretching modes. The position of this band for pure α -CD is 3371 cm^{-1} , and is shifted to higher frequency 3410 cm^{-1} when it forms the IC with triblock copolymer. This shift maybe due to association of the CD O-H groups with the included polymer chain. The bands observed in the region $2700\text{--}3000\text{ cm}^{-1}$ for triblock- α CD-IC and pure α -CD are different. Since there is overlap between the absorbance of the C-H stretching mode of pure α -CD (at 2931 cm^{-1}) and that of the triblock copolymer (multiple peak at about 2945 cm^{-1} with a sharp shoulder at 2866), the new bands appearing at about 2925 cm^{-1} with a shoulder at 2868 cm^{-1} can be confirmed in the difference spectrum (see Fig. 11), and are most probably attributed to

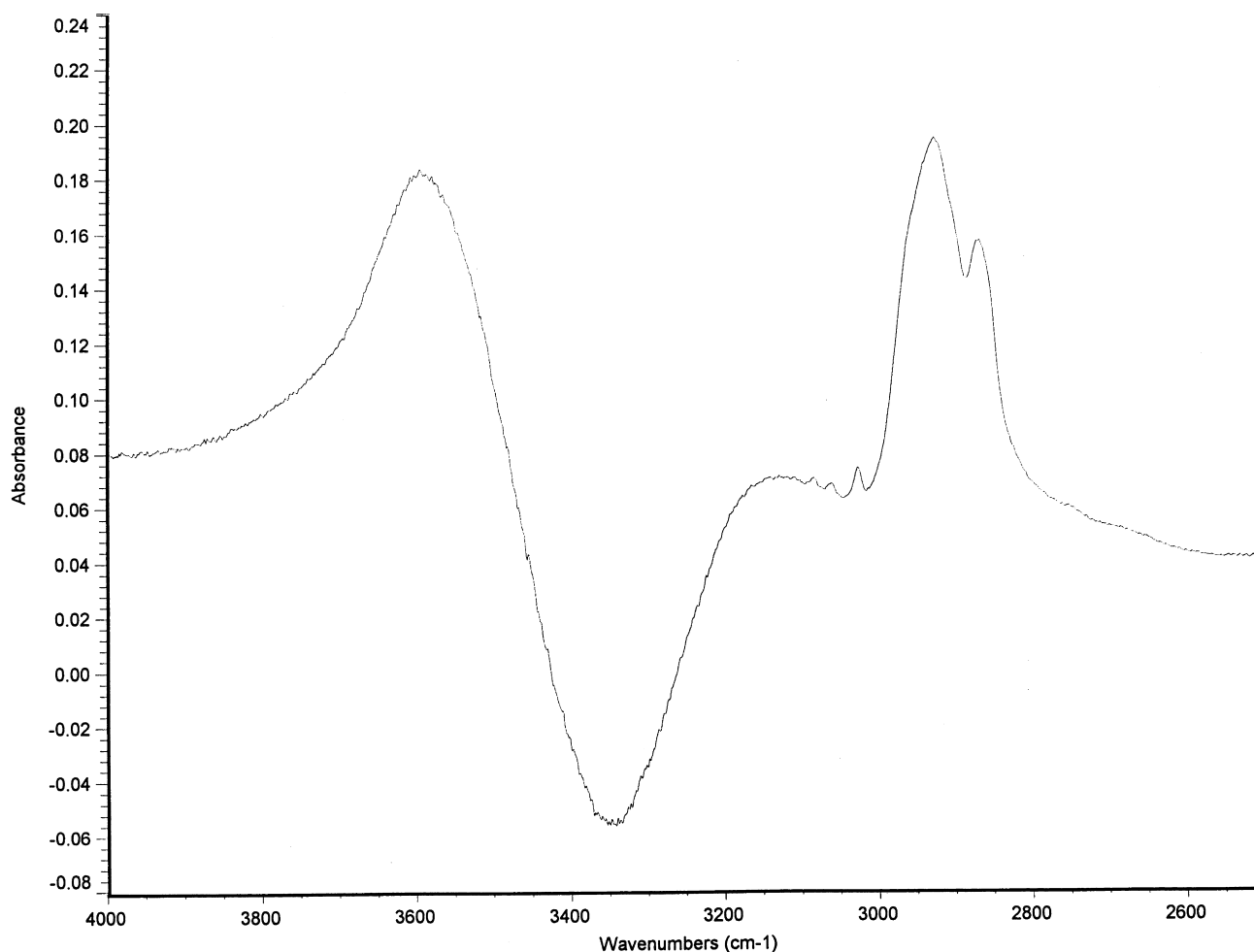


Fig. 11. FTIR spectrum difference between Fig. 10(a) and (b).

included triblock copolymer chains in the IC sample. A new band appeared at 1737 cm^{-1} in the IC spectrum, which was absent from the α -CD spectrum, and may be assigned to the C=O stretching band for the PCL block included inside the α -CD channel. Changes in the relative intensity of multiple peaks in the region $1500\text{--}1200\text{ cm}^{-1}$ can be observed in the triblock- α CD-IC, compared with α -CD. These bands are assigned to C-H, CH₂ and O-H bending modes.

Fig. 12 shows the FTIR spectra of PCL-PEO-PCL- γ CD-IC, γ -CD and PCL-PEO-PCL samples. Comparing the spectra of triblock- γ CD-IC and γ -CD, we obtain observation similar to the triblock- α CD-IC: The center for O-H stretching modes shifted to higher frequency. A new band appeared at 2927 cm^{-1} with a shoulder at 2850 cm^{-1} , which is different from γ -CD. An obvious new band at 1730 cm^{-1} due to C=O can also be observed.

3.4. NMR spectroscopy

The CP/MAS/DD ^{13}C NMR spectra of PCL-PEO-PCL- α CD-IC, α -CD and PCL-PEO-PCL are presented in Fig. 13. The α -CD assumes a less symmetrical conformation in

the crystal when it does not include a guest in the cavity [22], so the spectrum shows multiple resonances for each carbon type of α -CD. However, in the spectrum of the triblock- α CD-IC, each glucose carbon can be observed as a single peak. This indicates that α -CD adopts a symmetrical conformation and each glucose unit of α -CD is in a similar environment. The X-ray studies of single crystals showed that α -CD adopts a less symmetrical conformation when it does not include guests in the cavity and adopts a symmetrical conformation when it includes guests in the cavities [19–20]. Thus our CP/MAS/DD spectra of the pure α -CD and triblock- α CD-IC are consistent with the results by X-ray. The principal resonances due to the triblock copolymer in the channels can be identified by comparison to the spectrum of pure triblock copolymer. Therefore, combined with the X-ray, FTIR and DSC results, the triblock copolymer chains are thought to be included inside the channels of α -CD.

Fig. 14(b) shows the one pulse ^{13}C NMR spectra which gives stronger signals to the relatively mobile carbons of the sample than does CP/MAS/DD ^{13}C NMR. The relative intensities of the peaks of PCL-PEO-PCL to those of

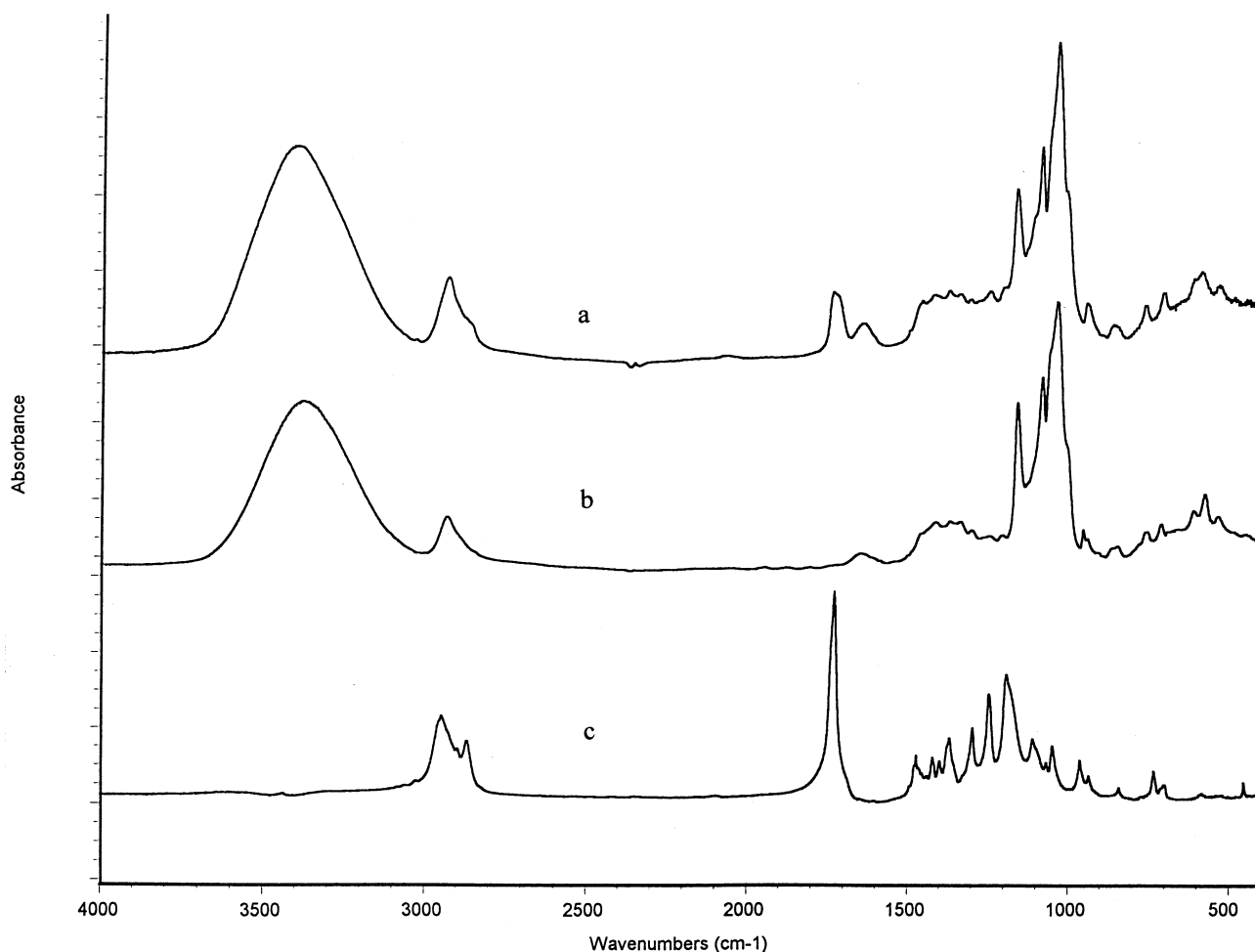


Fig. 12. FTIR spectra of: (a) PCL-PEO-PCL- γ CD-IC; (b) γ -cyclodextrin; (c) PCL-PEO-PCL.

α -CD are much stronger in Fig. 14(b) than those in Fig. 14(a), indicating that the triblock copolymer chains are not so rigid as α -CD in the IC. This is consistent with the view that crystalline triblock- α CD-IC has a channel structure, with α -CD forming the crystal frame of the inclusion compound.

The carbonyl carbon shows multiple resonances in the CP/MAS/DD spectrum, and three of its methylene carbons also show multiple resonances, which can be seen more clearly in the one pulse experiment. Multiple resonances can be attributed to more than a single conformational or packing environment. Our molecular modeling [23] of polyesters suggested that the most stable *trans* conformer accounts for at least 40% of all channel conformers found for PCL. The remaining conformers found to fit in the channel were identified as the kink ($g^{\pm}tg^{\pm}$) type. It was also shown that there was no conformational interconversion possible in the channel. Therefore the higher energy kink conformations are not expected to be present in the channel, because of the increased entropy attendant with the presence of rapidly interconverting channel conformers is not realized. So it is assumed that only the all-*trans* conformation resides in the narrow channel. Therefore we attribute

the multiple resonances observed for carbonyl and methylene carbons of PCL in the channel to distinct crystalline packing environments.

Fig. 15 presents the CP/MAS/DD ^{13}C NMR spectra of PCL-PEO-PCL- γ CD-IC, γ -CD and PCL-PEO-PCL. Comparing with the resolved peaks of each carbon type of the γ -CD, the triblock- γ CD-IC shows single peaks for each glucose carbon, which confirm the channel structure of the IC. The principal resonances due to the triblock copolymer in the channels can be identified by comparison to the spectrum of pure triblock copolymer, which can be seen more clearly in the one pulse experiment (see Fig. 16(a)). Therefore, triblock copolymer chain is thought to be included inside the channels formed by orderly stacked γ -CD molecules. There is no splitting of resonances corresponding to the carbonyl and methylene peaks of the PCL block, which indicates that all the triblock chains have similar crystalline packing environments.

In summary, we have confirmed that PCL-PEO-PCL- α CD-IC and PCL-PEO-PCL- γ CD-IC were formed via a heating technique. Both of them have much different crystal structures and thermal behavior compared to their bulk

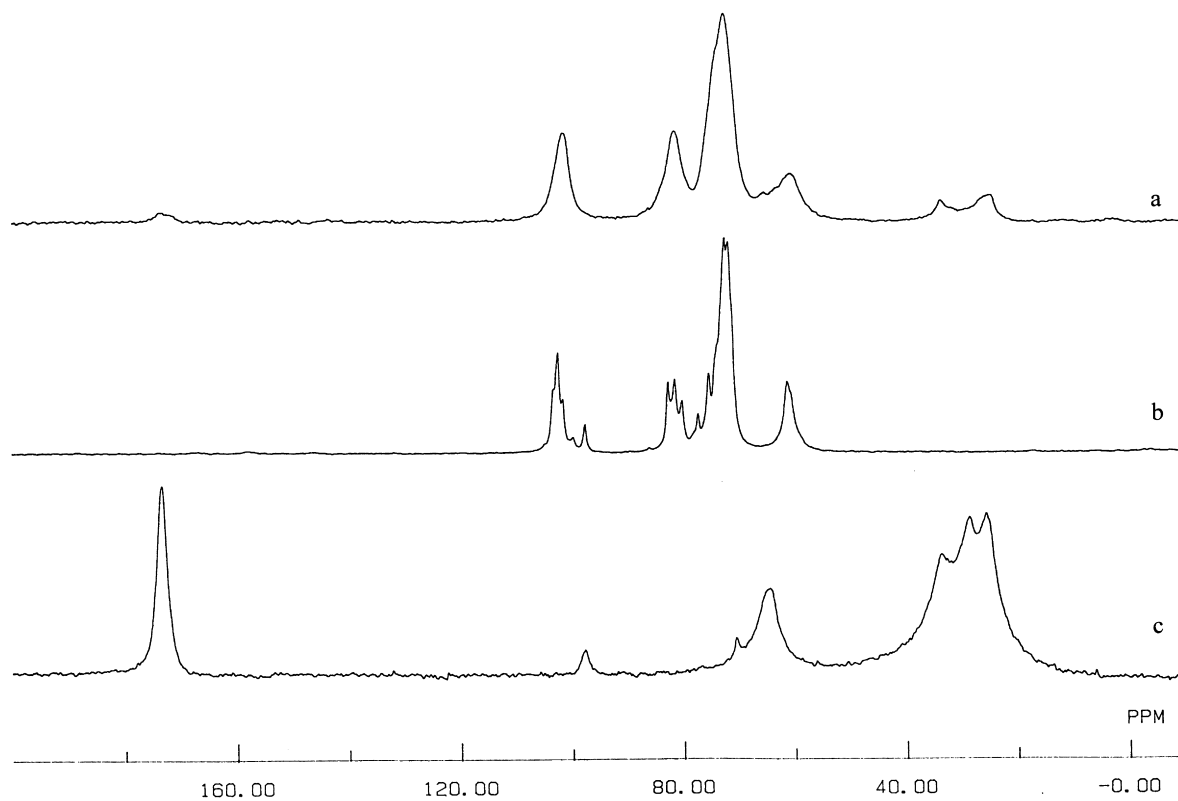


Fig. 13. CP/MAS/DD ^{13}C NMR spectra of: (a) PCL-PEO-PCL- α CD-IC; (b) α -cyclodextrin; (c) PCL-PEO-PCL.

polymers. They are confirmed to have IC channel structures by DSC, FTIR, X-ray and solid state ^{13}C NMR. Further study on their detailed complex structures, stoichiometries and molecular motions of the triblock copolymer included inside the channels are underway.

Acknowledgements

We are grateful to the Army Research Office (MURI#-DAAH04-96-1-0018-01) and North Carolina State University for supporting this work.

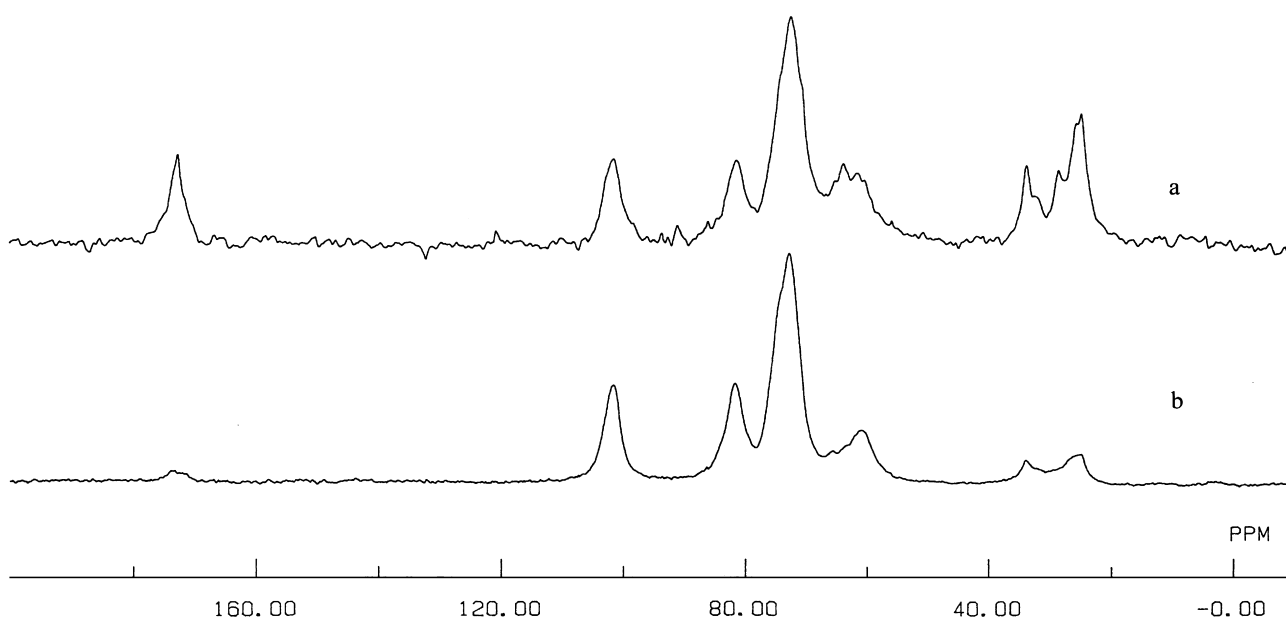


Fig. 14. ^{13}C NMR MAS/DD: (a) single pulse; and (b) cross-polarization, of PCL-PEO-PCL- α CD-IC.

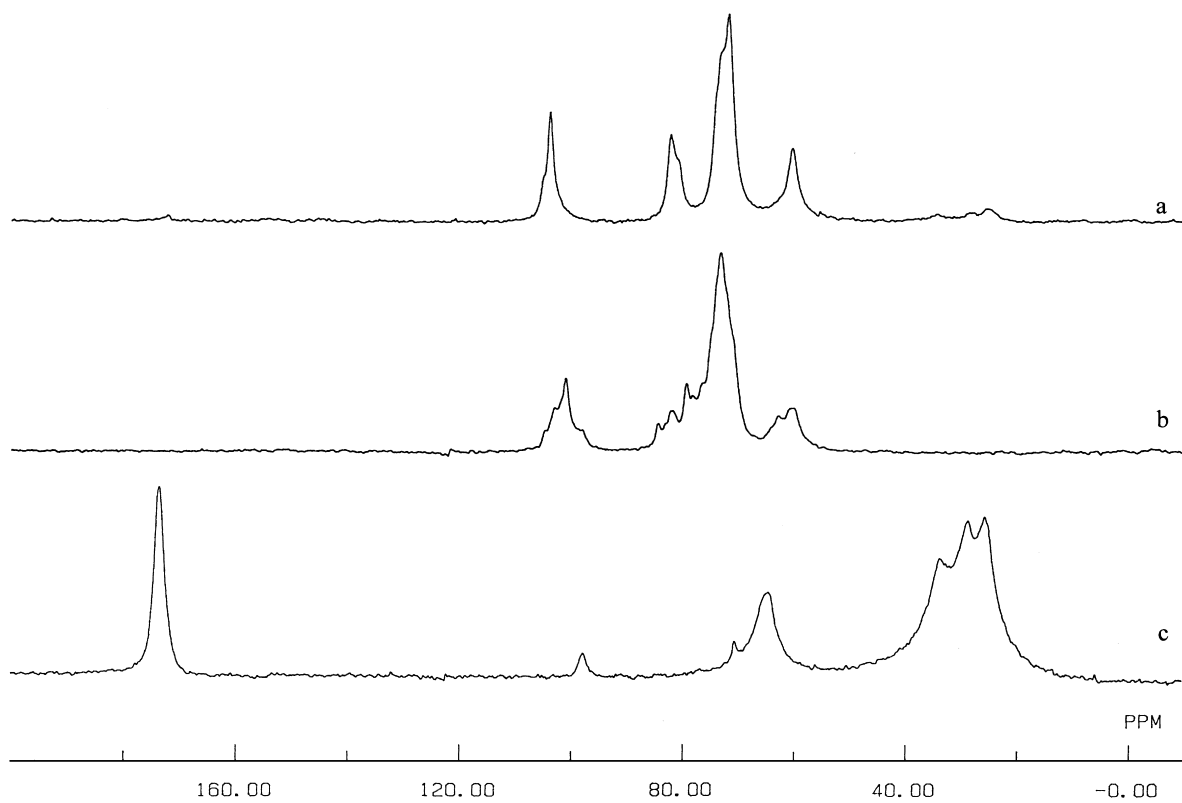


Fig. 15. CP/MAS/DD ^{13}C NMR spectra of: (a) PCL-PEO-PCL- γ CD-IC; (b) γ -cyclodextrin; (c) PCL-PEO-PCL.

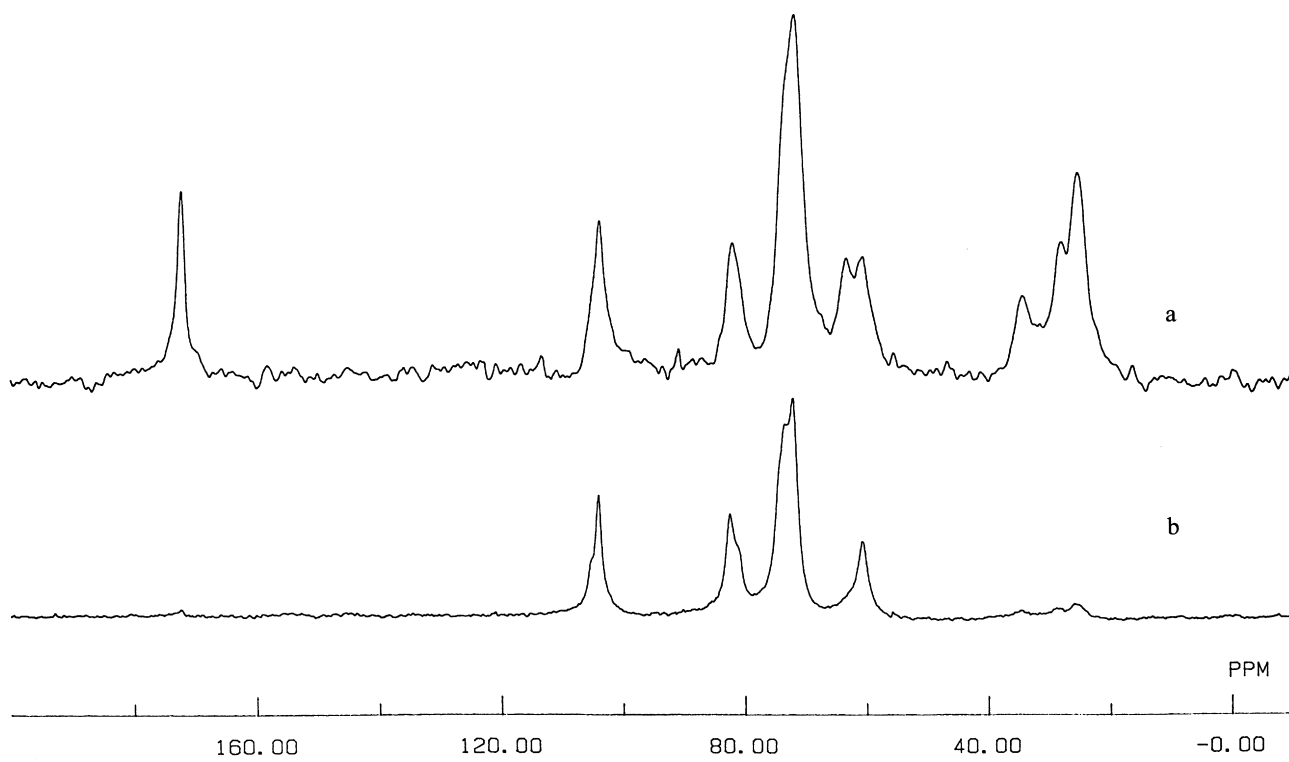


Fig. 16. ^{13}C NMR MAS/DD: (a) single pulse; and (b) cross-polarization, of PCL-PEO-PCL- γ CD-IC.

References

- [1] Flory PJ. Principles of polymer chemistry, Ithaca, NY: Cornell University Press, 1953.
- [2] Bender ML, Komiyama M. Cyclodextrin chemistry, Berlin: Springer, 1978.
- [3] Szejtli J. Cyclodextrins and their inclusion complexes, Budapest, Hungary: Akademiai Kiado, 1982.
- [4] Harada A, Kamachi M. *Macromolecules* 1990;23:2821.
- [5] Harada A, Li J, Kamachi M. *Macromolecules* 1993;26:5698.
- [6] Harada A, Okada M, Li J, Kamachi M. *Macromolecules* 1995;28:8406.
- [7] Harada A, Suzuki S, Okada M, Kamachi M. *Macromolecules* 1996;29:5611.
- [8] Huang L, Allen E, Tonelli AE. *Polymer* 1998;39:4857.
- [9] Harada A, Kawaguchi Y, Nishiyama T, Kamachi M. *Macromolecules: Rapid Communication* 1997;18:535.
- [10] Topchieva IN, Blyumenfel'd AL, Klyamkin AA, Polyakov VA, Kabanov VA. *Polymer Science* 1994;36:221.
- [11] Panova IG, Gerasimov VI, Grokhovskaya TE, Topchieva IN. *Doklady Chemistry* 1996;347:58.
- [12] Panova IG, Gerasimov VI, Tashlitskii VN, Topchieva IN, Kabanov VA. *Polymer Science A* 1997;39:452.
- [13] Saenger W. In: Attwood J, Davies J, MacNicol D, editors. *Inclusion Compounds*, 2. London: Academic Press, 1984 chap. 8.
- [14] Szejtli J. *Cyclodextrin technology*, Dordrecht: Kluwer Academic, 1998 p. 450.
- [15] Harada A, Li J, Kamachi M. *Nature* 1994;370:126.
- [16] Lu J, Tonelli AE. In preparation.
- [17] Vasanthan N, Shin ID, Huang L, Nojima S, Tonelli AE. *Macromolecules* 1997;30:3014.
- [18] Choi C, Davis DD, Tonelli AE. *Macromolecules* 1993;26:1468.
- [19] McMullan RK, Saenger W, Fayos J, Mootz D. *Carbohydrate Research* 1973;31:37.
- [20] Takeo K, Kuge T. *Agricultural and Biological Chemistry* 1970;34:1787.
- [21] Gidley MJ, Bociek SM. *Journal of American Chemical Society* 1988;110:3820.
- [22] Lindner K, Saenger W. *Biochemical and Biophysical Research Communications* 1980;92:933.
- [23] Tonelli AE. *Macromolecules* 1991;24:1275.