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Inclusion compounds formed between cyclodextrins and nylon 6

Lei Huang, Emily Allen, Alan E. Tonelli*

Fiber and Polymer Science, College of Textiles, North Carolina State University, PO Box 8301, Raleigh, NC 27695-8301, USA

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Abstract

High performance properties are increasingly needed in fibers for industrial applications. Such properties have been achieved in both flexible and intrinsically stiff polymers, but only through specialized and expensive spinning methods. In this work, the potential of achieving high performance mechanical behavior in nylon 6 using a conventional spinning process was explored. We report the formation of high-molecular-weight polymer inclusion compounds (ICs) between α- and β-cyclodextrins (α- and β-CDs) and nylon 6 ($M_n = 12$ kg mol^{-1}). Both high-molecular-weight polymer ICs were successfully made by a heating technique. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), and Fourier transform infrared (FTIR) spectroscopy have been utilized to observe the nylon 6 polymer chains included inside the channels formed by the cyclodextrins. DSC and TGA scans showed the high-temperature stable nylon 6-CD-IC samples contain no free crystalline nylon 6 polymer, and the much higher decomposition temperatures observed for these nylon-CD-ICs may imply that polymer chains included inside the polymer CD-IC channels can greatly improve cyclodextrins' stabilities. The nylon 6-α-CD-IC and nylon 6-β-CD-IC X-ray diffraction patterns were very similar to those of valeric acid-α-CD-IC and 1-propanol-β-CD-IC, which were confirmed to be channel crystal structures by single crystal X-ray diffraction. A new band which was absent from the pure cyclodextrin spectrum appeared at 1729 cm^{-1} for nylon 6-CD-ICs in their FTIR spectra and may be characteristic for CDs in their channel-forming ICs.

Keywords: Inclusion compounds; Cyclodextrins; Nylon 6

1. Introduction

High performance properties are increasingly needed in fibers for industrial applications. Such properties have been achieved in both flexible and intrinsically stiff polymers, but only through specialized and expensive spinning methods, especially for the flexible polymers since polymers generally crystallize in the form of lamellar structures in which the chains lie in folded configurations. The conventional oriented fibers obtained by drawing still contain fragments of those lamellae with straight stem segments parallel to the draw direction. The orientation of crystalline lamellae does not necessarily mean that the individual polymer chains are also fully extended. Even a perfectly packed stack of regularly folded single crystals, which would exhibit a near perfect orientation of the macromolecules, would have virtually zero strength along the chain axis [1], and experimental results have demonstrated that the demands of high performance applications from polymeric fibers could not be accomplished solely by pursuing high degrees of molecular orientation and large amounts of crystallinity [2]. To obtain full chain extension, the chains which may otherwise lie in random folded states must also be extended. The utilization of inclusion compounds (ICs) may help us to resolve this problem which has been discussed for almost two decades.

ICs are crystalline adducts in which one component (the host) crystallizes into a matrix, isolating the guest component into cavities of well-defined geometries. Instead of being held together by classical chemical bonds, they are linked by weak forces essentially steric in origin, i.e. related to the shape and dimension and not to the chemical nature of the molecules [3]. In polymer-ICs [3,4], the guest polymer chains are confined to narrow, cylindrical channels created by the host, small-molecule lattice like urea (U), perhydrotriphenylene (PHTP), and cyclodextrin (CD), where the polymers are highly extended and stretched, as a consequence of being squeezed, and are separated from neighboring polymer chains by the IC channel walls composed exclusively of the small-molecule host lattice (see Fig. 1).

It has been found [5] that the extended conformations have been retained for polymers coalesced after collapse of their IC structure. We can coalesce the polymer chains

* Corresponding author. Tel.: +1-919-515-6635; Fax.: +1-919-515-6532; E-mail: alan_tonelli@nesu.edu

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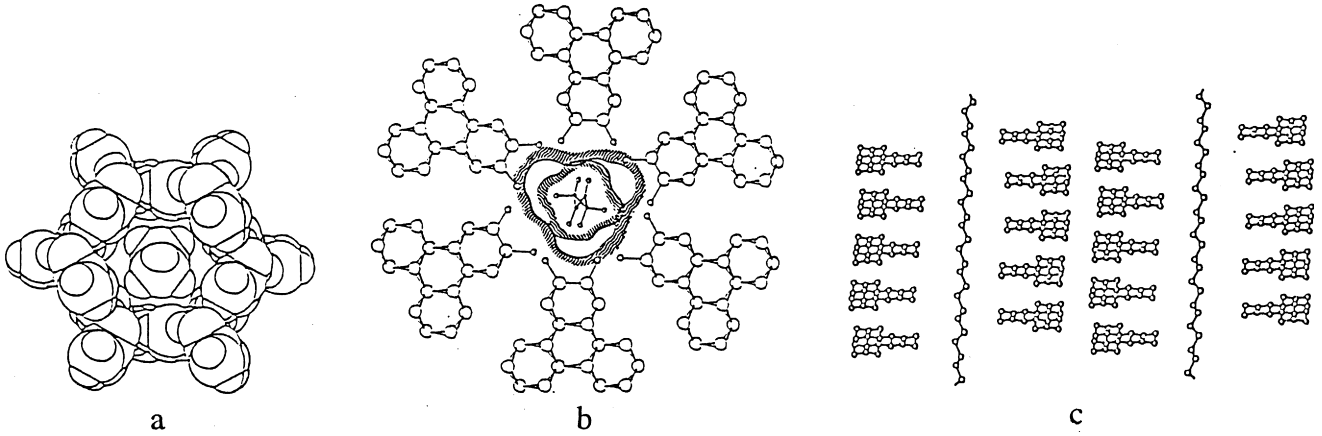

Fig. 1. View down the channel of the (a) *n*-hexadecane-U-IC and (b) polybutadiene-PHTP-IC crystals; (c) view perpendicular to the channel of the polybutadiene-PHTP-IC crystal.

from their ICs by exposure to a solvent for the small-molecule host (like water for CD), but which is not a solvent for the polymer [6]. After coalescence by solvent or heat treatment of their ICs, crystallizable polymers are observed to crystallize in an extended-chain morphology accompanied by less chain-folding than occurs when crystallization takes place from disordered melt or solution environments, so we expect that films and fibers formed from polymer ICs during their coalescence will exhibit improved properties, like tensile strength, modulus, etc., because of their chain-extended morphology.

In addition, embedding polymer-IC crystals into a carrier polymer, followed by in situ release and coalescence of the included polymers from their IC crystals, offers a means to obtain molecular polymer–polymer composite materials with unique morphologies which might be used to nucleate extended-chain crystallization in the carrier polymer or find applications in the control–release area (see Fig. 2). Depending on whether or not the IC-included and carrier polymers are identical, it may be possible to study a polymer's self or mutual diffusion, dye diffusion in fiber-forming polymers, and, for chemically distinct polymers, probe the development (both the organization and kinetics) of phased-separated morphologies.

Here, we choose cyclodextrins (CDs), cyclic carbohydrates, as the host small molecules which can form inclusion complexes with a wide range of guest compounds. Since the discovery of CDs, a large number of inclusion compounds of CDs with various low-molecular-weight compounds have been prepared and characterized. However, there are few reports on the inclusion compounds formed between CDs and fiber-forming polymers [3,4,7].

Cyclodextrin ICs formed with low-molecular-weight guests can either have channel or cage structures. Fig. 3 presents the chemical structures for α- and β-cyclodextrins, and Fig. 4 presents the schematic descriptions of channel-type, cage *herringbone*-type and cage brick-type cyclodextrin IC crystal structures [8]. The average diameters of cyclodextrins' ''doughnut-shape'' cavities are 5.5 Å for α- and 7.0 Å for β-cyclodextrins, respectively. 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 cyclodextrin molecule is closed on both sides by adjacent molecules. Normally, the channel

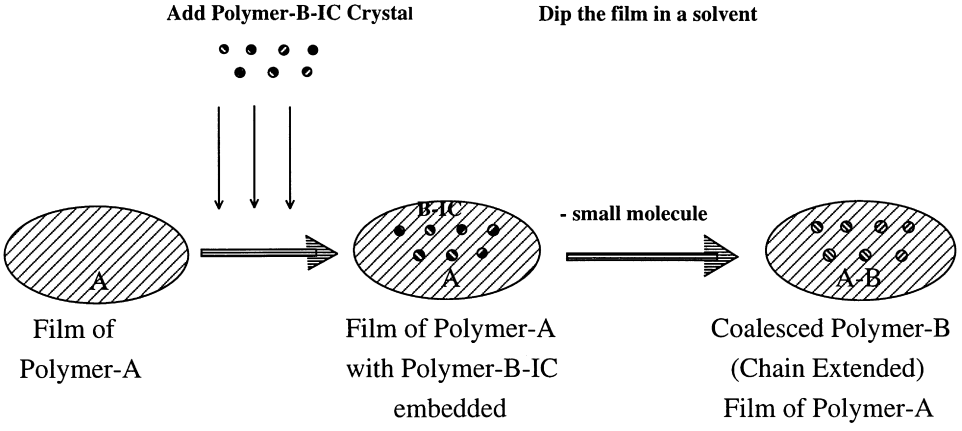

Fig. 2. Mechanism for coalescence of polymer-B from its inclusion compound into a polymer-A carrier phase.

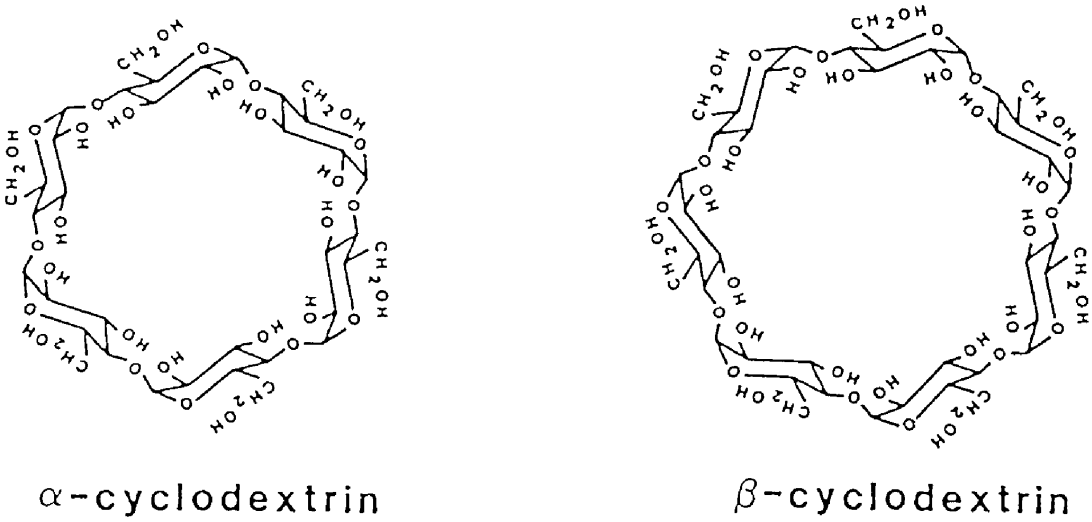

Fig. 3. The chemical structures for α-cyclodextrin and β-cyclodextrin.

structures can be assigned to polymer-CD-IC samples due to 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.

Nylon 6, which is a protein-like, wholly man-made synthetic material, is the polymerization product of ϵ-caprolactam. Its properties are dominated by the presence of amide groups along the backbone of the nylon 6 chain resulting in inter- and intramolecular hydrogen bonding, which influences its chemical and physical properties. Since it was announced to the public in 1938 [9], nylon 6 has been used in a wide variety of applications, including textile fibers used in apparel, as industrial cords and in engineering plastics, and in producing carpets, plastic gears and bushings, electric parts, and fishing line and ropes. However, its interactions with other polymers and its intra- and interchain interactions are still not fully understood.

Molecular modeling of single, isolated chains in polymer-ICs offers a means to interpret the experimental observations. Tonelli [10] has modeled polymer chains included in their IC channels by restricting the conformations accessible to small-chain fragments (e.g. 9–20 backbone bonds) to those which fit into a cylinder whose diameter (for urea $D = 5.5$ Å) mimics the observed channel cross-section. After establishing the population of channel conformers, a test is performed to determine the possibility of interconverting between them without any portion of the polymer chain fragment leaving the channel during any step in the interconversion process.

The rotational isomeric state (RIS) model [11] has been used to determine the conformations of aliphatic nylons that are able to fit into a channel with a diameter of 5.5 Å for urea and PHTP IC compounds. This was achieved by a two-step procedure:

1. From all possible RIS conformations available to the free polymer chain, those which fit into the channel found in inclusion compounds were identified;
2. A test was performed to determine whether or not it was possible to interconvert between these channel conformations while the polymer chain remained inside the channel.

Nylon 6 chains are able to adopt only five distinct conformations whose diameters are appropriate to the channels of $D = 5.25$–5.50 Å. In addition to the all-trans, planar zigzag conformation, kink conformers with (g $\pm$ tg $\mp$) sequences were found to fit in these channels. However, it

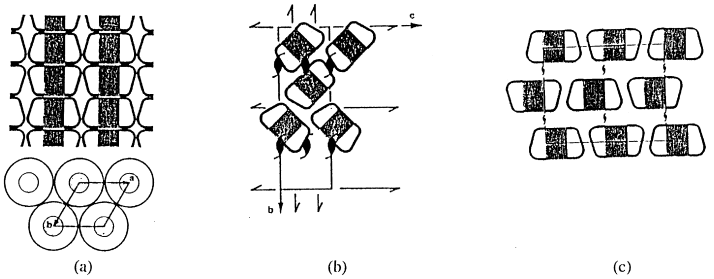

Fig. 4. Schematic description of: (a) channel-type, (b) cage herringbone-type, and (c) cage brick-type crystal structures formed by crystalline cyclodextrin inclusion complexes.

was not possible to interconvert between these channel conformers without some portion of each polymer chain leaving the channel.

In the work presented here, nylon 6-CD-ICs are prepared via heating techniques. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and Fourier transform infrared (FTIR) spectroscopy are used to characterize the ICs and the extended nylon 6 polymer chains isolated in the narrow CD-IC channels. This is the first stage in our research into the potential for achieving high performance mechanical behavior in nylon 6 using a conventional spinning process. The fiber-forming polymer-IC model study will also help us to understand the interactions occurring between polymers and their effects on blend miscibility, compatibility, morphologies, structures, and properties.

2. Experimental

2.1. Materials.

Nylon 6 pellet samples with molecular weight of about 12 kg mol^{-1} were obtained from Allied Signal. Cyclodextrins were obtained from Cerestar. Both were used after drying in a vacuum oven at 70°C for 12 h.

2.2. Preparation of the physical mixtures

The nylon 6 pellets were ground into a granular powder with a Wiley mill. The physical mixtures of nylon 6 and CDs were made by mixing nylon 6 and CD powders together at room temperature in a 1:1 (nylon 6 monomer unit:CD) molar ratio, which was indicated by computer model studies [10].

2.3. Preparation of IC samples by solution heating technique

Nylon 6 (0.15 g) was dissolved in 15 ml of formic acid, 7.25 g of α-cyclodextrin and 3.0 g of β-cyclodextrin were dissolved in 50 ml of distilled water while all the solutions were stirred on a hot plate at 70°C. Then the nylon 6 solution was added slowly to the CD aqueous solutions using an addition funnel, and the mixed solutions of polymer and CD were kept on a hot plate for 3 h at 70°C, then cooled to room temperature while stirring for another 6 h. After storing quiescently and uncovered for 24 h in a hood, the white precipitate was filtered and dried in a vacuum oven.

3. Characterization

3.1. Thermal property analysis

Thermal characteristics of samples were determined with a Perkin-Elmer Model 7 series/UNIX different scanning calorimeter and thermogravimetric analyzer. 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 by two heat/cool cycles between 25 and 250°C at a heating rate of 10°C min^{-1} and a cooling rate of 100°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 at a heating rate of 10°C min^{-1}. Both instruments used nitrogen as the purge gas.

3.2. 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 Cu Kα 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 the diffracting intensities were recorded every 0.05° from 2θ scans in the range 5–40°.

3.3. Infrared spectroscopy

Absorbance Fourier transform infrared spectra were recorded on a Nicolet 510p FTIR 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.

4. Results and discussion

4.1. Thermal property analysis

Fig. 5 and Fig. 6 show the TGA scans for cyclodextrins, the physical mixtures of cyclodextrins and nylon 6, and the nylon 6-CD-ICs up to 400°C, respectively. From Fig. 5 we can see that α-cyclodextrin and a physical mixture of α-cyclodextrin and nylon 6 both started to decompose at 313°C. The most striking feature for the nylon 6-α-CD-IC is that it showed a higher decomposition temperature (328°C) than pure α-CDs (313°C).

In Fig. 6, it is seen that the physical mixture of β-cyclodextrin and nylon 6 started to decompose at 324°C, while the nylon 6-β-CD-IC showed a higher decomposition temperature at 333°C. This phenomenon of higher decomposition temperatures in polymer-CD-ICs may imply that the polymer chains included inside the polymer CD-IC channels can improve cyclodextrin's thermal stability. These rather high temperature stable polymer-CD-ICs might also provide a great potential benefit in several areas, such as using polymer ICs in the fabrication of

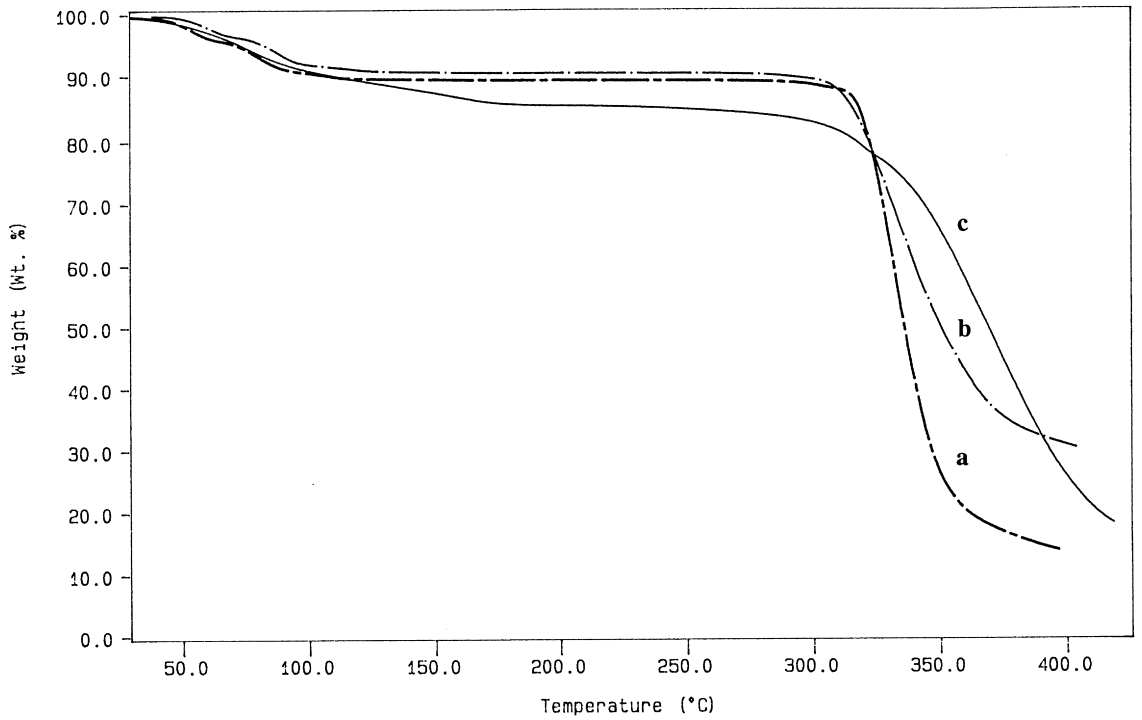

Fig. 5. TGA scans of (a) α-CD, (b) α-CD and nylon 6 physical mixture, and (c) nylon 6-β-CD-IC (10°C min^{-1}).

polymer–polymer molecular composites. Normally, other kinds of polymer ICs, like those formed with urea, and PHTP as hosts, are not stable in IC structures at temperatures above 140–180°C [3].

Since cyclodextrins and their ICs will decompose while melting, we only tested them below their melting temperatures in DSC (i.e. below 250°C). Fig. 7 shows DSC curves for a pure bulk nylon 6 sample. It has a melting temperature of 217°C for the first heating curve, and after quenching to 25°C at 100°C min^{-1} and holding at 25°C for 3 min, it shows a melting temperature of 220°C for the second heating curve. Under the same testing conditions,

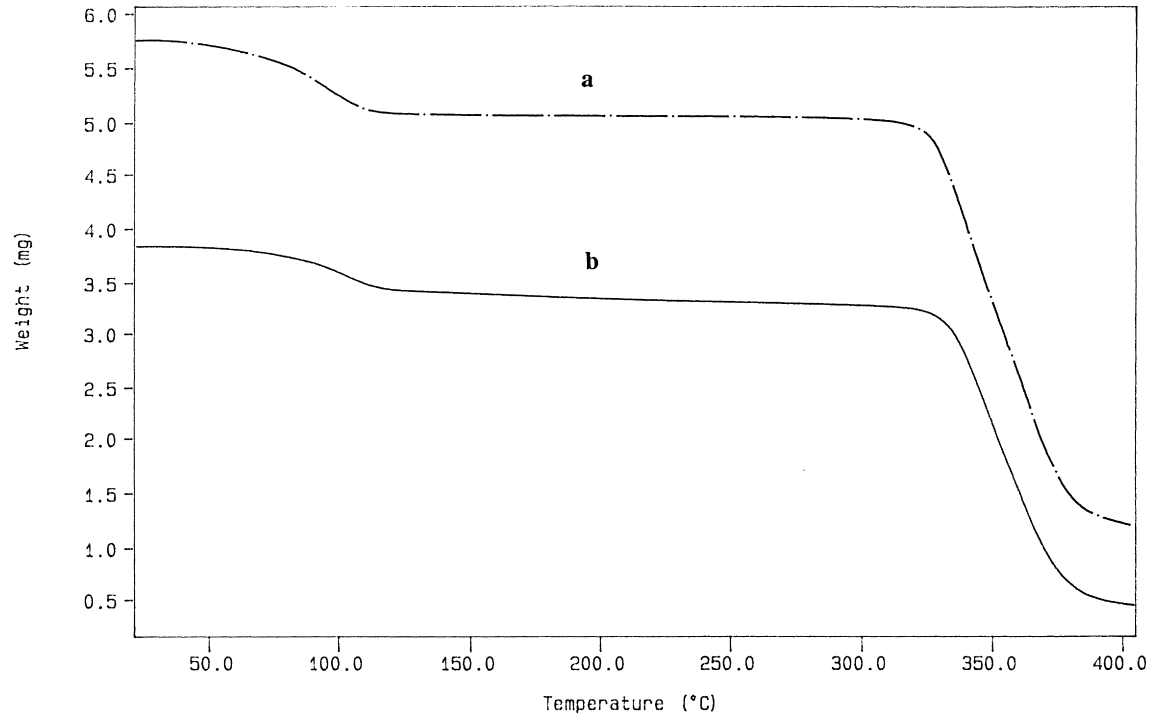

Fig. 6. TGA scans of (a) β-CD and nylon 6 physical mixture, and (b) nylon 6-β-CD-IC (10°C min^{-1}).

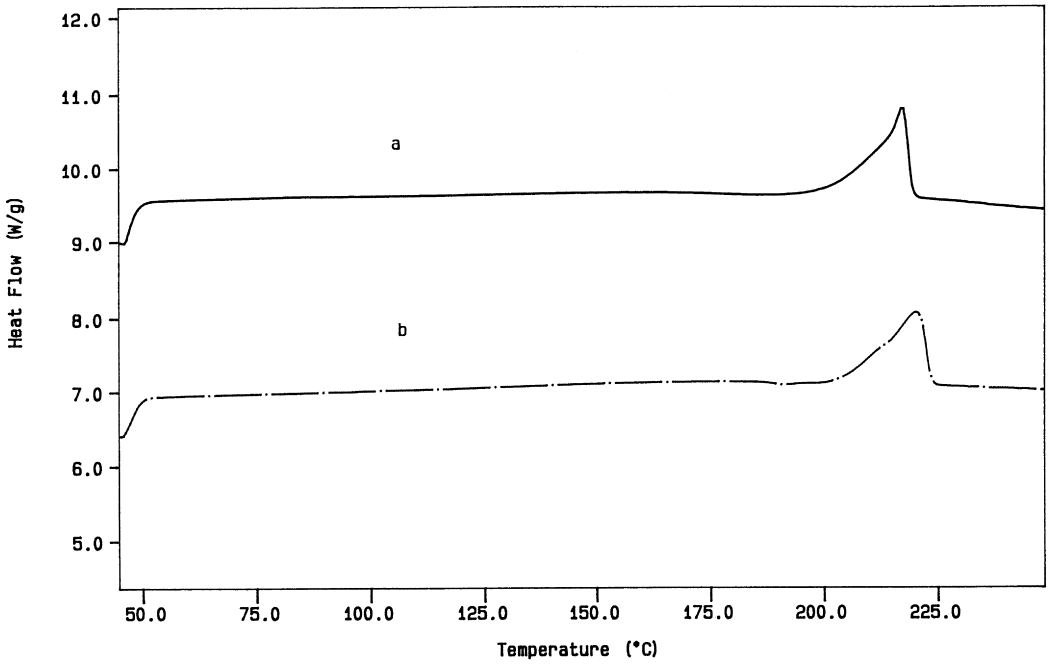

Fig. 7. DSC thermograms for pure nylon 6 showing: (a) the first heating; (b) the second heating (10°C min^{-1}).

we recorded the DSC curves for nylon 6-α-CD-I and nylon 6-β-CD-IC which are shown in Fig. 8 and Fig. 9. By comparing them with Fig. 7, the absence of nylon 6 melting peaks (around 217°C) in nylon 6-CD-IC scans may indicate that there is no free crystalline nylon 6 polymer in the nylon 6-CD-ICs. So we expect that most of the nylon 6 chains may be included inside the channels which are provided by orderly stacked α- and β- cyclodextrin molecules. The two peaks, which are at 192°C in Fig. 8 and 160°C in Fig. 9 and appeared in the first heating curves but disappeared in the second heating curves, are probably due to a small amount of excess cyclodextrins remaining in the IC samples which formed cage crystal structures with moisture. After heating to 250°C, the moisture was evaporated and these peaks disappear in the second heating curves.

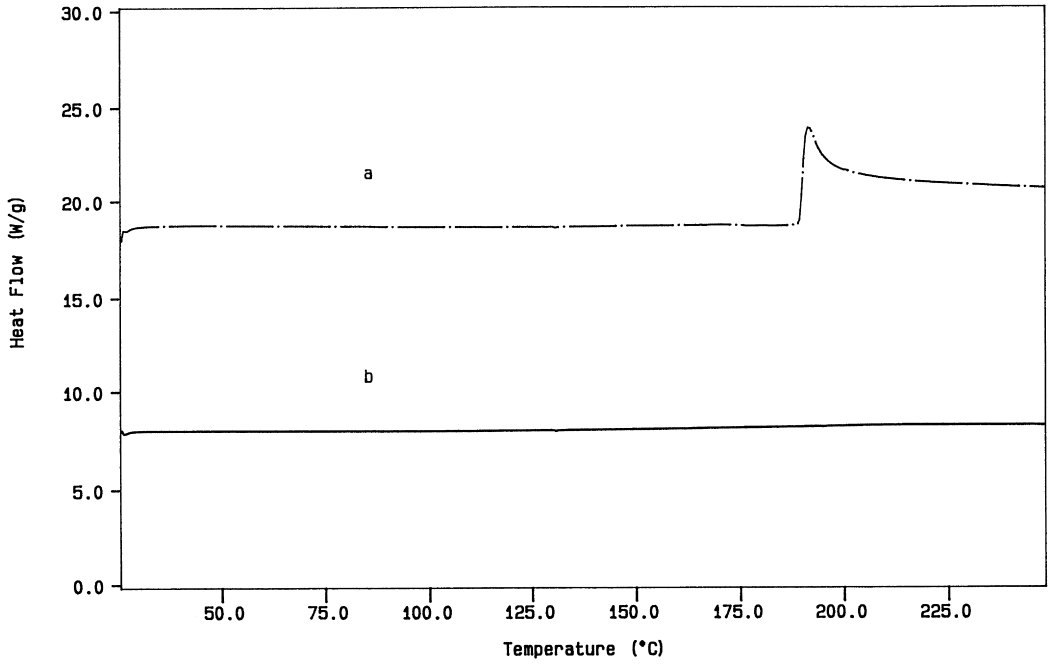

Fig. 8. DSC thermograms for nylon 6-α-CD-IC showing: (a) the first heating; (b) the second heating (10°C min^{-1}).

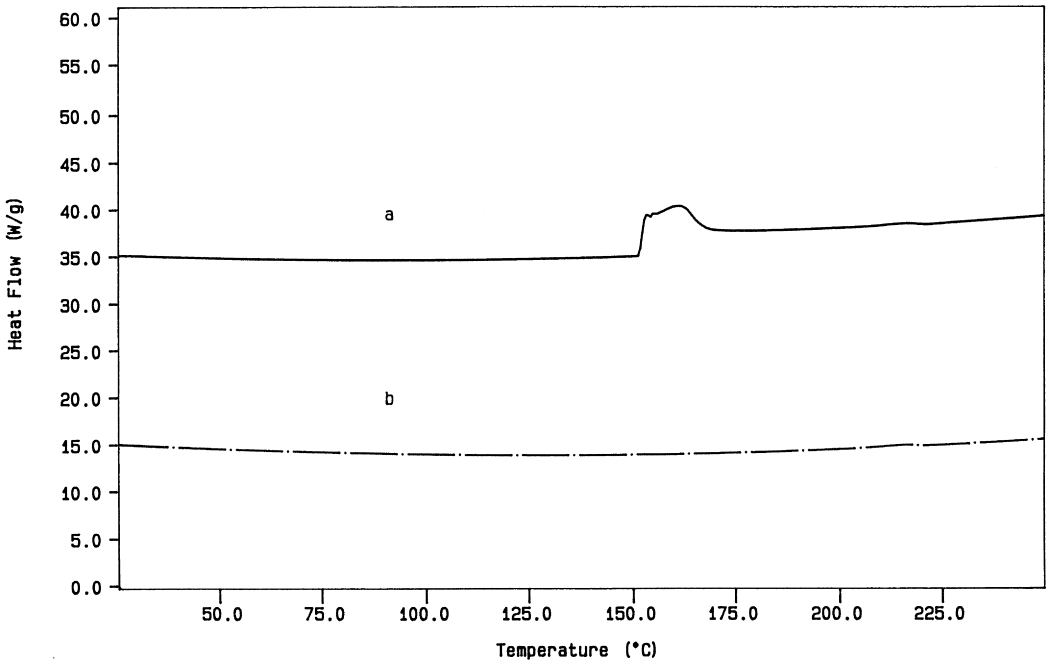

Fig. 9. DSC thermograms for nylon 6-β-CD-IC showing: (a) the first heating; (b) the second heating (10°C min^{-1}).

4.2. X-ray diffraction

The structure of nylon 6 can be described in terms of a two-phase model which is assumed to be composed of alternating crystalline and amorphous regions. Nylon 6 is known to exist in at least two polymorphic crystalline forms. One is a monoclinic structure [12] for the α-form with $a = 9.56$ Å, $b = 17.24$ Å (chain axis), $c = 8.01$ Å and $\beta = 67.5°$, where the molecules are in the fully extended planar configuration and the hydrogen bonds are between anti-parallel chains. The other is the γ-form which is characterized by a shortened chain repeat distance, compared with the fully extended α-form, with $a = 9.33$ Å, $b = 16.88$ Å (chain axis), $c = 4.78$ Å and $\beta = 121°$ [13]. From the wide-angle X-ray diffraction pattern of the nylon 6 sample (Fig. 10d), we observed a single broad peak centered around 22° (2θ) which appears to originate from a mixture of small imperfect α- and γ-structures.

Fig. 10 presents the comparison of wide-angle X-ray diffraction patterns observed for α-CD, nylon 6, α-CD and nylon 6 physical mixture, and nylon 6-α-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. The nylon 6-α-CD-IC showed a diffraction pattern quite different from the diffractograms of nylon 6 and α-cyclodextrin, and this constitutes primary evidence that a different crystal type was formed. There is also the strong diffraction peak at approximately 20.0 (2θ), which was previously suggested to be a possible indicator for the α-CD channels which include polymers inside [14,15].

By comparing the X-ray diffraction of valeric acid-CD-IC and propionic acid-CD-IC, whose inclusion structures are already known as channel-type and cage-type respectively [16,17], we observe that nylon 6-α-CD-IC's diffraction pattern is much more similar to that of valeric acid-CD-IC (see Fig. 11). This is very strong evidence for the proposed channel-type polymer-CD-IC structure mentioned earlier.

Fig. 12 is the comparison of wide-angle X-ray diffraction patterns observed for pure β-CD, nylon 6-β-CD-IC, and pure nylon 6 powder samples at room temperature from $2\theta = 5$ to 40°. Like nylon 6-α-CD-IC, the diffractogram of nylon 6-β-CD-IC also showed quite a different diffraction pattern from that of β-CD, and this constitutes primary evidence that a different crystal type was formed.

Fig. 13 shows the patterns of β-CD (c) and the complexes of β-CD with nylon 6 (a) and with 1-propanol (b). It is shown that all the samples are crystalline and the pattern of the nylon 6-β-CD-IC is different from that of β-CD, which was reported to be a cage crystal structure when it forms a β-CD·12H_2O complex with water [18], but is similar to that of the complex with 1-propanol, which has been proven to have a channel structure by the X-ray study of a single crystal of the complex [19]. We may need some further study on nylon 6-β-CD-IC, because of its complicated diffraction pattern, but the results here indicate that, in the nylon 6-β-CD-IC sample, the CD exhibits a different packing from that in free β-CD and has a channel structure as in its complex with 1-propanol.

4.3. FTIR spectroscopy

Fig. 14 and Fig. 15 show the FTIR spectra in the region

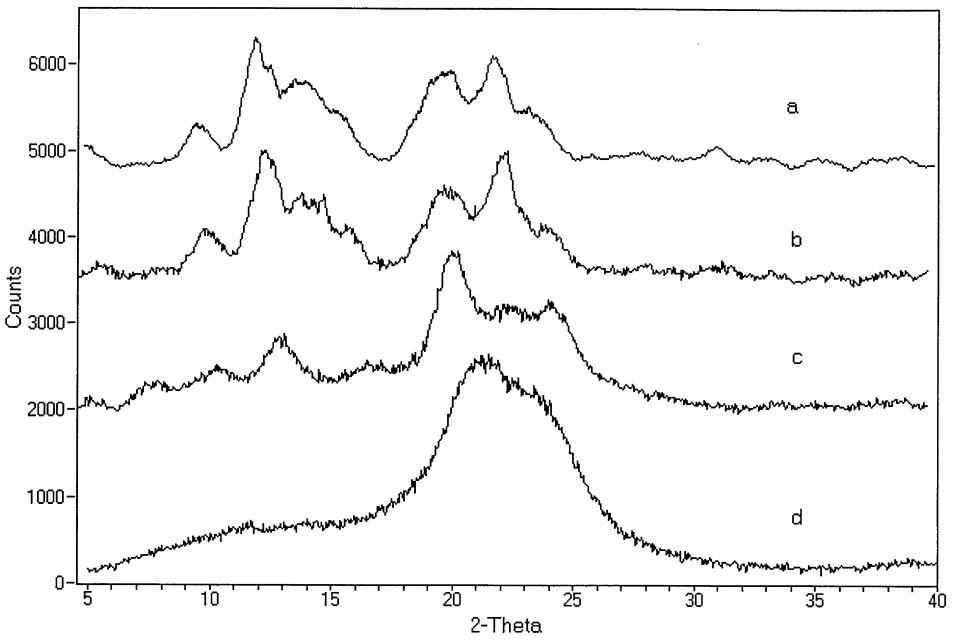

Fig. 10. Wide-angle X-ray diffraction of (a) α-CD, (b) α-CD and nylon 6 mixture, (c) nylon 6-α-CD-IC, and (d) nylon 6.

from 400 to 4000 cm^{-1} obtained for cyclodextrins, nylon 6 and nylon 6-CD-ICs. We can see that the two nylon 6-CD-ICs' spectra are almost the same. The extremely broad band whose center was at 3386 cm^{-1} is assigned to the symmetric and antisymmetric O–H stretching modes for pure CDs and is extremely broad.

The bands observed in the 3000–2000 cm^{-1} region for CDs (Fig. 14A and Fig. 15A) and nylon 6-CD-ICs (Fig. 14B and Fig. 15B) are slightly different. Nylon 6 (Fig. 14C and Fig. 15C) has several strong bands due to the C–H stretching mode at 3081, 2935 cm^{-1} (the C–H antisymmetric stretching mode) and at 2866 cm^{-1} (the C–H symmetric stretching mode). At slightly lower frequency, the small band at around 3030 cm^{-1} and a broad shoulder (around 2855 cm^{-1}) appeared in the nylon 6-CD-ICs' spectra, which were different from the cyclodextrins' spectra and were most probably contributed by the included nylon 6 segments in their IC sample.

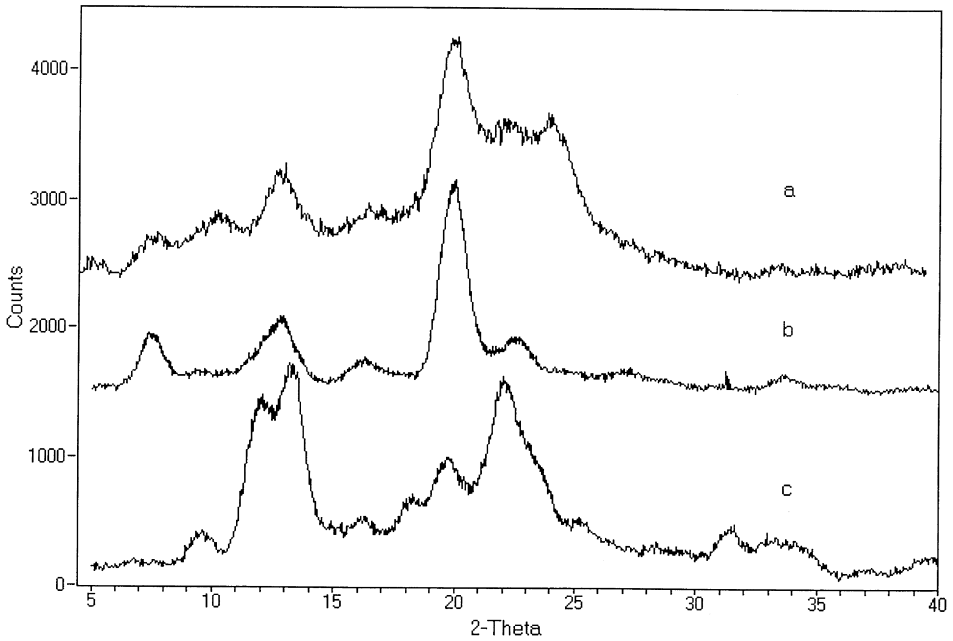

Fig. 11. Wide-angle X-ray diffraction of (a) nylon 6-α-CD-IC, (b) valeric acid-α-CD-IC, and (c) propionic acid-α-CD-IC.

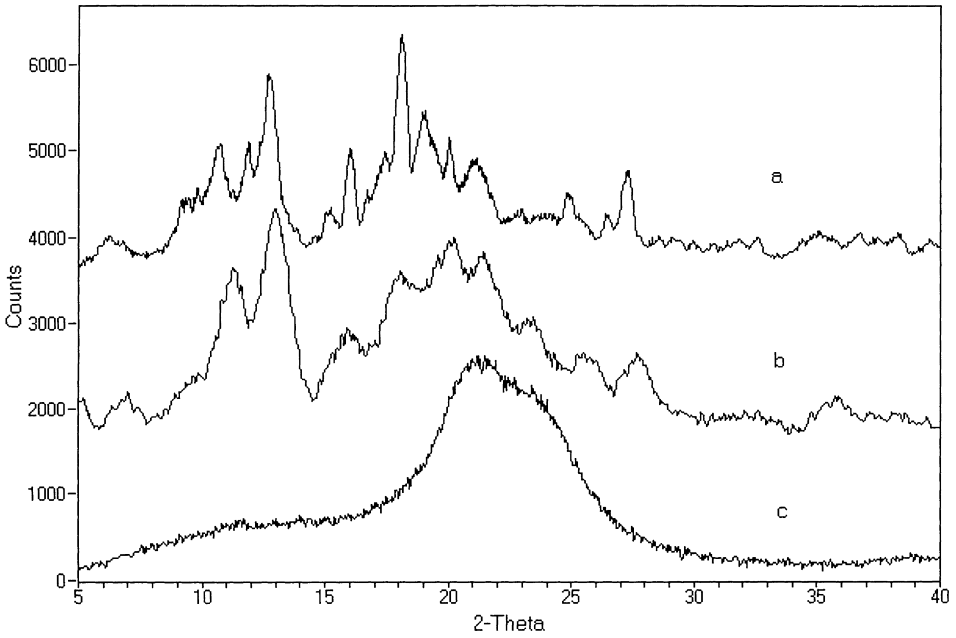

Fig. 12. Wide-angle X-ray diffraction of (a) β-CD, (b) nylon 6-β-CD-IC, and (c) nylon 6.

A new band appeared at 1727 cm^{-1} in the nylon 6-CD-IC spectra which was absent from the cyclodextrins' spectra. It is most probably due to the carbonyl stretching from nylon 6 molecules. The changes in relative intensity of the 1493 and 1453 cm^{-1} bands were also observed in the nylon 6-CD-IC samples. Bands in the 1200–800 cm^{-1} region were very similar for both cyclodextrins and nylon 6-CD-ICs. These bands are referred to as stretching modes of the glucosidic group coupled with C–C and C–O stretching modes [20].

In summary, we report that for the first time high-molecular-weight polymer-ICs between CDs and nylon 6 were successfully made by a heating technique. DSC, TGA, WAXD, and FTIR have been utilized to observe the nylon 6 chains included inside the channels formed by CDs. Nylon 6-CD-ICs have very different crystal structures and thermal behavior compared to the bulk polymer. The long polymer chains have been included inside the channels which are provided by the orderly stacked cyclodextrin molecules, and the success of including the same polymer chain, nylon 6, in channels of different sizes offered by α- and β-cyclodextrins suggests several more interesting research topics, such as studying the polymer chain's conformational

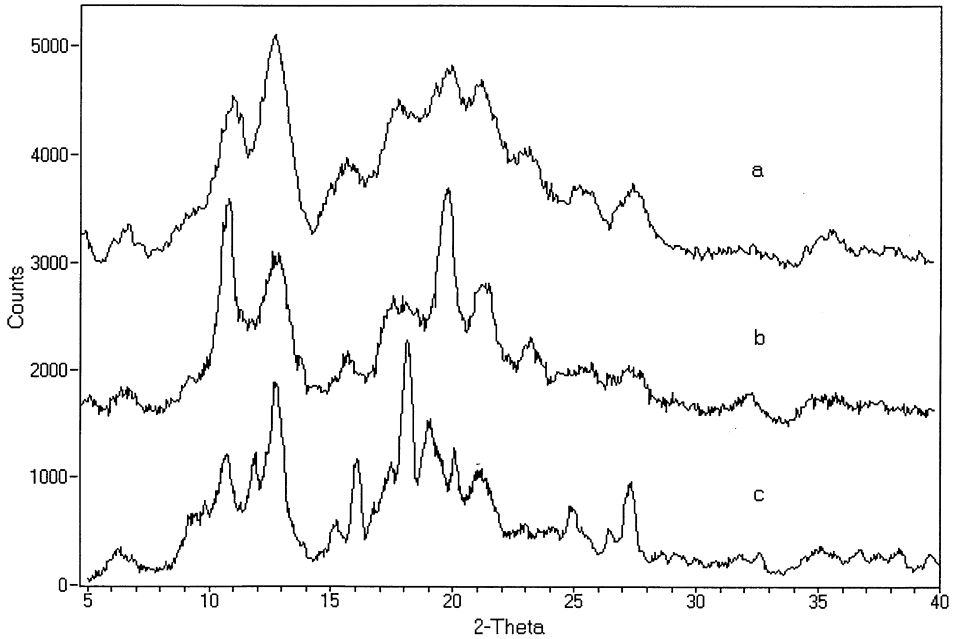

Fig. 13. Wide-angle X-ray diffraction of (a) nylon 6-β-CD-IC, (b) 1-propanol-β-CD-IC, and (c) β-CD.

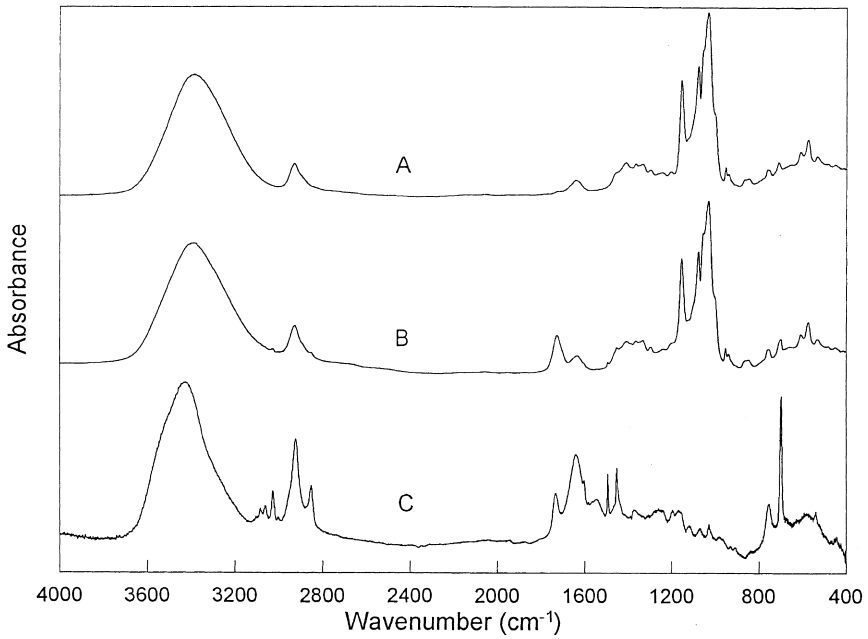

Fig. 14. Fourier transform infrared spectra in the region between 400 and 4000 cm^{-1}: (A) α-cyclodextrin, (B) nylon 6-α-CD-IC, and (C) nylon 6 (12k).

and motional behavior in different controlled environments. Further analyses of the structure, stoichiometry, and stability of these polymer-CD-ICs is in progress, and we are approaching a new way to produce more elongated, higher modulus, more stable and stronger fibers by using fiber-forming polymer inclusion compounds in the conventional spinning techniques.

The overall objective of this study was to develop extended chain structures and high performance characteristics in nylon 6 films and fibers. Achievement of such a goal in a relatively flexible polymer has been known to be difficult. If the targeted structure and properties could be realized in nylon 6 using conventional procedures, this would mark a significant step forward in the manufacture of man-made fibers for industrial applications.

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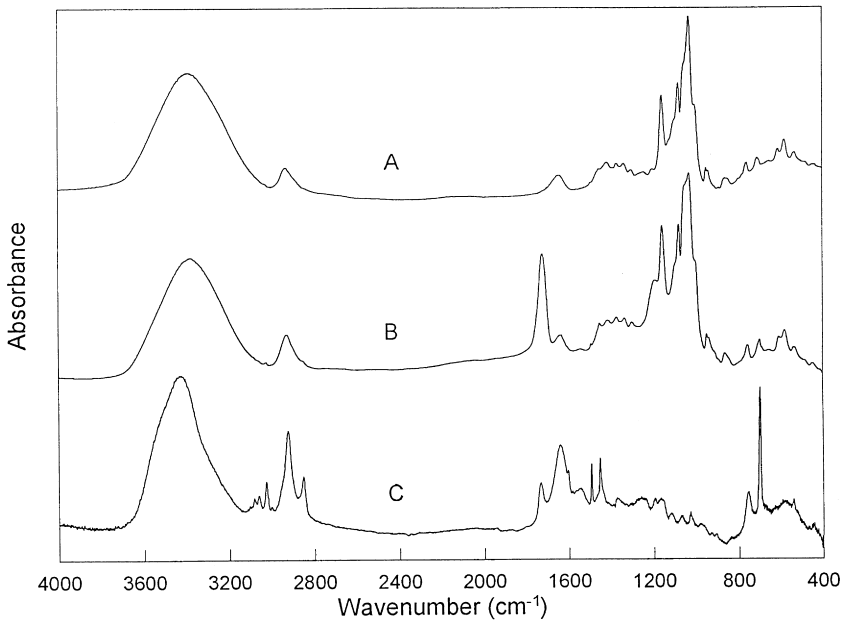

Fig. 15. Fourier transform infrared spectra in the region between 400 and 4000 cm^{-1}: (A) β-cyclodextrin, (B) nylon 6-β-CD-IC, and (C) nylon 6 (12k).

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