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Formation and characterization of the inclusion complexes between poly(dimethylsiloxane) and polyacrylonitrile with γ-cyclodextrin

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Abstract

Poly(dimethylsiloxane) and polyacrylonitrile have been observed to form inclusion complexes (ICs) with γ-cyclodextrin. These complexes were prepared by a solution-heating technique. Their structural features were observed with the use of: FTIR, TGA, WAXS, and ^{13}C-NMR. FTIR identifies absorption peaks of the guest polymer molecules in the cyclodextrin. Thermal decomposition shows that the ICs have a higher thermal stability than the pure γ-cyclodextrin. The wide angle X-ray diffraction of the complexes indicates that the ICs form channel structures. CP-MAS ^{13}C-NMR spectra of the ICs show that γ-cyclodextrin, in the presence of a polymer guest, adopts a more symmetric conformation when compared to its pure state. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclodextrins; Poly(dimethylisiloxane) (PDMS); Polyacrylonitrile (PAN)

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1. Introduction

The phenomenon of polymer inclusion complexation is now generally well known. It has been observed that cyclodextrins acting as a host can include within their narrow channels large molecular guests such as polymers. Harada and Kamachi first reported in 1990 the formation of inclusion complexes (ICs) between cyclodextrins (CD) and low molecular weight hydrophilic polymers — poly(ethylene glycol) [1] and poly(propylene glycol) [2]. Since then ICs of cyclodextrins with hydrophobic polymers, such as polyisobutylene [3], high molecular weight poly(ε-caprolactone) [4], nylon-6 [5], triblock copolymer of poly(ε-caprolactone)-poly(ethylene oxide)-poly(ε-caprolactone) [6], poly(L-lactic acid) [7], and hydrophilic, high molecular weight poly(ethylene oxide) [4] have been reported. In a recent communication Harada and co-workers [8] reported the formation of an IC of γ-CD with an hydrophobic inorganic polymer — poly(dimethylsiloxane).

Cyclodextrins are a family of cyclic oligosaccharides consisting of glucose units joined by α-1,4-glycosidic linkages. Most of the reported research on polymer-CD ICs have used the α, β, and γ forms of CD. These various forms are essentially defined by the number of glucose units in the molecules, with the α, β, and γ CDs having six, seven, and eight glucose units, respectively. The average diameter of the γ-cyclodextrin cavity is between 7.5–8.3 Å with a height of about 7.9 Å [9] (see Fig. 1). The crystal structures of the ICs between cyclodextrins and their guests are of two types: channel and cage structures [10]. Fig. 2 shows the various crystalline forms of CD-ICs. Due to the long chain nature of polymers, the crystalline structure of polymer-CD-ICs is generally of the channel type.

In this work, we are interested in taking advantage of the physical structure of the cyclodextrin molecule to investigate the possibility of separating cyclic oligomers from their linear chains in polymer samples. Also, because of the ability of CDs to isolate single chains of polymers within their cavities, polymer-CD-ICs provide a unique solid state environment to study only the intramolecular contribution of the single chains to the dynamics of polymer motions, and therefore their properties [11]. We are motivated to use polymer-CD-ICs as model systems to further elucidate the intrinsic dynamic mobility and conformations of extended polymers, such as found in liquid-crystalline and semi-crystalline bulk polymer samples. We have selected two polymers for our current study: poly(dimethylisiloxane) (PDMS) and polyacrylonitrile (PAN).

It is well established that at the low molecular weight end, PDMS contains a number of cyclic species. One of our goals is to determine if through the process of PDMS-γ-CD-IC formation we can clean PDMS by removing the cyclic oligomers. In addition, based on improved X-ray diffraction

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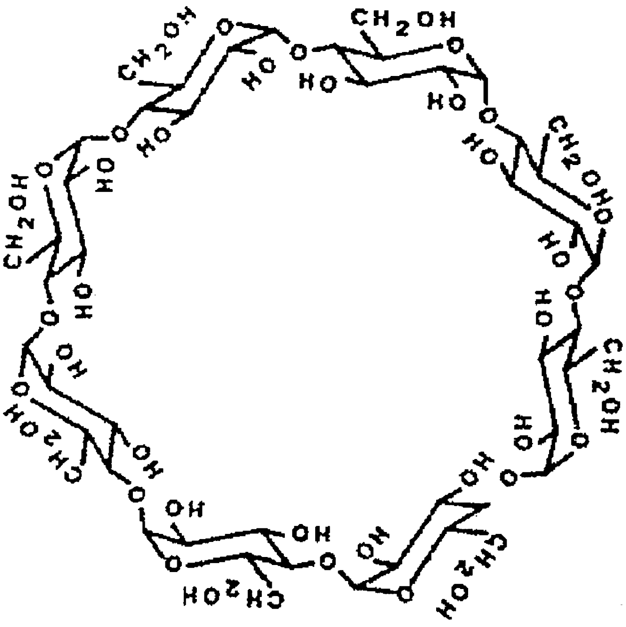


Fig. 1. Molecular structure of γ-CD.

data and analysis, Albouy [12] has recently suggested a new crystalline conformation for PDMS. His investigation supports an extended 4_1-helical PDMS conformation, which is similar to a suggestion made earlier by Flory [13] and more recently supported by solid-state NMR observations on crystalline PDMS by Schilling et al. [14]. The 4_1-helical PDMS conformation is much more extended and narrower in cross-section than the broad, ribbon-like 2_1-helical conformation proposed earlier for crystalline PDMS by Damaschun [15] in 1962. Isolated PDMS chains confined to the ~8 Å channels in the PDMS-γ-CD-IC can (cannot) adopt the extended, narrow 4_1-helical (broad, ribbonlike 2_1-helical) conformations proposed for crystalline PDMS chains. Thus, a comparison of the ^{13}C and ^{29}Si NMR resonance frequencies observed for PDMS chains in its γ-CD-IC and bulk crystals can possibly confirm Abouy's recently proposed conformation for crystalline PDMS.

With respect to PAN, the conformation it adopts in the bulk has been the subject of debate [16–21]. However, using a 2-D, double-quantum NMR spectroscopic technique (DOQSY), Kaji and Schmidt-Rohr [22], concluded that the *para*-crystallinity in atactic PAN is due to the relatively high *trans*/*gauche* ratio (90:10) of the polymer chain backbone bonds. We think that knowledge of the conformations and dynamic motions of single PAN chains in PAN-γ-CD-IC may help to develop a general understanding of the conformations and dynamic motions of its bulk solid. At the very least, observation of PAN chains isolated in the narrow channels of its γ-CD-IC crystals will assist in highlighting the relative contributions made by inter- and intramolecular interactions to its bulk properties. In this connection, we have recently synthesized PANs with a wide range of stereoregularities. We want to learn whether or not the conformations and motions of their chains isolated in the narrow PAN-γ-CD-IC channels differ, with the hope that this information might aid in our understanding the physical properties exhibited by bulk PAN's with different stereosequences. This approach has been successful in prior studies of *trans*-1,4-polyisoprene, polyethylene, and *trans*-1,4-polybutadiene, in their inclusion compounds with perhydrotriphenylene [23–25].

In this work, we report the formation and characterization of ICs between PDMS and PAN with γ-CD, as the initial step in addressing the above goals.

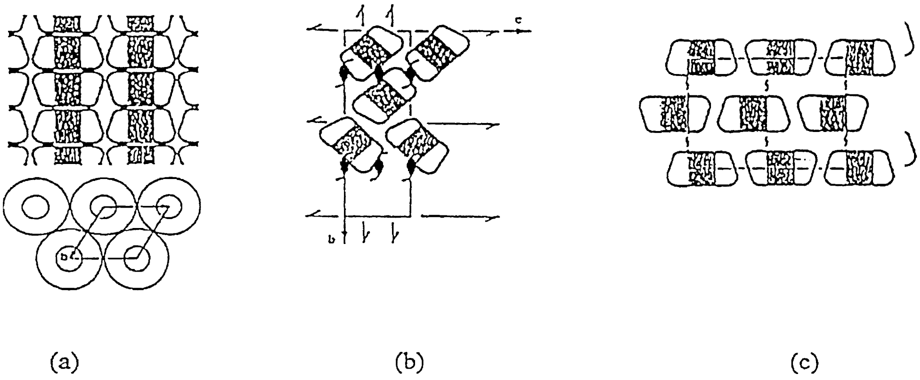
2. Experimental

2.1. Materials

Commercial grades of PDMS with various molecular weights were used as received from United Chemical Technologies. PAN and cyclodextrins obtained from Aldrich and Cerestar, respectively, were also used as received.

2.2. Method of IC formation by solution heating method

PDMS-γ-CD-ICs: 1.0 g of PDMS samples (MW = 237, 770, 1250, and 62,700) were slowly added into a saturated



(a) (b) (c)

Fig. 2. Schematic description of the various crystalline structures of cyclodextrin ICs: (a) channel type, (b) cage *herringbone* type, (c) cage brick type.

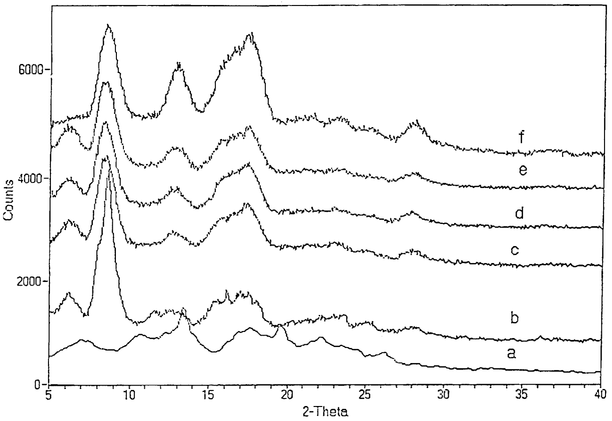


Fig. 3. Wide Angle X-ray Diffraction of (a) pure γ-CD, (b) 1-propanol-γ-CD-IC, (c)–(f) PDMS-γ-CD-ICs of various molecular weights 237, 770, 1250, and 62,700 g mol^{-1}, respectively.

solution of γ-CD (11.6 g dissolved in 50 ml of distilled water). The mixture was stirred on a hot plate at 60–65°C.

PAN-γ-CD-IC: 0.25–0.5 g of PAN was first dissolved in *N,N*-Dimethylformamide solution at about 90°C. The polymer solution was then slowly added to a saturated solution of γ-CD.

All of the polymer γ-CD mixtures were stirred on a hot plate at between 60–70°C, for 3 h, then cooled to room temperature, while stirring for another 4 h. The resulting white precipitate was allowed to rest for 24 h, and then filtered and dried in a vacuum oven. Attempts at IC formation between PDMS and PAN with α- and β-CD were not successful.

2.3. Characterization

X-ray diffraction. Wide angle X-ray diffraction patterns of the powder samples were obtained at room temperature using a Siemens type-F X-ray diffractometer. The source of X-rays was Ni-filtered, CuK$_\alpha$ radiation with a wavelength of 1.54 Å. The current and voltage supplied were 20 mA and 30 kV, respectively. Samples were placed into a circular sample holder with scotch tape and the detector collected data at a rate of ($2\theta = 5°$) min^{-1} between $2\theta = 5$ and 40°.

Infrared spectroscopy. Infrared absorption spectra were collected using a Nicolet 510P FTIR spectrometer with OMNIC software. The frequencies observed were in the mid-IR region of 4000–400 cm^{-1} with a resolution of 2 cm^{-1} and a total of 64 scans. A new background was obtained for every sample. The samples were thoroughly mixed with KBr and then pressed into pellet form.

Thermal analysis. The thermal properties of the ICs were determined using the Perkin Elmer Pyris 1 thermogravimetric analyzer, with samples of 5–10 mg. Samples were placed in platinum pans left to hang in the furnace, and a heating rate of 20°min^{-1} was used in the temperature range of 30–400°C.

NMR spectroscopy. High resolution solid state ^{13}C-NMR spectra were obtained using a Chemagnetics 200S spectrometer at 50 MHz under cross-polarization (CP), magic-angle spinning (MAS) using a Zirconia rotor spinning between 3.5 and 4.0 KHz. The optimum Hartmann–Hahn and magic-angle conditions were calibrated using *p*-di-*tert*-butylbenzene (PDTBB) 31.0 ppm versus tetramethylsilane (TMS). High power dipolar decoupling (DD) was applied at about 47 KHz during acquisition. The spectral width was 15 KHz stored in a 2 K memory that was zero-filled to 8 K before Fourier transformation.

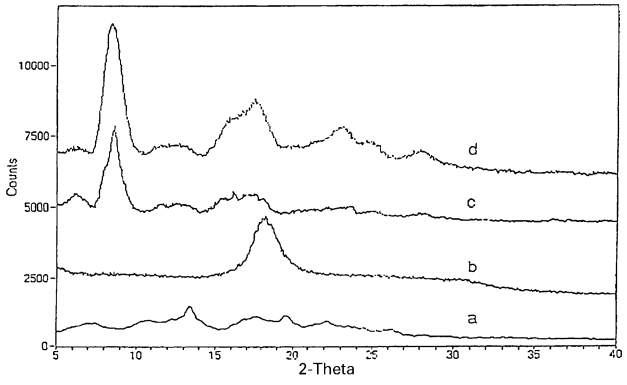


Fig. 4. Wide angle X-ray diffraction of: (a) pure γ-CD, (b) pure PAN, (c) 1-propanol-γ-CD-IC, and (d) PAN-γ-CD-IC.

3. Results and discussion

X-ray Diffraction: Fig. 3 presents the wide angle X-ray diffractograms of (a) pure γ-CD, (b) 1-propanol-γ-CD-IC, and (c)–(f) PDMS-γ-CD-ICs of various molecular weights. In this figure, we compare the known diffraction pattern of 1-propanol-γ-CD-IC that has been identified from the structure of its single crystal to be of the channel form [26], with those of pure γ-CD and PDMS-γ-CD-ICs. The key feature that serves as a fingerprint for the channel type structure of γ-CD-ICs is the peak at about $2\theta \cong 8.0°$. As can be observed, this feature is not present in the pure γ-CD, which adopts a cage structure, but is observed in all the PDMS-γ-CD-IC samples. This strongly supports the inclusion of PDMS chains within the cylindrical cavities of γ-CD.

Similarly in Fig. 4 is shown the wide angle X-ray diffractogram of pure (a) γ-CD, (b) pure PAN, (c) 1-propanol-γ-CD-IC, and (d) PAN-γ-CD-IC. Again we observe the correspondence of the $2\theta \cong 8.0°$ in the 1-propanol-γ-CD-IC with that of PAN-γ-CD-IC. Also the diffraction pattern of the PAN-γ-CD-IC is different from those of pure γ-CD and pure PAN.

FTIR Spectroscopy: Shown in Fig. 5 are the FTIR spectra of PDMS-γ-CD-IC, pure PDMS and pure γ-CD in the frequency region of 800–1600 cm^{-1}. The key feature in this spectrum is the absorption due to the symmetric C–H deformation modes [27] of methyl groups at 1263 cm^{-1}.

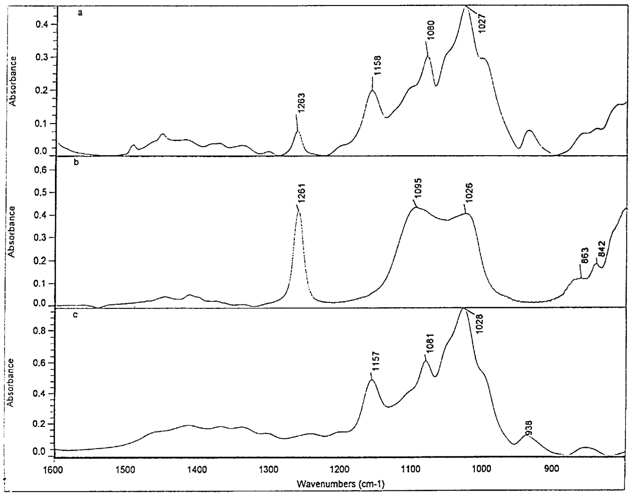


Fig. 5. FTIR spectra in the region between 800 and 1600 cm^{-1}: (a) PDMS-γ-CD-IC, (b) pure PDMS (MW = 1250), and (c) pure γ-CD.

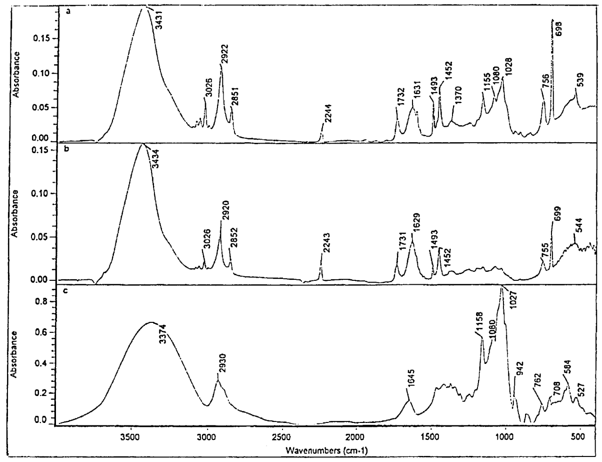


Fig. 7. FTIR spectra in the region between 400 and 4000 cm^{-1}: (a) PAN-γ-CD-IC, (b) pure PAN, (c) pure γ-CD.

This band is present in the absorption spectrum of PDMS-γ-CD-IC (5a), while it is clearly absent in the absorption spectrum of pure γ-CD (5c). This observation also suggests the inclusion of PDMS within the channels of γ-CD. Fig. 6 similarly presents absorption spectra within the frequency range of 800–1600 cm^{-1} of the ICs of PDMS of various molecular weights with γ-CD, and again the 1263 cm^{-1} absorption band is observed.

FTIR was also used to infer the formation of PAN-γ-CD-IC from the results presented in Fig. 7, where the absorption spectra of PAN-γ-CD-IC, pure PAN, and pure γ-CD in the region between 400 and 4000 cm^{-1} are shown. The key absorption frequencies of PAN [28] are 2920 and 2851 cm^{-1} assigned to the anti-symmetric and symmetric stretch respectively of the CH2 group, the C≡N stretching vibration at 2243 cm^{-1} and the CH2 vibrations at 1493 and 1452 cm^{-1}. These bands appear in the absorption spectrum of PAN-γ-CD-IC, but are absent in the absorption spectrum of pure γ-CD, again suggesting the inclusion of PAN in the narrow channels of the PAN-γ-CD-IC.

Thermal analysis. The TGA thermograms of pure γ-CD and the ICs of PDMS with γ-CD are presented in Fig. 8. The samples were subjected to thermal treatment at a heating rate of 20°min^{-1} between 25 and 400°C. However, for sharper focus, we show in Fig. 8 only the data for the temperature range between 280–380°C. These results show that with the lower molecular weight (237 and 770) samples of PDMS-γ-CD-IC, in Fig. 8a and b, respectively, the onset of thermal decomposition starts at about 310°C. This is 16°C lower than the onset of thermal decomposition in pure-γ-CD at about 326°C, Fig. 8c. While for samples

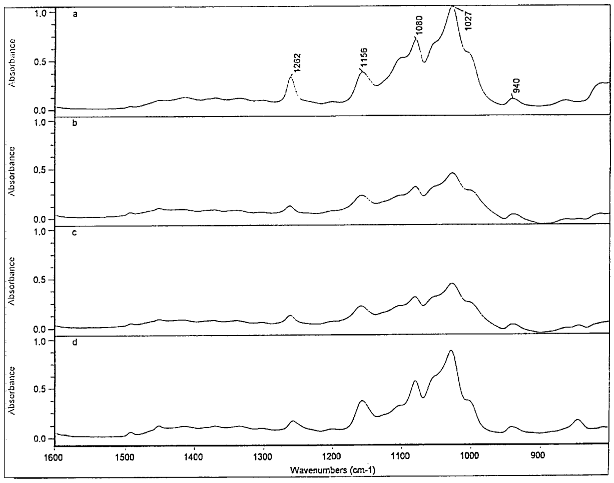


Fig. 6. FTIR spectra in the region between 800 and 1600 cm^{-1} of PDMS of various molecular weights within γ-CD-ICs: (a) 62,700, (b) 1250, (c) 770, and (d) 327.

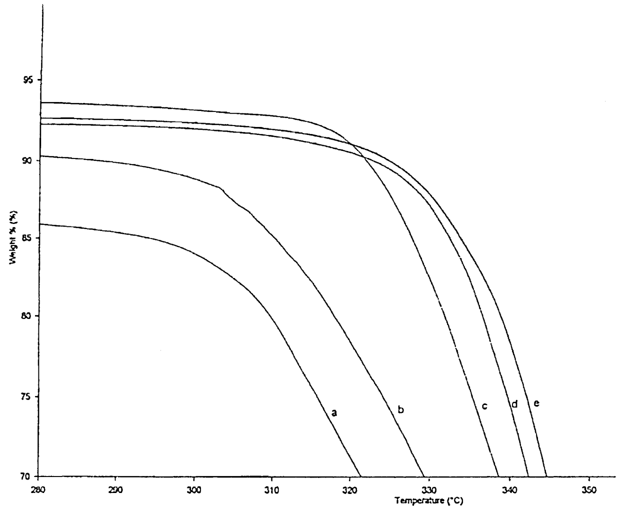


Fig. 8. TGA scans of pure γ-CD and PDMS-γ-CD-IC of various molecular weights: (a) 237, (b) 770, (c) pure γ-CD, (d) 1250, (e) 62,700.

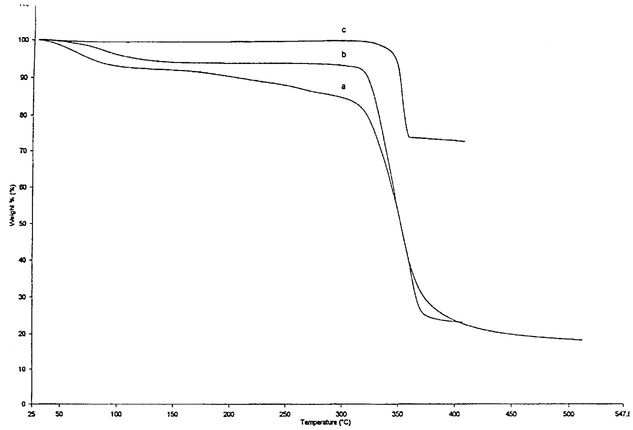


Fig. 9. TGA scans of: (a) PAN-γ-CD-IC, (b) pure γ-CD, (c) pure PAN.

with higher molecular weight (1250 and 62,700), Fig. 8d and e, respectively, the onset of thermal decomposition started at about 335°C, which is 11°C higher than that of pure-γ-CD. This suggests that the thermal stability of the ICs is influenced by the molecular weight of the guest polymer.

In Fig. 9, the TGA thermograms of PAN-γ-CD-IC, pure γ-CD, and pure PAN are shown. Here the onset of thermal decomposition of the IC is at about 331°C, which is slightly higher than that of the pure γ-CD at 326°C. This suggests a higher thermal stability of the IC over the pure γ-CD.

Solid-state CP/MAS ^{13}C-NMR Spectroscopy. The solid-state CP/MAS ^{13}C-NMR spectra of free CDs show splitting in several of the carbon resonances. This indicates that the CD crystals are in a rigid, non-symmetric conformation. With the presence of a guest in the cavities of the channel crystal structure, the carbon resonances of the cyclodextrins show reduced splitting and are broader indicating the crystals have adopted more symmetric and possibly dynamic conformations. In Fig. 10 is shown the CP/MAS ^{13}C-NMR spectra of (a) PDMS-γ-CD-IC, and (b) pure γ-CD. In Fig. 10a, we observe the resonance of the methyl group of PDMS at 1.84 ppm. Also the resonances of the CD carbons in the IC are well defined compared to the split resonances of the free γ-CD. This is further evidence supporting the formation of an IC between PDMS and γ-CD.

In the CP/MAS ^{13}C-NMR spectra of PAN-γ-CD-IC and pure PAN, which are not presented here, we noticed that the resonances of the γ-CD carbons are fewer in number when compared to those of the free γ-CD. Once again this suggests the presence of an included guest enabling the γ-CD molecules to adopt more symmetric conformations in the γ-CD-IC channel form crystal. The resonance of the nitrile carbon at 119.4 ppm, and the resonances of the methylene and methine carbons at 36.3 and 30.9 ppm, which are not clearly distinguished in the bulk PAN sample, are observed when the IC is formed. This further suggests that in PAN-γ-CD-IC the guest PAN chains are isolated in the narrow channels of the host crystalline lattice formed by γ-CD.

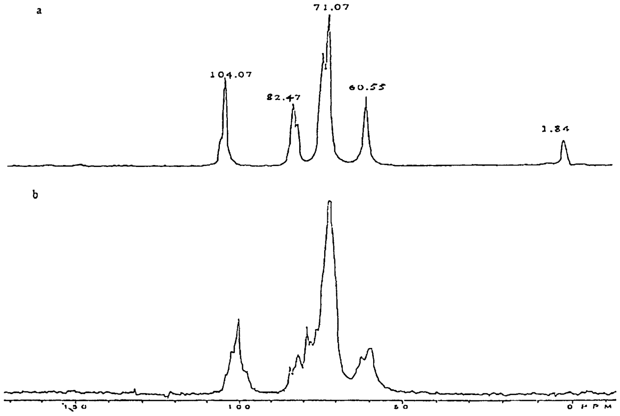


Fig. 10. CP/MAS of ^{13}C-NMR spectra of (a) PDMS-γ-CD-IC, (b) pure γ-CD.

In summary, we confirm the formation of ICs of PDMS and PAN with γ-CD. Both complexes are observed to be of the channel type from characterization using FTIR, TGA, WAXS, and solid-state ^{13}C NMR. After coalescence of the polymers from their ICs, we now have PDMS samples with no cycles and PAN chains possibly organized into a solid-state morphology different from samples generated by melt or solution processing. We further intend to study the dynamic motions of the isolated PAN chains in the γ-CD and compare them to the motions observed for the chains in bulk PAN samples, including those coalesced from their γ-CD-IC crystals. This should aid in the elucidation of the nature of inter/intramolecular interactions and the assessment of how importantly polymer chain cooperativity affects the bulk properties of PAN.

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