Available online at www.sciencedirect.com

SCIENCE DIRECT®

European Polymer Journal 41 (2005) 2483–2487

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Preparation of β-cyclodextrin–polyaniline complex in supercritical CO_2

Bo Wang, Jun He *, Donghai Sun, Rui Zhang, Buxing Han *,
Ying Huang, Guangying Yang

Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 10 September 2004; received in revised form 25 February 2005; accepted 28 April 2005

Abstract

A method is proposed to prepare β-cyclodextrin (β-CD)/polyaniline (PANI) inclusion complex. In this route, benzoyl peroxide (BPO, the oxidant) is first encapsulated into the cavity of β-CD. Aniline is then carried into the cavity of β-CD by supercritical (SC) CO_2, which polymerizes in situ to form inclusion complex. The product is characterized by FT-IR, UV–Vis, ^1H NMR and XRD techniques. The results suggest that the columnar inclusion complexes may be formed.

Keywords: Inclusion complex; Supercritical CO_2; β-Cyclodextrin; Polyaniline

1. Introduction

Cyclodextrins (CDs), such as α-, β-, γ-CD, are cyclic molecules consisting of six to eight glucose units. The cylindrical structure with the hydrophobic cavities about 0.7 nm in depth and 0.5–0.8 nm in diameter yields various unique properties. For example, they can form complexes with various small molecules by including them into the cavity [1]. Since the report that CDs can thread onto a polymer chain [2,3], much interest has been concentrated on preparing inclusion complexes of CDs and polymers [4–6].

Polyaniline (PANI) has emerged as one of the most promising organic conducting polymers due to its high environmental stability, facile redox, pH switch behavior, and low cost [7,8]. Polymerization of aniline within the cavity of clay [9] and zeolite [10] have been reported. Recently, Ito and co-workers [11,12] found that it was possible for PANI to form inclusion complex with β-CD in organic solvents at low temperature, and Yuan et al. developed an in situ polymerization method in aqueous solution [13]. However each of the method have disadvantages, such as the residue of solvent in the product and difficulty in dealing with the product after the reaction, so finding a better solvent to prepare complex is desirable.

There has been increasing interest in using supercritical carbon dioxide (SC CO_2) as a substitute for conventional organic solvents because it has high diffusivity, low viscosity, near zero surface tension, mild critical parameters, and it is nontoxic, nonflammable, and inexpensive. In recent

---

* Corresponding authors. Tel.: +86 10 62562821; fax: +86 10 62559397.

E-mail addresses: hejun@iccas.ac.cn (J. He), hanbx@iccas.ac.cn (B. Han).

0014-3057/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2005.04.036

years, SC CO_2 has been used widely in materials science [14–16], such as preparing polymer–polymer composites [17,18], impregnation of carbon nanotubes with metal [19] and polymer [20], impregnating different additives into polymer matrices [21].

In this work, we report the preparation of inclusion complex between β-CD and PANI using SC CO_2 for the first time. In this process, benzoyl peroxide (BPO) was encapsulated into β-CD as an oxidant, aniline was then carried into the cavity of β-CD by SC CO_2 where aniline was polymerized to form inclusion complex because aniline is partially soluble in SC CO_2 [22,23]. After the reaction, SC CO_2 can be easily removed only by releasing the pressure, and there is no residue of solvent in the product. We believe that the environmentally benign method can be used to prepare some other CD-based complexes.

2. Experimental

2.1. Materials

β-cyclodextrin was purchased from Aldrich Co. and used as received. Aniline (A. R. grade) was provided by Beijing Chemical Reagent Center. Benzoyl peroxide (BPO) was recrystallized twice from methanol. CO_2 with a purity of 99.95% was supplied by Beijing Analytical Instrument Factory and used as received.

2.2. Preparation of inclusion complex

BPO (0.15 g) was first dissolved in 10 ml ethanol. The solution was mixed with 45 ml aqueous β-CD solution (1.5 wt.%) with vigorously stirring, and white precipitate was obtained. The precipitate was washed with acetone to remove excess BPO, and BPO–β-CD complex was obtained by centrifugation.

BPO–β-CD complex (4 g) was loaded into a stainless steel cell of 30 ml. A small glass tube with 0.2 g of aniline was placed into the cell. The BPO–β-CD complex and aniline in the cell was separated by the wall of the glass tube. The cell was placed in a water bath of 35.0 °C. CO_2 was compressed into the cell up to 16 MPa. The aniline dissolved in SC CO_2 diffused into BPO–β-CD complex and polymerized. After a reaction time of 12 h, the system was depressurized to atmospheric pressure. Blue powder was observed at the bottom of cell. The powder was washed with water and acetone to remove excess free β-CD and oligomers in the product.

2.3. Characterization

The FT-IR spectra of the samples pressed in a KBr pellet were collected on a Bruker IR spectrometer (TENSOR 27). UV–Vis spectra were determined on a TU-1201 model spectrophotometer (resolution: 0.5 nm). ^1H NMR spectra were recorded with DM-300 (Bruker) spectrometer in DMSO-d_6. X-ray power diffraction (XRD) analysis was carried out by a D/MAX. RB diffraction-meter (made in Japan) with Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 200 mA. The scanning speed and the step were 2°/min and 0.02°, respectively.

3. Results and discussion

3.1. FT-IR

The FT-IR spectra of β-CD, PANI, the product and the physical mixture of PANI and β-CD are shown in Fig. 1. Compared with the spectrum of the pure β-CD, the spectrum of the product shows peaks that related to the PANI, the peak at 1605 and 1330 cm^{-1} corresponding to the stretching of N=Q=N ring and the aromatic C–N stretching in PANI, where Q represents the quinoid structure. This confirms the existence of the PANI in the product. For pure PANI, the two peaks mentioned above are at 1570 and 1306 cm^{-1} [24], respectively. In the physical mixture of the PANI and β-CD, the wave numbers of these two peaks are the same with those of pure PANI. All these suggest that PANI and β-CD in the product are not simply blended. The N atoms of the polymer chain probably provide the electron to form hydrogen bond [25]. As a result, the wave numbers of the two peaks of PANI in the inclusion complex are different from that of pure PANI and in the physical mixture of PANI and β-CD.

3.2. UV–Vis

It is well-known that PANI is insoluble in water and common organic solvents due to its conjugation

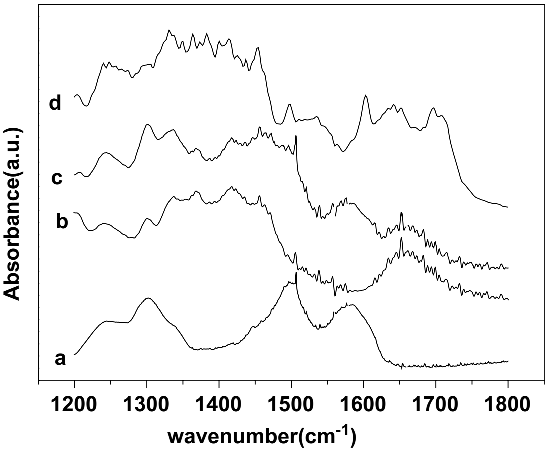

Fig. 1. FT-IR spectra of PANI (a), β-CD (b), physical mixture of PANI and β-CD (c), and product (d).

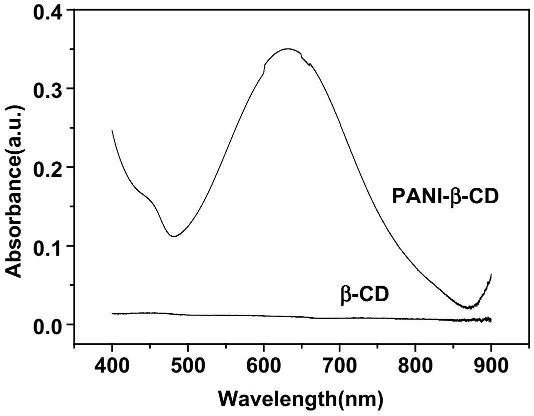

Fig. 2. The UV–Vis spectra of β-CD and PANI-β-CD inclusion complex in DMSO.

structure. But the product of this work is partly soluble in DMSO (dimethyl sulfoxide) and some other organic solvents. The enhanced solubility may come from the stronger solvation between the β-CD and the solvents. As a result, the compact coil structure of the polymer is transferred into an expanded coil or linear structure as reported by other authors [26]. UV–Vis spectra of pure β-CD and the product in DMSO are shown in Fig. 2. It can be seen that the complex has absorption band at about 630 nm, while the pure β-CD has no absorbance between 400 and 900 nm. So this band is likely to attribute to the excitation band of the quinoid ring on the chain of the PANI [27,28]. Furthermore, the CO group present in β-CD molecule may form hydrogen bond with the H that present on the N atoms of the polymer chain. So the polarons become weak, which results in the weak absorbance at higher wavelength [25].

3.3. ^{1}H NMR

^{1}H NMR spectra of pure β-CD and the complex are shown in Fig. 3. The assignment of chemical shift of pure β-CD is illustrated in Fig. 3a [29,30]. For the complex (Fig. 3b), the chemical shift at 4.85 ppm is assigned to the glucose ring in β-CD [30], and that at about 7 ppm is likely attributed to the benzene ring in PANI [31]. As aniline and oligomers were washed away by acetone, the result also confirmed the existence of PANI and β-CD in the products. After integration of the peaks in Fig. 3b, it

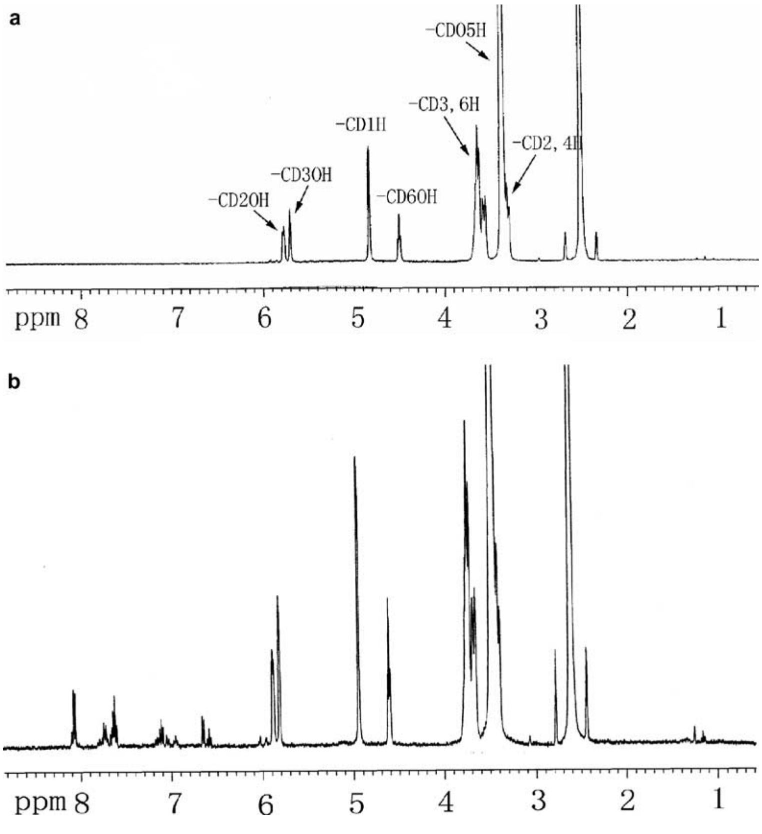

Fig. 3. ^{1}H NMR spectra of β-CD (a) and PANI-β-CD complex (b) in DMSO-d_6.

Table 1
^{1}H NMR data for the β-CD and PANI-β-CD complex

	β-CD (ppm)	PANI-β-CD (ppm)
β-CD-H1	4.82	4.82
β-CD-H2	3.31	3.31
β-CD-H3	3.56	3.66
β-CD-H4	3.35	3.36
β-CD-H5	3.51	3.61
β-CD-H6	3.63	3.64
β-CD-2-OH	5.76	5.76
β-CD-3-OH	5.68	5.69
β-CD-6-OH	4.48	4.49

can be known that the ratio of PANI and β-CD in the complex is about 1:1. Furthermore, as can be seen from Table 1, compared to pure β-CD, the chemical shift of the interior protons H-3, H-5 in the product [29] have movee upfield, which is perhaps due to the direct interaction of these protons with PANI molecule. In contrast, the chemical shifts of outer protons H-2 and H-4 [29] are relatively unchanged, indicating the interaction occurs inside the cavity instead of the exterior of the torus. The shifts were detectable and producible. Therefore, this provides further evidence for the formation of the inclusion complex.

3.4. XRD

X-ray diffraction (XRD) can give useful information about inclusion complex of CDs and other polymers, their structure can be classified as cage-type or column-type [32]. We also use XRD to characterize the product in this work. The XRD patterns of pure β-CD and the product are given in Fig. 4. From the figure it can be seen that the number of reflection peaks of the product is less than that of pure β-CD. The pattern has two major peaks at 2θ = 11.80 and 17.72, suggesting that the β-CD molecules in the complex are in more ordered form [33]. The pattern of complex is similar to that of the columnar inclusion complexes between β-CD and poly (1,3-dioxolane) (PDXL) [34] or poly (propylene glycol) (PPG) [35]. This implies that the β-CD molecules may be rearranged one by one and thread on the chain of PANI in the product. Based on the chemical structures of PANI and β-CD, we deduce that the inclusion complex is a pseudopolyrotaxane.

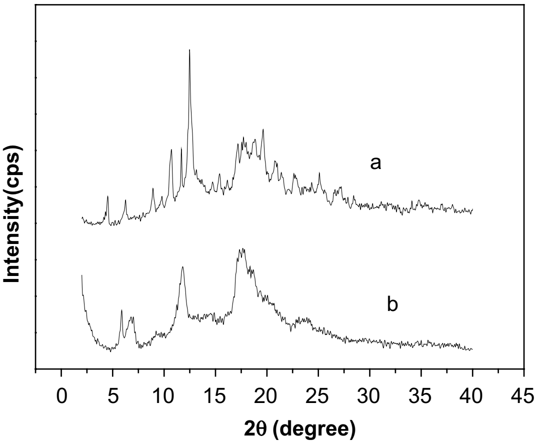

Fig. 4. The X-ray diffraction of β-CD (a) and PANI-β-CD inclusion complex (b).

4. Conclusions

In summary, the inclusion complex between polyaniline and β-CD was prepared in SC CO_2. The formation of inclusion complex was confirmed by UV–Vis and FT-IR. The ^{1}H NMR and XRD analysis suggests that the β-CD molecules is threaded onto the chain of PANI and forms columnar inclusion complex. SC CO_2 is a useful medium to synthesize inclusion CDs/polymer complexes.

Acknowledgement

This work was supported by National Natural Science Foundation of China (20373080, 20133030).

References

[1] Szejtli J. Cyclodextrins and their inclusion complexes. Budapest: Akademial Kiado; 1982.
[2] Harada A, Li J, Kamachi M. Nature 1992;356:325.
[3] Harada A, Li J, Kamachi M. Macromolecules 1993;26:5698.
[4] Steinbrunn MB, Wenz G. Angew Chem Int Ed 1996;35:2139.
[5] Weicknmeier M, Weng Z. Macromol Rapid Commun 1997;18:1109.
[6] Okada M, Kamachi M, Harada A. J Phys Chem B 1999;103:2067.
[7] Jelle BP, Hagen GJ. J Electrochem Soc 1993;140:3560.
[8] Lindfors T, Ivaska A. J Electroanal Chem 2002;531:43.
[9] Wu Q, Xue Z, Qi Z, Wang F. Polymer 2000;41:2029.
[10] Enzel P, Bein T. J Phys Chem 1989;93:6270.
[11] Yoshida K, Shimomura T, Ito K, Hayakawa R. Langmuir 1999;15:910.
[12] Shimoura T, Yoshida K, Ito K, Hayakawa R. Polym Adv Technol 2000;11:83.
[13] Yuan GL, Kuramoto N, Takeshi M. Poly Adv Technol 2003;14:428.
[14] Cooper AI, Holmes AB. Adv Mater 1999;11:1270.
[15] Kendall JL, Canelas DA, Young JL, Desimone JM. Chem Rev 1999;19:543.

[16] Mchugh MA, Krukonis VJ. Supercritical fluid extraction: principle and practice. 2nd ed.. Boston: Butterworth–Heinemann; 1994.

[17] Watkins JJ, Mccarthy TJ. Macromolecules 1994;27:4845.

[18] Li D, Han BX. Macromolecules 2000;33:4550.

[19] Watkins JJ, Blackburn JM, Mccarthy TJ. Chem Mater 1999;11:213.

[20] Ye XR, Lin YH, Wang CM, Wai CM. Adv Mater 2003;15: 316.

[21] Morley KS, Marr PC, Webb PB, Berry AR, Allison FJ, Moldovan G, et al. J Mater Chem 2002;12:1898.

[22] Kainz S, Brinkmann A, Leitner W, Pfaltz A. J Am Chem Soc 1999;121:6421.

[23] Wagner KD, Brudi K, Dahmen N, Schmieder H. J Supercrit Fluid 1999;15:109.

[24] Fu YP, Weiss RA. Synth Met 1997;84:103.

[25] Chen SA, Lee HT. Synth Met 1992;47:233.

[26] MacDiarmid AG, Epstein AJ. Synth Met 1994;65:103.

[27] Zhang WJ, Feng J, Macdiarmid G, Epstein J. Synth Met 1997;84:119.

[28] Wilbur JM, Sandreczki TC, Brown IM, Leopold DJ, Mohite S. Synth Met 1996;82:175.

[29] Forgo P, Vincze I, Kövér KE. Steroids 2003;68:321.

[30] Manolikar MK, Sawant MR. Chemosphere 2003;51:811.

[31] Abd El-Ghaffar MA, Youssef EAM, Darwish WM, Helaly FM. J Elastomers Plast 1998;30:168.

[32] Mcmullan RK, Saenger W, Fayos J, Mootz D. Carbonhydr Res 1973;31:211.

[33] Jiao H, Goh SH, Valiyaveettil S. Macromolecules 2001;34: 1542.

[34] Li JY, Yan DY. Macromolecules 2001;34:211.

[35] Harada A, Kamachi M. Chem Commun 1990:1322.