

Reorganization of the Chain Packing Between Poly(ethylene isophthalate) Chains via Coalescence from Their Inclusion Compound Formed with γ -Cyclodextrin

Kyeong Pang, Ben Schmidt, Richard Kotek, Alan Tonelli

Textile Engineering, Chemistry, and Science (TECS), College of Textiles, North Carolina State University, Raleigh, North Carolina 27695-8301

Received 5 January 2006; accepted 13 February 2006

DOI 10.1002/app.25217

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Amorphous poly(ethylene isophthalate) (PEI) was synthesized, and was used for preparing an inclusion compound (IC) with γ -cyclodextrin (γ -CD). Coalesced polymer was produced by washing the PEI- γ -CD-IC with hot water. Wide angle X-ray diffraction, Fourier transform infrared, and differential scanning calorimetry analyses were employed to verify formation of PEI- γ -CD-IC and to compare the as-synthesized and coalesced PEI samples. These observations suggested that the conformations and morphology/chain-packing of PEI were changed via coalescence from its γ -CD inclusion compound. The glass-transition temperature of the amorphous coalesced PEI is 15–20°C higher than the

T_g observed for the as-synthesized sample, even when observed in the second heat after cooling from well above T_g at 260°C. The amorphous as-synthesized PEI retains its randomly-coiling structure, while coalesced PEI has at least partially retained, the highly extended and parallel chains from the narrow channels of the inclusion compound, resulting in better/tighter packing among the PEI chains manifested by a higher T_g . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 6049–6053, 2006

Key words: poly(ethylene isophthalate); synthesis; γ -cyclodextrin; inclusion complex; coalesced PEI

INTRODUCTION

Cyclodextrins are cyclic oligosaccharides obtained by enzymatic digestion of starch (Fig. 1). They consist of six, seven, and eight glucose units linked by 1,4- α -glucosidic bonds for α -, β -, and γ -cyclodextrin, respectively. Their shallow truncated cone shapes make them act as host molecules for the inclusion of both small and long molecule guests, including aromatic esters,^{1–3} which may lead to the formation of noncovalent, crystalline inclusion compounds. Packing of the CD molecules within the crystal lattice occurs in one of two principal modes (Fig. 1): cage and channel structure.⁴ In the cage structure, both ends of the cavity are blocked by adjacent CDs. CDs usually adopt this cage structure in its pure crystal hydrates. In the channel structure, the CDs are stacked to form endless columns in the crystal. In polymer-CD inclusion compounds, CD molecules are stacked into the channel structure, and the guest polymer chains are included in the CD columns.

Bullions et al.² produced poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (PC) samples by the coalescence of their segregated, extended

chains from the narrow channels of the crystalline inclusion compounds (ICs) formed with γ -cyclodextrin (γ -CD) host. They reported that the coalesced PC crystallized in a predominantly chain extended morphology, whereas the coalesced PET crystallized in a chain-folded morphology.² More importantly, in the case of PET crystallized during coalescence from its γ -CD-IC, the noncrystalline portions of the sample were found to predominantly adopt highly extended $g^{\pm} t g^{\mp}$ kink conformations, which resulted in the following behaviors: (i) coalesced-PET was repeatedly and rapidly crystallizable from the melt, and (ii) a glass-transition (T_g) was not observed for the coalesced sample of PET.

In this study, we investigate the potential changes in the bulk behavior of the structurally related and usually amorphous polymer, poly(ethylene isophthalate) (PEI),^{5,6} after coalescence from its inclusion compound formed with host γ -CD.

EXPERIMENTAL

Materials

Poly(ethylene isophthalate) (PEI) was synthesized in our laboratory from pure isophthalic acid (IPA) and ethylene glycol (EG supplied by Amoco and Dupont, respectively). Zinc acetate and antimony trioxide were obtained from Aldrich. γ -Cyclodextrin (γ -CD)

Correspondence to: A. Tonelli (alan_tonelli@ncsu.edu).

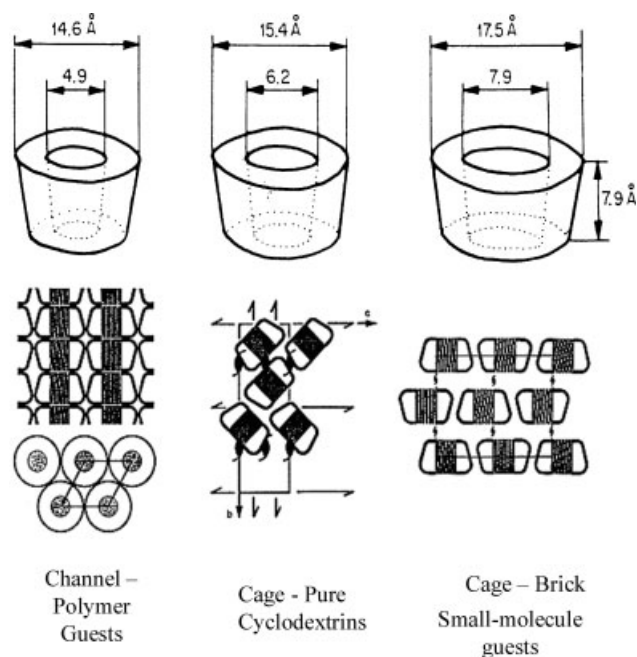


Figure 1 Structures and molecular dimensions of α -, β -, and γ -cyclodextrins (top) and cyclodextrin crystal structures (bottom).

was obtained from Cerestar (Hammond, IN). Tri-fluoroacetic acid (TFA), chloroform (CLF), and 1,1,2,2-tetrachloroethane (TCE) were all obtained from Aldrich.

Synthesis of PEI

The synthesis was carried out in two different steps. IPA and EG in a molar ratio of IPA/EG = 1/2.5 and the catalysts, zinc acetate (0.15 wt % based on weight of IPA) and antimony trioxide (0.05 wt % based on weight of IPA) were added into a reactor. In the first step, the esterification reaction was conducted at 200°C under nitrogen atmosphere. The reaction mixture was stirred at a constant speed. During the reaction, water was distilled and collected as a byproduct. In the second step (polycondensation), the oligomers, made in the first step, were heated at 222 and 264°C and a vacuum was applied slowly. The condensation reaction was continued for 5 h. The resultant PEI has a molecular weight of $\sim 20,000$ g/mol as estimated by its solution viscosity.

Preparation of PEI- γ -CD inclusion compound

PEI solution was prepared by dissolution of 0.5 g of PEI in 20 mL of solvent (TFA/CLF 1/4 mixture or TCE) at 55°C. The solution was stirred for 45 min. A saturated aqueous solution of γ -CD was prepared by dissolution of 2 g of γ -CD in 10 mL of deionized water at room temperature. The γ -CD solution was

slowly added into the PEI solution, and a white gel-like foam formed on top of the liquid mixture. The precipitated mixture was stirred for 3 h in the 55°C oil bath. It was then cooled down to room temperature, allowed to settle for about 24 h, and was finally vacuum-filtered and dried in a vacuum oven at 50°C.

Preparation of γ -CD/solvent control

1 g of γ -CD was dissolved in 5 mL of deionized water at 55°C. The γ -CD solution was added dropwise into the solvent (TFA/CLF 1/4 v/v mixture). During the addition, a white foam was formed. The foam was filtered and dried under vacuum at 60°C for 15 h after stirring for 24 h at 50°C.

Preparation of PEI/solvent control

The procedure for PEI- γ -CD-IC formation was duplicated except that γ -CD was not dissolved in the deionized water that was added to the TFA/CLF solution of PEI.

Preparation of coalesced PEI

Coalesced PEI was obtained by washing the PEI- γ -CD-IC several times with boiling water over a period of 5–6 h, filtering off the coalesced PEI, and then drying the PEI precipitate under vacuum at 50°C.

Preparation of a PEI/ γ -CD physical mixture

A few percent of γ -CD were suspended in the TFA/CLF solution of PEI used to make the PEI- γ -CD-IC. This suspension was quickly poured into a large excess of acetone, which caused the PEI to precipitate, creating a PEI/ γ -CD physical mixture.

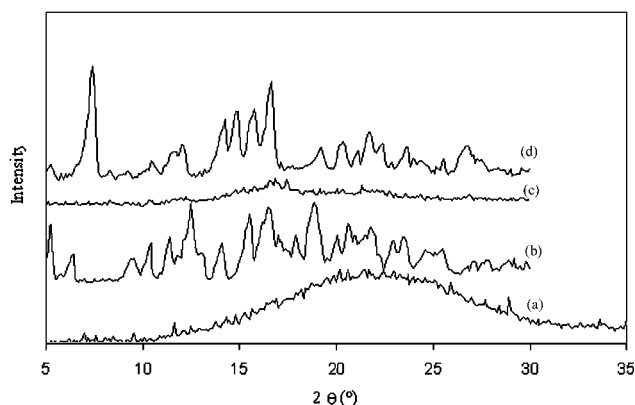


Figure 2 WAXD results for PEI samples: (a) as synthesized PEI, (b) γ -cyclodextrin, and PEI- γ -CD inclusion compounds prepared in (c) tetrachloroethane and (d) in trifluoroacetic acid/chloroform mixed solvent.

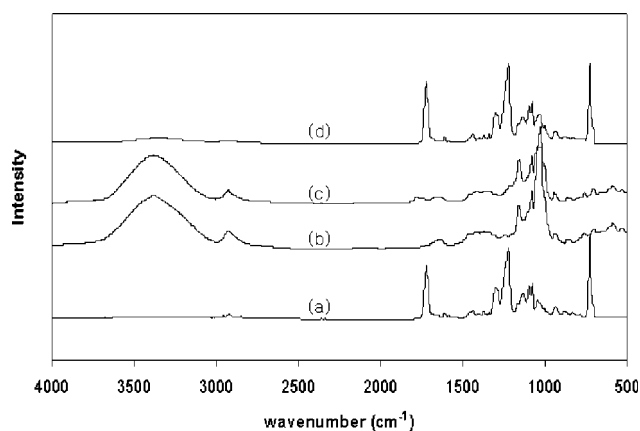


Figure 3 FTIR spectra of (a) as-synthesized PEI; (b) γ -cyclodextrin; (c) PEI- γ -CD-IC; and (d) coalesced PEI.

Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) measurements were carried out with a Siemens type-F X-ray diffractometer. A Ni-filtered Cu $K\alpha$ radiation source (1.54 Å) was used for the measurement. The supplied voltage and current were 30 kV and 20 mA, respectively. All specimens were scanned from $2\theta = 5$ to 30 or 35° at a rate of $2\theta = 2^\circ/\text{min}$.

Differential scanning calorimetric analyses

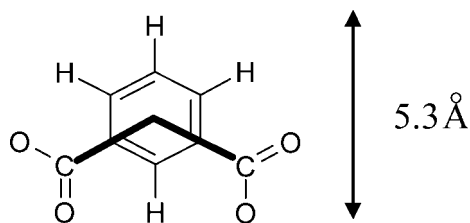
The DSC scans were performed with a PerkinElmer DSC-7 differential scanning calorimeter. The measurements were run from 25 to 260°C at heating and cooling rates of $10^\circ\text{C}/\text{min}$.

Fourier-transform infrared spectroscopy

The FTIR spectral analyses were carried out in a Nicolet 510P FTIR spectrometer between 4000 and 400 cm^{-1} with samples in the form of pressed KBr pellets.

RESULTS AND DISCUSSION

The minimal cross-sectional dimensions of a PEI polymer chain was approximated as 5.3 \AA .



Thus, though α -CD is likely too small, PEI may fit in both β - and γ -CD hosts (Fig. 1). However, the crystalline packing of β -CD in its channel and cage

structures is well-known to be difficult to distinguish by powder X-ray diffraction.⁷ In the case of γ -CD, however, cage and channel structures can easily be distinguished by X-ray diffraction.² As a consequence, γ -CD was chosen as the host for PEI in our investigation.

Figure 2 shows WAXD patterns for PEI, γ -CD, and their inclusion compounds. As-synthesized PEI is amorphous as seen in its X-ray pattern, which, though not shown, is virtually identical to the X-ray pattern exhibited by coalesced PEI. Channel-structure inclusion compounds formed by γ -CD are well-known to show a strong peak at $2\theta = 7.5^\circ$ in their diffraction patterns, which has been suggested as an indicator for the channel structure.² The peak at $2\theta = 7.5^\circ$ is shown clearly in the pattern of PEI- γ -CD-IC obtained with the TFA/CLF solvent system. That means there was almost no free PEI and all polymer chains occupied the narrow cylindrical channels created by the stacks of γ -CD (Fig. 1) in the inclusion compound sample prepared with TFA/CLF solvent. On the other hand, the X-ray pattern of the solid precipitate obtained with TCE does not show the indicator peak. The polymer chains do not occupy the channels of γ -CD, because the γ -CDs are not packed into the channel structure, but rather the cage structure, when using the TCE solvent system. Instead, the narrow cavities of γ -CDs might be occupied by solvent molecules in this case.

Figure 3 shows FTIR spectra for PEI, γ -CD, and their inclusion compound. For γ -CD, the band at 1080 cm^{-1} is contributed by coupled C—C/C—O stretching vibrations, and the band at 1158 cm^{-1} is attributed to the antisymmetric stretching vibration of the C—O—C glycosidic bridge.² The PEI- γ -CD-IC obtained from TFA/CLF shows almost the same spectrum as pure γ -CD except for the peak at 1760 cm^{-1} , which is assigned to the carbonyl group of PEI. This means PEI and γ -CD make an inclusion compound under the TFA/CLF environment of poly-

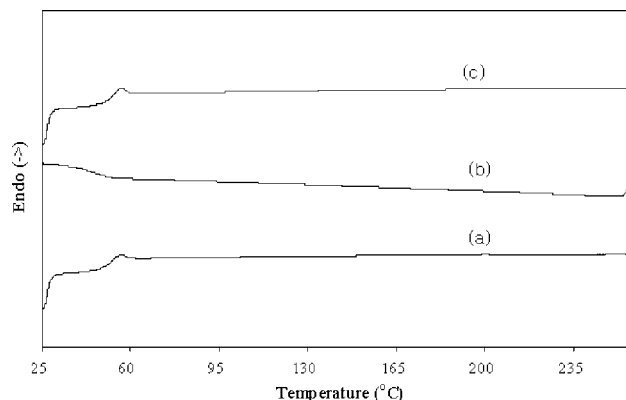


Figure 4 DSC scans for as-synthesized PEI; (a) first heating, (b) cooling, and (c) second heating.

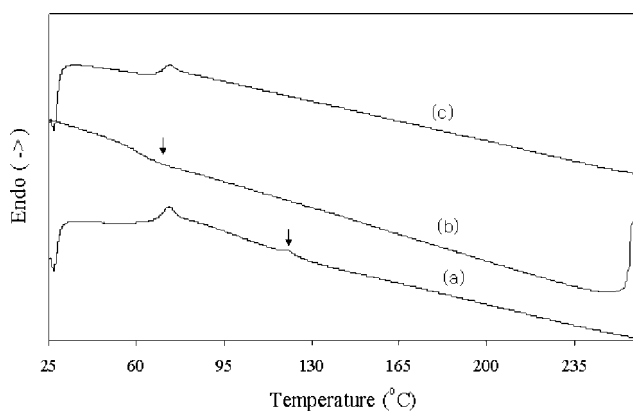


Figure 5 DSC scans for coalesced PEI; (a) first heating, (b) cooling, and (c) second heating.

mer-IC fabrication. The spectrum for IC-coalesced PEI (spectrum (d) in Fig. 3) is almost the same as that of as-synthesized PEI (spectrum (a) in Fig. 3), though the small broad peak beyond 3000 cm^{-1} in the spectrum of IC-coalesced PEI might be from the hydroxyl groups of water remaining in the sample. This means that the host γ -CDs were nearly completely removed by washing the inclusion compound with boiling water to coalesce the included PEI.

Changes in the thermal behavior of PEI coalesced from PEI- γ -CD-IC were investigated via DSC. All samples were heated from 25 to 260°C and then cooled down to 25°C and heated again to 260°C . The heating and cooling rates were $10^\circ\text{C}/\text{min}$. The DSC curves for as-synthesized PEI are shown in Figure 4. They do not show any melting or crystallization peaks. Both the first heating and second heating scans show glass transition temperatures in the range ~ 50 – 55°C . The as-synthesized PEI was originally an amorphous material and did not crystallize during heating or cooling at $10^\circ\text{C}/\text{min}$ in the DSC (Fig. 4). Although not present here, the DSC observations made on the PEI control were virtually identical to the results presented in Figure 4 for as-synthesized PEI.

Figure 5 shows the DSC scans for the PEI sample obtained by hot water coalescence from PEI- γ -CD-

IC. The first heating curve (a) shows a glass transition and a very small endothermic peak at 70 and 120°C , respectively, the latter with an enthalpy (ΔH) of 0.467 J/g . For comparison, the heat of fusion of 100% crystalline PET is $\sim 120\text{ J/g}$.⁸ The cooling curve [Fig. 5(b)] shows what appears to be a small, broad glass transition at $\sim 65^\circ\text{C}$. The second heating curve [Fig. 5(c)] shows only a glass transition temperature at virtually the same temperature as observed in the first heating.

The small endothermic peak observed at 120°C in the first heat of coalesced PEI may be attributed to the vaporization of residual moisture from a small amount of remnant γ -CD in the coalesced PEI sample, because, though not shown, a similar small endotherm was observed in the DSC scan of the PEI/ γ -CD physical mixture.

The glass transition temperature of coalesced PEI is ~ 15 – 20°C higher than that of the as-synthesized PEI, though both appear completely amorphous. The glass transition shifted to a higher temperature after the inclusion in and coalescence from its inclusion compound with γ -CD. Usually polymer chains in amorphous regions start to move at the glass transition temperature. The coalesced PEI chains only begin to move at a temperature significantly higher than as-synthesized PEI chains, probably because the coalesced PEI chains are extended and their packing is more orderly than in the as-synthesized totally amorphous PEI with its randomly coiling chains. The greater extension and tighter packing of coalesced PEI chains apparently remains even after heating well above T_g to 260°C , because nearly identical elevated T_g s are observed during the first and second DSC heating scans. These observations somewhat parallel those observed previously for coalesced PET,² where in the noncrystalline sample regions chains were also more tightly packed.

The process of coalescing PEI from its inclusion compound with γ -CD has resulted in the extension and parallelization of PEI chains during the formation of the inclusion compound, which do not completely disappear after the removal of γ -CD by washing with

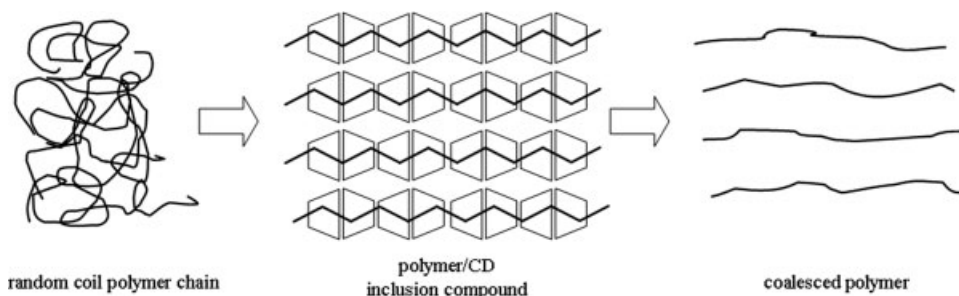


Figure 6 Schematic representation of polymer chain packing in PEI controlled by the formation of and subsequent coalescence from its γ -CD-inclusion compound.

hot water and coalescence of the PEI chains. A schematic representation of our view of the formation of and coalescence from PEI- γ -CD-IC is shown in Figure 6. The 15–20°C elevation in T_g of amorphous PEI produced by inclusion in and coalescence from PEI- γ -CD-IC is significant, the more so because the coalesced amorphous PEI with tighter chain-packing does not disorder even after heating above its T_g to 260°C.

CONCLUSIONS

PEI, its inclusion compound with γ -CD, and PEI coalesced from the IC were produced and characterized. The T_g exhibited by the amorphous coalesced PEI is substantially higher (\sim 15–20°C) than that of the as-synthesized PEI, even during the second heating of the coalesced sample. These observations are consistent with the completely amorphous, randomly-coil-

ing and the more extended and parallel, less randomly-coiling natures of PEI chains in as-synthesized and coalesced samples, respectively.

References

1. Lamcharfi, E.; Kunesch, G.; Meyer, C.; Robert, B. *Spectrochimica Acta, Part A* 1995, 51, 1861.
2. Bullions, T. A.; Wei, M.; Porbeni, F. E.; Gerber, M. J.; Peet, J.; Balik, M.; White, J. L.; Tonelli, A. E. *J Polym Sci, Part B: Polym Phys* 2002, 40, 992.
3. Bullions, T. A.; Edeki, E. M.; Porbeni, F. E.; Wei, M.; Shuai, X.; Rusa, C. C.; Tonelli, A. E. *J Polym Sci, Part B: Polym Phys* 2003, 41, 139.
4. Rusa, C. C.; Bullions, T. A.; Fox, J.; Porbeni, F. E.; Wang, X.; Tonelli, A. E. *Langmuir* 2002, 18, 10016.
5. Li, B.; Yu, J.; Lee, S.; Ree, M. *Eur Polym J* 1999, 35, 1607.
6. Sanz, A.; Nogales, A.; Ezquerro, T. A.; Lotti, N.; Finelli, L. *Phys Rev* 2004, 70, 021502.
7. Huang, L.; Taylor, H.; Gerber, M.; Orndorff, P.; Horton, J.; Tonelli, A. E. *J Appl Polym Sci* 1999, 74, 937.
8. Robert, R. C. *Polymer* 1969, 10, 113.