

# Constrained polymer chain behavior observed in their non-stoichiometric cyclodextrin inclusion complexes

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**Abstract** Much has been learned from inclusion compounds (IC's) formed between guest polymers and host cyclodextrins (CDs) [polymer-CD-ICs] by examining the properties of the fully covered guest polymers, as well as those coalesced neat bulk samples of guest polymers obtained upon removal of the host CDs. However, what can be gained from studying the properties of the restrained unthreaded portions of polymer chains that “dangle” from non-stoichiometric (n-s)-polymer-CD-IC's? We attempt to assist in answering this question by observing (n-s)-polymer-CD-IC's formed between amorphous atactic-poly(methyl methacrylate) (PMMA) and  $\gamma$ -CD, as well as the IC formed between a synthesized poly( $\epsilon$ -caprolactone)-poly(propylene glycol)-poly( $\epsilon$ -caprolactone) (PCL-PPG-PCL) triblock copolymer and  $\beta$ -CD, which was presumed to have threaded and unthreaded PPG and PCL blocks. Though our (n-s)-PMMA- $\gamma$ -CD-IC samples were found to exhibit extremely heterogeneous behaviors, glass transition temperature increases of up to 27 °C above that of neat PMMA were observed. X-ray diffraction data indicates modest  $\gamma$ -CD crystallinity at partial coverages of PMMA, with a crystal structure similar to that of the IC with full coverage. On the other hand, XRD, DSC and FTIR data revealed an almost total disruption of PCL block crystallinity upon complexation of PCL-PPG-PCL with  $\beta$ -CD, suggesting either partial threading and coverage of the PCL blocks by  $\beta$ -CD or their partial mixing with the PPG blocks covered with  $\beta$ -CD.

**Keywords** Non-stoichiometric polymer-CD-ICs · PMMA · PCL-PPG-PCL triblock

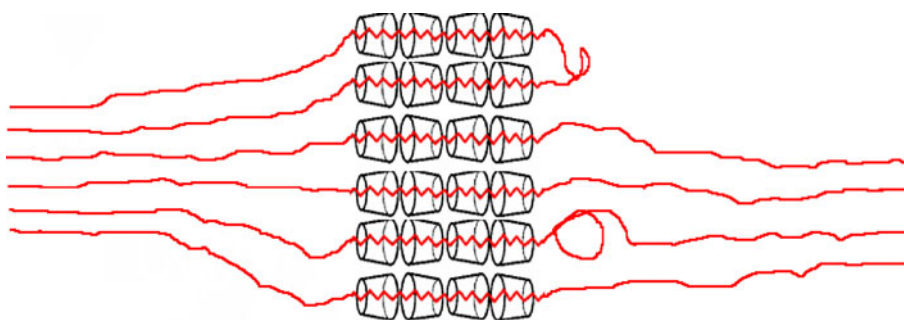
## Introduction

Though much has been learned by examining polymer properties after removal of host cyclodextrins (CDs) from their inclusion compounds (ICs) formed with CDs, or by studying the physical properties of the fully covered polymers in their CD-IC's [1], what can be gained from observing the properties of the unthreaded, yet restrained, “dangling” portions of polymers when we form partially covered, “non-stoichiometric” (n-s)-polymer-CD-IC's? As suggested in Fig. 1, (n-s)-polymer-CD-IC's are inclusion complexes that contain a CD:polymer repeat unit ratio lower than that necessary to completely cover all of each partially included polymer. The impetus for forming (n-s)-polymer-CD-IC's is the resulting unthreaded portions of polymer chains “dangling” out of the crystalline CD channels. These unthreaded chain portions are consequently restrained and closely packed, similar to a polymer brush, and are likely to display significant property differences from bulk samples of the same polymers.

Dong et al. [2–4] have recently explored (n-s)-poly( $\epsilon$ -caprolactone) (PCL)- $\alpha$ -CD-IC nucleation of melt-crystallized bulk PCL. They found that such nucleation produces a strong increase in the crystallization rate and thermal stability of the bulk material. The elastic storage modulus ( $G'$ ) was observed to increase with nucleation, as well as a higher loss component ( $G''$ ) during glass transition. Increases in the Young's modulus and yield stress of 200 and 130%, respectively, were also reported for PCL nucleated with (n-s)-PCL- $\alpha$ -CD-IC [2]. Recent work in our laboratory [5] has shown that in (n-s)-CD-IC's of nylon-6 (N6) improved physical properties, such as increased melt crystallization temperatures, are observed for the dangling N6 segments. This behavior permits (n-s)-N6-CD-IC's to be used as efficient nucleating agents for bulk N6 samples.

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**Fig. 1** Extended and highly oriented nature of un-included portions of polymer chains in their (n-s)-CD-ICs. (Note, though not drawn here, it is likely that both ends of the un-included chain portions may be further constrained by inclusion in other CD-IC crystals)



Luo et al. [6, 7] also formed (n-s)-PCL- $\alpha$ -CD-ICs and tested their physical properties. They observed that with a relatively high percentage of uncovered polymer chains ( $\sim 70\%$  uncovered PCL repeat units) and many interconnected small channel  $\alpha$ -CD-IC crystals, their (n-s)-PCL- $\alpha$ -CD-ICs behaved as a type of cross-linked, shape-memory material. Depending on the degree of coverage, recovery ratios of  $\sim 90$ – $95\%$ , and a storage modulus significantly higher than bulk as-received PCL were observed. However thermal degradation, was actually faster than for the as-received PCL.

The current view seems to be that some partially covered chains in (n-s)-polymer-CD-ICs are included in more than one CD crystal. The uncovered chain length (and subsequently, the measured properties) should vary depending on many factors, including stoichiometry (coverage), polymer crystallinity and molecular weight, and degree of CD aggregation.

Here we describe attempts to form (n-s)-IC's between completely amorphous poly (methyl methacrylate) (PMMA) and  $\gamma$ -CD with different stoichiometric ratios, and to study the behavior of the resulting uncovered portions of the PMMA chains. In an attempt to control the location of host CD molecules on guest polymer chains in (n-s)-polymer-CD-ICs, a PCL-poly (propylene glycol) (PPG)-PCL triblock copolymer was also synthesized and an IC formed with host  $\beta$ -CD. It was expected [8] that the host  $\beta$ -CDs would localize on the central PPG blocks, leaving the end PCL blocks unthreaded, thereby permitting changes in the behavior of the “dangling” PCL chains to be observed. While the un-included portions of PMMA chains are unable to crystallize, the PCL end blocks are, and, so, by comparing these two (n-s)-polymer-CD-ICs we hoped to further our understanding of the behavior of CD-constrained polymers.

## Materials and methods

PMMA ( $M_w = 15,000$  g/mol), PPG ( $M_w = 3,000$  g/mol),  $\epsilon$ -caprolactone, SnOct<sub>2</sub>, and all solvents were obtained from Sigma-Aldrich.

## PCL-PPG-PCL triblock copolymer synthesis

Polymerization of the PCL-PPG-PCL was based on the technique Shuai et al. [9] used to produce a similar polymer. 1.0 g of PPG ( $M_w = 3,000$  g/mol, dried in vacuum oven overnight), 3.0 g of  $\epsilon$ -caprolactone (twice distilled and dried with CaH<sub>2</sub>), and 16 mg of Tin(II) 2-ethylhexanoate (SnOct<sub>2</sub>) were placed in a vial, flushed with dry argon and capped, and heated at 110 °C for 3 days. The sample was dissolved in dichloromethane, precipitated in cold methanol, filtered, and dried. 2.08 g were collected, giving a yield of  $\sim 50\%$ .

Proton NMR of the triblock copolymer observed in solution suggested that the PCL:PPG repeat unit ratio was 1.8:1. Knowing that our center block consists of 3,000 g/mol PPG (approximately 52 repeat units), and assuming equal polymerization of PCL from both ends of each PPG block, we can suggest that our PCL end blocks are approximately 46 repeat units long (or  $\sim 5,300$  g/mol).

## IC formation techniques

For a majority of the (n-s) and fully covered  $\gamma$ -CD-IC samples, a method similar to that of Uyar et al. [10] was implemented. PMMA (varying molar amounts) was dissolved in 50 mL of dioxane and stirred in an oil bath at 50 °C. An appropriate amount of  $\gamma$ -CD (depending on the desired stoichiometric ratio of the sample) was dissolved in 5 mL of deionized water and then added drop-wise to the polymer solution. Upon addition of the  $\gamma$ -CD solution to the PMMA/dioxane (a non-solvent for  $\gamma$ -CD) solution, a white precipitate was formed. Though the initial precipitate was presumably mostly  $\gamma$ -CD, a PMMA- $\gamma$ -CD IC was nevertheless formed over time. The samples were stirred in the heated oil bath for 1 h, then allowed to cool for three days while stirring. They were then filtered through Whatman #6 cellulose filters and dried at elevated temperature in a vacuum oven to remove any excess solvent.

In addition, two attempts were made to form PMMA- $\gamma$ -CD-ICs using solid  $\gamma$ -CD and either pure liquid or a solution of PMMA. In the former case, solid PMMA and  $\gamma$ -CD were mixed and heated at 105 °C, while in the latter instance, solid  $\gamma$ -CD was suspended in a PMMA/dioxane solution.

To form the PCL-PPG-PCL- $\beta$ -CD-IC, 0.251 g of the synthesized triblock was dissolved in 25 mL of dichloromethane. 0.87 g of  $\beta$ -CD was dissolved in 4 mL of DMSO and added drop-wise to the polymer solution. The sample was sonicated for 10 min and allowed to stir for 3 days at room temperature. This material was filtered and dried overnight under vacuum. Unfortunately, the sample weight was not recorded, leaving us unable to provide the yield. It is important to note that all sample coverage values provided are merely the starting stoichiometric ratios. While a sample may be labeled as an 80% (n-s)-CD-IC, for example, the true coverage value is likely less than 80%, as it is unlikely that all CDs thread onto and remain on the polymers.

### Characterization techniques

#### DSC

DSC thermograms were collected on a TA Instruments Q1000 Differential Scanning Calorimeter, with an attached liquid nitrogen cooling system. Various heating and cooling rates were used, depending on the sample, and are noted where appropriate. Hermetically sealed aluminum pans were used in all instances. DSC data were analyzed using Universal Analysis, part of TA's Thermal Advantage software. Melting and crystallization temperatures and enthalpies were all determined automatically by the software based on the collected data.

#### XRD

X-ray diffraction data was collected on a Philips XLF, APTS X-ray diffractometer with an OMNI Instruments customized automount and copper tube, producing an X-ray wavelength of 1.54 Å.

#### NMR

NMR spectra were collected on a Bruker 500 MHz NMR spectrometer, with analyses typically performed using ACD SpecManager (software version 10.02). Zero filling was used to bring the point count up to 65536 and an apodization of 0.3 was used during Fourier transformation. The HDO peak was used as a reference at 4.75 ppm versus TMS.

## Results and discussion

### IC formation

PMMA-IC formation with solid  $\gamma$ -CD was monitored using solution proton NMR and X-ray diffraction techniques. The goal of these experiments was to determine whether or

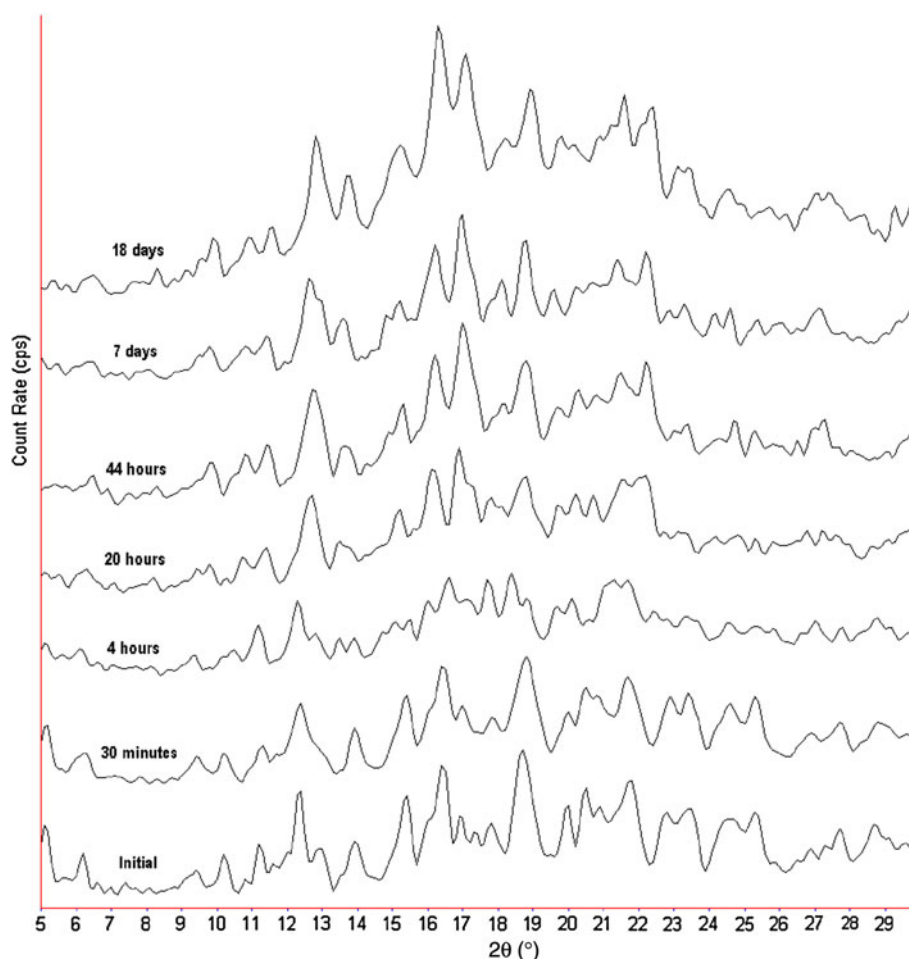
not inclusion of PMMA into solid  $\gamma$ -CD was observable via either method, and, if successful, to determine the structures of these IC's. Similar experiments were not, however, performed on our PCL-PPG-PCL triblock copolymer sample, as inclusion of the PCL-PPG-PCL triblock copolymer was observed here by precipitation similar to previously reported methods using  $\gamma$ -CD [9].

Solid state IC formation between PMMA and  $\gamma$ -CD at 105 °C was probed by X-ray diffraction and Fig. 2 presents the progression of XRD patterns observed over 18 days. A slow transition from the cage crystal structure (as manifested by peaks at  $2\theta = 12.4, 15.2, 16.5,$  and  $18.8^\circ$  [11]) can be observed. At 4 h, the cage crystal structure seems to have been mostly disrupted, and as we progress to 20 and 44 h, the formation of strong peaks at  $2\theta = 16.3$  and  $17.1^\circ$  can be observed. Unexpectedly, there is a distinct absence of the characteristic channel  $\gamma$ -CD diffraction peak at  $2\theta = 7.5^\circ$ , corresponding to the 200 plane of the channel crystal structure [12]. The absence of a strong channel  $\gamma$ -CD peak may indicate that while the PMMA is acting to disrupt the cage crystalline structure, the formation of an extensive channel crystalline structure has yet to occur.

To determine if the changing diffraction behavior of our PMMA/ $\gamma$ -CD sample was the result of an inclusion process, a physical mixture of PMMA and  $\alpha$ -CD, which is unable to thread over PMMA, was prepared in a similar fashion. XRD patterns were collected after spending increasing times at 105 °C to determine whether there was a deviation from the initial diffraction pattern. Though not shown here, in the PMMA/ $\alpha$ -CD mixture, the only change observed was a small increase in the relative size of the  $2\theta = 20.5^\circ$  peak. No disruption of the initial cage pattern was ever observed. This supports the observation that the threading of liquid PMMA chains into solid  $\gamma$ -CD is likely the cause for the changes observed in X-ray diffraction patterns seen in Fig. 2.

Proton NMR spectra were collected for mixtures of PMMA and  $\gamma$ -CD in  $d_8$ -dioxane. While PMMA is soluble in dioxane,  $\gamma$ -CD is not and remains as a precipitate. Because the  $\gamma$ -CD is insoluble, it remains "invisible" to the NMR instrument and contributes no peaks to the solution spectrum. It was expected that, if inclusion were taking place, we would begin to see a reduction of the PMMA peaks and an increase in the water peak, as complexing PMMA drove the water out of the  $\gamma$ -CD cavities and into the dioxane. Figure 3 presents the NMR results for this mixture at various times over the course of a month. While the peak integrations are not included, it is clear the water peak increased over time relative to the solvent peak and shifted slightly downfield. (Proton resonances are observed for  $d_8$ -dioxane, because it is not completely deuterated) The initial water:dioxane peak ratio was 0.23:1, while after a month it was 0.95:1, a significant increase. While the

**Fig. 2** XRD patterns of a physical mixture of PMMA and  $\gamma$ -CD observed after spending various times at 105 °C (A 1:3  $\gamma$ -CD :PMMA repeat unit stoichiometric ratio, corresponding to full coverage was employed)

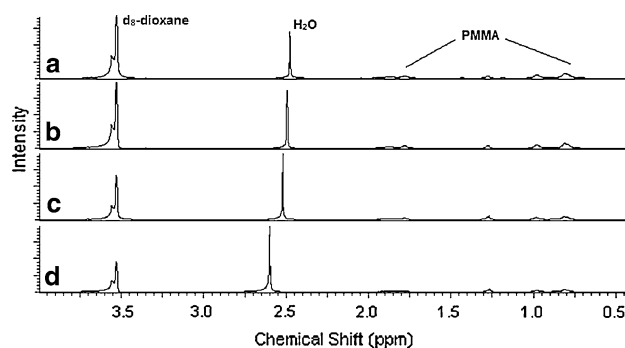


initial PMMA concentration was relatively low, integration of PMMA peaks demonstrated no change in PMMA concentration after a month. Thus, we can conclude that the PMMA was likely not including inside the insoluble  $\gamma$ -CD. It is possible that dioxane was instead including, causing the observed increase in water concentration.

A slight shifting of the H<sub>2</sub>O peak can also be observed over the course of the experiment. This may be a result of the changing H<sub>2</sub>O/d<sub>8</sub>-dioxane ratio, as the peak shift for the H<sub>2</sub>O resonance is highly dependent on many variables, including solvent composition.

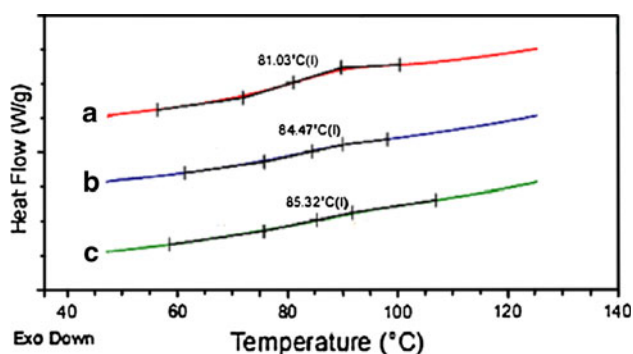
#### Analyses of PMMA and PCL-PPG-PCL copolymer (n-s)-ICs

Physical mixtures of PMMA with  $\gamma$ -CD and  $\alpha$ -CD were made and examined under repeated DSC runs at increased heating times and monitored for the  $T_{g,s}$  of PMMA. The as-received PMMA was also subjected to this heating profile and compared to the physical mixtures. The samples underwent 5 °C/min heating/cooling cycles and were allowed to anneal after each heating step for 2, 2, 5, and



**Fig. 3** NMR spectra of a PMMA (soluble) and  $\gamma$ -CD (insoluble) mixture initially (a) and after 20 h (b), 8 days (c), and 1 month (d) [solvent: d<sub>8</sub>-dioxane]

10 min at 130 °C and 15 min at 150 °C before the final heating. Figure 4 presents the stacked DSC thermograms for the three samples, where each heating step for a particular sample is shown one on top of another without any vertical or horizontal translation. It is evident from the near perfect superposition of all heating scans, that they are due only to the partial mixing of both components and not threading of PMMA by the  $\gamma$ -CD. The absence of changes in the DSC

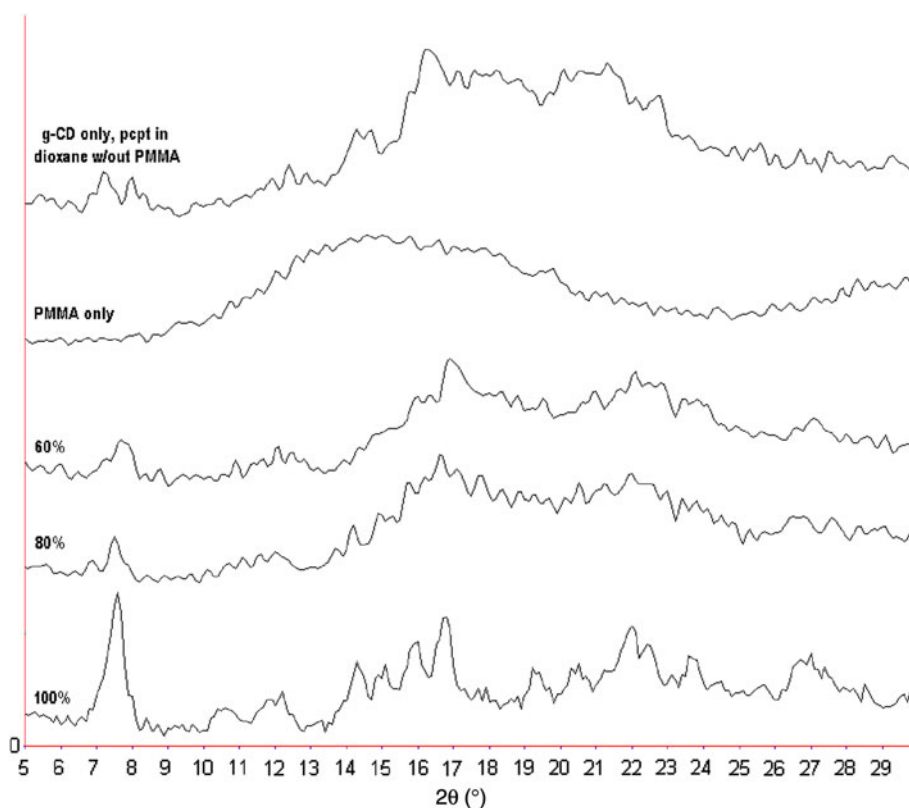


**Fig. 4** Multiple superimposed sequential DSC heating scans for as-received PMMA (a), a PMMA/ $\alpha$ -CD physical mixture (b), and a PMMA/ $\gamma$ -CD physical mixture (c)

signatures of the samples between and during each heating suggests that no solid-state inclusion has taken place within this time frame. So the slightly increased PMMA  $T_g$ s observed upon introduction of CD crystals must be a consequence of their mixing.

X-ray diffraction observations of various (n-s)-PMMA- $\gamma$ -CD-IC samples made in solution, as well as as-received PMMA and a precipitated  $\gamma$ -CD (channel structure) [13] are collected in Fig. 5, where we see that the atactic PMMA is completely amorphous. The (n-s)-PMMA- $\gamma$ -CD-ICs with assumed coverages of 60 and 80%, though likely lower, begin to show some channel crystalline characteristics,

**Fig. 5** XRD patterns of precipitated  $\gamma$ -CD, as-received PMMA, and PMMA- $\gamma$ -CD ICs with 60, 80, and 100% coverages



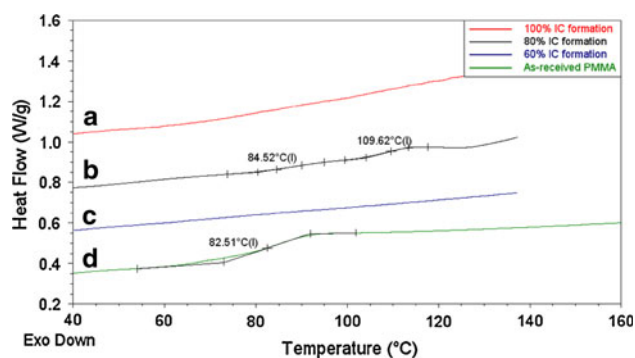
though their X-ray diffractograms are somewhat ill-defined. At perfect stoichiometry (1  $\gamma$ -CD:3 PMMA repeat units), or 100% coverage, there is a large increase in long range crystalline order, as demonstrated by the well-defined diffraction peaks characteristic of the channel  $\gamma$ -CD structure [12]. From this data, we can conclude that, at least for PMMA, a large degree of long-range crystalline order does not develop until the  $\gamma$ -CD coverage approaches 100%.

DSC observations of these same samples presented in Figs. 6 and 7 reveal a somewhat perplexing combination of behaviors that suggests restricted dangling PMMA chains are likely present in at least some of our samples. As seen in Fig. 7, one 80% coverage sample demonstrated a single  $T_g$  at 102 °C, an increase of 20° over as-received PMMA. However, another DSC sample taken from the same IC batch demonstrates two separate  $T_g$ s.

Additionally, it can be observed that the 60% covered IC sample has no glass transition (Fig. 6), even though it presumably contains a higher percentage of uncovered polymer than the 80% coverage sample.

This behavior strongly suggests that after filtration and washing, the (n-s)-PMMA- $\gamma$ -CD-IC samples remain heterogeneous. Multiple samples from the same batch of IC yielded strikingly different DSC behavior, presumably due to a drastic difference in the amount of uncovered polymer and the presence of non-complexed  $\gamma$ -CD and PMMA, which in the latter case maybe mixing. Figure 7





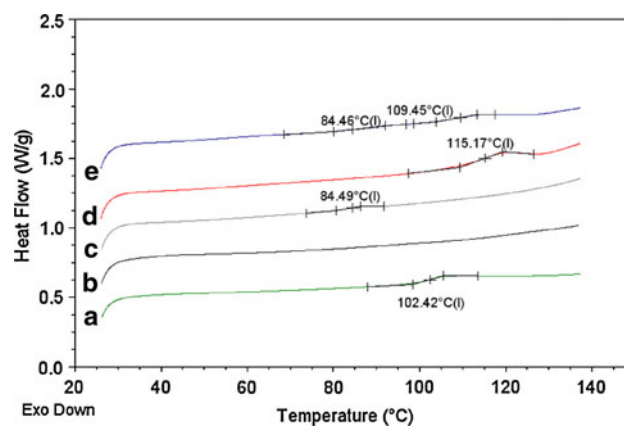
**Fig. 6** DSC scans of PMMA IC's with a CD coverage of 100% (a), 80% (b), and 60% (c), and as-received PMMA (d)

demonstrates the variety of different DSC behaviors observed when sampling the same (n-s)-PMMA- $\gamma$ -CD-IC. One particular behavior to note is the variability of the same sample before and after heating above the  $T_g$  of PMMA. Scans d and e in Fig. 7 are the first and second heatings observed for the same sample, respectively. Observed glass transitions change not only among various samples taken from the same IC batch, but also among the same samples depending on their thermal history.

Though the heterogeneity of our (n-s)-PMMA- $\gamma$ -CD-IC samples prohibits identification of the relationship between  $\gamma$ -CD coverage and glass transition behavior, it is worth noting the presence of an observable  $T_g$  significantly higher than that of as-received PMMA. This suggests that it is possible to create (n-s)-PMMA- $\gamma$ -CD-ICs with partially uncovered yet restricted chains resulting in an increased  $T_g$ . In contrast, Tu et al. [14] observed a  $T_g$  for poly (N-isopropyl acrylamide) (PNIPAM) in an  $\alpha$ -CD-IC formed with a poly (ethylene oxide) (PEO)-b-PNIPAM diblock copolymer, where only the PEO blocks are included, that was lower than the  $T_g$  of bulk PNIPAM homopolymer.

While a (n-s)-PMMA- $\gamma$ -CD-IC could potentially have any portions of its polymer chains located in a channel  $\gamma$ -CD crystal, a triblock copolymer with a center block that can thread and complex with a particular CD and with end blocks that do not complex with the same CD would appear to be an excellent candidate for producing a controllable (n-s)-polymer-CD-IC with uncomplexed yet restrained chains “dangling” from the crystalline IC surfaces. Consequently, a PCL-PPG-PCL triblock copolymer was synthesized from a hydroxyl-terminated 3,000 g/mol PPG and  $\epsilon$ -caprolactone. An IC was then formed with  $\beta$ -CD, under the initial assumption that all the  $\beta$ -CD would reside on the PPG center block.

Figures 8 and 9 present DSC scans of the neat triblock copolymer and its IC formed with  $\beta$ -CD, respectively. For the as-synthesized copolymer, we can observe a single  $T_g$  at  $-64$  °C. Low molecular weight PPG was observed by us to have a  $T_g$  of approximately  $-73$  °C, while PCL [15] has

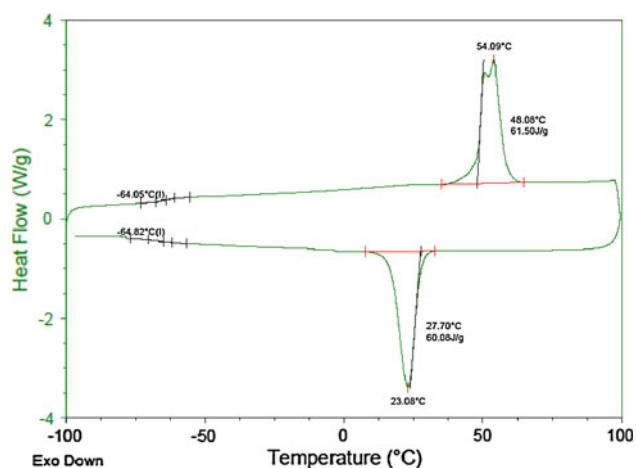


**Fig. 7** Multiple DSC samples obtained from the same batch of 80% coverage PMMA/ $\gamma$ -CD NS-IC (a–d) as well as two repeated runs of the same sample (d, e)

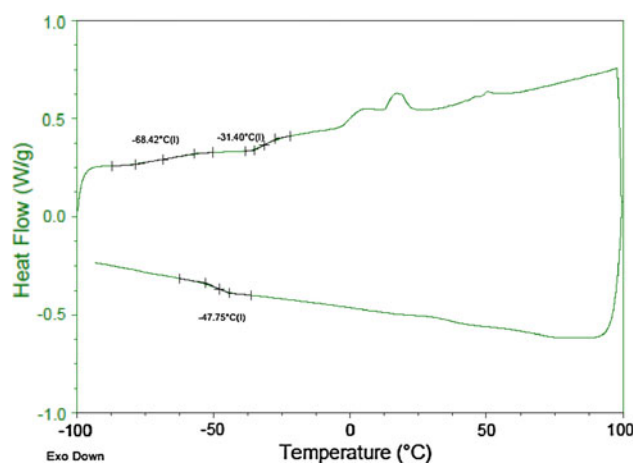
a  $T_g$  of approximately  $-56$  °C. It is likely that the observed  $T_g$  is that of the PPG, because the high crystallinity observed for the PCL end blocks ( $\sim 58\%$ ) [16] likely precludes their glass transition. Upon complexation, the  $T_g$  values undergo dramatic changes, while crystallization of the PCL blocks is largely suppressed. [Though not presented here, FTIR observations confirm both the absence and presence of  $\beta$ -CD and the substantial and absence of PCL crystallinity in neat PCL- PPG-PCL and PCL-PPG-PCL- $\beta$ -CD-IC, respectively.] The single  $T_g$  observed at  $-64$  °C for the uncomplexed neat triblock becomes two transitions in the  $\beta$ -CD-IC, one at  $-68$  °C and the other at  $-31$  °C. If the  $\beta$ -CD were exclusively covering only the central PPG block, it seems likely that we would no longer see a  $T_g$  for PPG and the PCL end blocks would still be largely crystalline.

Based on these observations, it seems likely that the  $\beta$ -CD has in some way at least partially mixed with or included the PCL blocks preventing their crystallization. The  $T_g$  present at  $-31$  °C is likely the PCL glass transition, now visible due to the very high amorphous PCL content, and elevated from that of neat PCL homopolymer by its partial threading into or mixing with  $\beta$ -CD threaded on the PPG blocks. The second  $T_g$  observed at  $-68$  °C, and only a few degrees lower and higher than observed for PPG in the uncomplexed neat triblock and neat homopolymer, respectively, would logically seem to be contributed by PPG blocks that are only very lightly threaded by  $\beta$ -CD.

It should be noted that very recently Tsai et al. [17] reported solution and solid state NMR observations made on  $\beta$ -CD-ICs formed with Pluronics {poly-(ethylene glycol)-PPG-poly-(ethylene glycol) triblocks [PEG-PPG-PEG]}, which indicated that only the central PPG blocks were selectively threaded by and complexed with the host  $\beta$ -CDs. Nevertheless, they also observed in the X-ray diffractograms of the pluronic- $\beta$ -CDs the complete absence of



**Fig. 8** DSC heating and cooling cycle of a PCL-PPG-PCL triblock copolymer



**Fig. 9** DSC heating and cooling cycle of PCL-PPG-PCL- $\beta$ -CD IC

crystallinity for the PEG blocks. This suggests at least some mixing between the PEG blocks and the included and  $\beta$ -CD-complexed PPG blocks. It is possible that a similar mixing is possible between the PCL blocks and the PPG blocks that are completely covered and complexed with  $\beta$ -CD in our PCL-PPG-PCL- $\beta$ -CD-IC. However, if this is the case, then the two  $T_g$ s observed for the PCL-PPG-PCL- $\beta$ -CD-IC remain difficult to understand. The insolubility of the triblock IC makes CD/polymer interaction study by NMR difficult. However, it may be possible to end-cap a partially covered sample, creating a soluble pseudo-polyrotaxane that can be studied by solution-NMR.

## Conclusions

While evidence of liquid PMMA and solid  $\gamma$ -CD interaction was observed through X-ray diffraction, the strong  $2\theta = 7.5^\circ$  peak generally indicative of the channel  $\gamma$ -CD

structure [12] was not observed. The same interaction was not observed in a liquid PMMA/solid  $\alpha$ -CD mixture, suggesting the threading of liquid PMMA into solid  $\gamma$ -CD likely played a role in the structural changes evidenced by X-ray. NMR observations of PMMA dissolved and  $\gamma$ -CD suspended in  $d_8$ -dioxane did not reveal IC formation as expected, but instead suggested that the solvent was slowly included and displaced the water inside the  $\gamma$ -CDs.

DSC studies of (n-s)-PMMA- $\gamma$ -CD-IC samples formed in solution suggested strongly heterogeneous materials that could perhaps be made more homogeneous upon annealing. The presence of a dramatically increased  $T_g$  observed in some samples (increases as high as 27 °C over neat PMMA) suggested that in certain environments, restriction of dangling PMMA chains may result in large increases in their glass transition temperature. It has been suggested [18–20] that, at least in DMSO solutions of end-capped rotaxanated and in solid unrotaxanated (n-s)-PEG- $\alpha$ -CD-ICs, the  $\alpha$ -CDs likely aggregate in small clusters of 3–4 CD's on each threaded chain. This would imply that only small crystallites dispersed along the entire length of the polymer chain might exist in some solid (n-s)-polymer-CD-ICs, and possibly explain the extreme heterogeneity of our (n-s)-PMMA- $\gamma$ -CD-IC samples.

An attempt at controlling/concentrating the location of CD molecules on (n-s)-polymer-CD-ICs was made by forming an IC with PCL-PPG-PCL triblock copolymer and  $\beta$ -CD. Initially, it was thought that the  $\beta$ -CD would only complex with the PPG center block, creating a type of “forced” (n-s)-polymer-CD-IC, and would permit examination of the properties of unincluded though restrained PCL blocks. However, DSC and FTIR observations showed that the  $\beta$ -CD also interacted with the PCL blocks in such a way as to almost entirely prevent their crystallization, leading instead to two glass-transitions. Surprisingly the DSC observations seem most consistent with partial threading of both PCL and PPG blocks by the host  $\beta$ -CDs, though  $\beta$ -CDs threaded on the central PPG blocks may also be mixing with the PCL end blocks.

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