Reorganization and improvement of bulk polymers by processing with their cyclodextrin inclusion compounds

Tamer Uyar[a], Cristian C. Rusa[a], Marcus A. Hunt[a], Evren Aslan[b],
Jale Hacaloglu[b], Alan E. Tonelli[a],*

[a]Fiber and Polymer Science Program, College of Textiles, North Carolina State University, Campus Box 8301, Raleigh, NC 27695-8301, USA
[b]Department of Chemistry, Middle East Technical University, Ankara 06531, Turkey

Abstract

The formation of polymer-cyclodextrin inclusion compounds of polycarbonate (PC), poly(methylmethacrylate) (PMMA) and poly(vinylacetate) (PVAc) guests with host γ-cyclodextrin (γ-CD) have been successfully achieved. Coalesced bulk polymer samples were obtained by removal of γ-CD from their inclusion compounds (ICs). The chemical and crystalline structures of ICs and coalesced PC, PMMA and PVAc were studied by Fourier transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (WAXD). The thermal transitions, thermal stability, and degradation mechanisms of the samples were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and direct insertion probe pyrolysis mass spectrometry (DIP-MS). FTIR findings indicated that the chain conformations of the bulk polymers were altered when they were included inside the CD channels and extended chain conformations were retained when coalesced from their ICs. Significant improvements were observed in the thermal transitions observed for the coalesced polymers, with glass transitions shifted to higher temperatures. The TGA results reveal that the thermal stabilities of coalesced polymers increased slightly compared to the corresponding as-received polymers. The DIP-MS observations indicated that the thermal stability and degradation products of the polymers are affected once the polymers chains are included inside the γ-CD-IC cavities.

1. Introduction

Cyclodextrins (CDs), cyclic starch oligomers, may be represented as shallow truncated cones consisting of 6, 7, or 8 glucose units, and are named alpha (α-), beta (β-), or gamma (γ-) cyclodextrins (CDs), respectively, (Fig. 1(a) and (b)). Although the depth of the cavities for the three CDs is the same (~ 7.9 Å), their cavity diameters are ~ 4.5, 7, and $8.5-9$ Å for α-, β- and γ-CD, respectively, [1]. CD molecules can complex and host both polar and non-polar molecules, as well as polymers (Fig. 1(f)), as guests inside their cavities due to their unique structure [2–7].

Our research group has recently reported that cyclodextrins (CDs) may act as hosts in the formation of inclusion compounds (ICs) with various high molecular weight polymers. Polymer-CD ICs are crystalline compounds obtained by threading of the doughnut shaped CD molecules onto the guest polymer chains. Once guest polymer chains are included inside the CD cavities, they are segregated from neighboring polymers chains by the walls of the CD crystalline lattice and are forced to adopt highly extended conformations by the narrow host CD channels. We have shown that coalescence of guest polymers from their CD IC crystals can result in a significant improvement of their physical properties caused by modification of the structures, morphologies, and even conformations that are observed for their coalesced bulk samples [8,9]. Recently, we have also developed a novel approach for forming intimately mixed polymer blends by coalescing (removal of CD) bulk polymer pairs from their common CD ICs [10–14].

Our successful attempt to prepare an intimately mixed ternary blend of PC/PMMA/PVAc by coalescence from their common γ-CD IC [13] was predicated on forming and

* Corresponding author. Tel.: +1 919 515 6588.
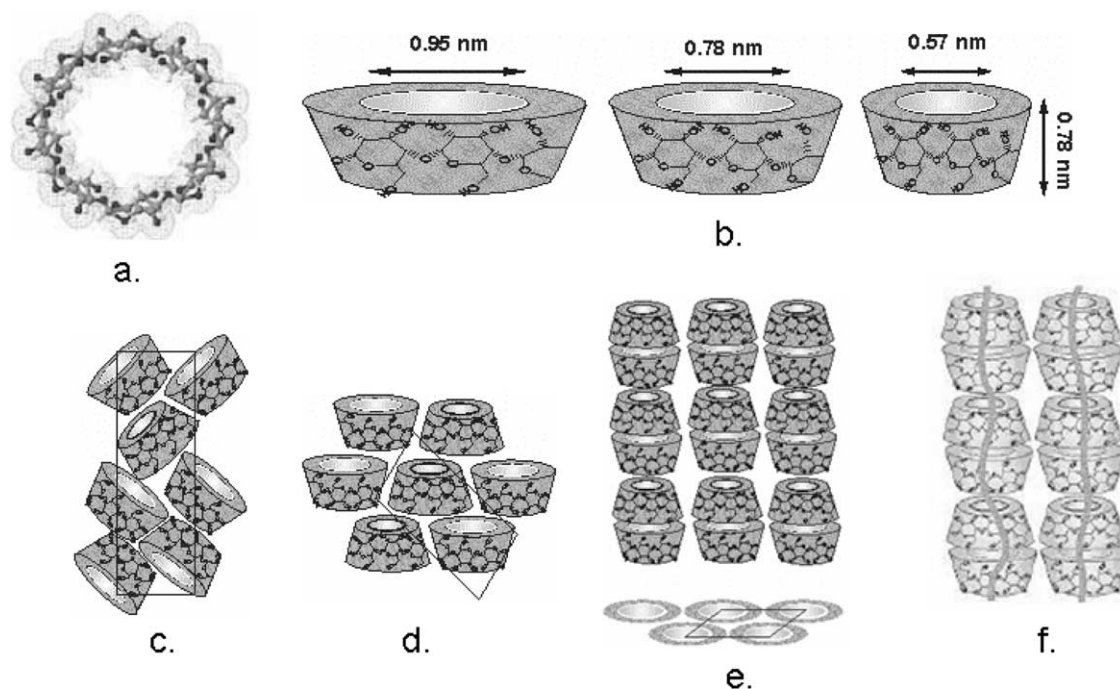 *E-mail address:* alan_tonelli@ncsu.edu (A.E. Tonelli).

Fig. 1. (a) γ-CD chemical structure; (b) approximate dimensions of α-CD, β-CD and γ-CD; schematic representation of packing structures of (c) cage-type; (d) layer-type CD; and (e) head-to-tail channel-type crystals; (f) cyclodextrin-inclusion compound (CD-IC) channels with included polymer guests.

coalescing from the constituent homopolymer and binary pair γ-CD ICs [14]. Here, we report the formation of ICs formed between γ-CD and polycarbonate (PC), poly (methylmethacrylate) (PMMA) and poly(vinylacetate) (PVAc) homopolymers. The coalesced bulk polymers were obtained by removal of γ-CD with water, which dissolves only the host CD molecules. FTIR study confirmed conformational changes for the coalesced polymer chains. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data showed that the coalesced polymers have distinct thermal behavior compared to the as-received polymers. Direct insertion probe pyrolysis mass spectrometry (DIP-MS) analysis indicated that the thermal stability and degradation products of the polymers are affected once the polymers chains are included inside the γ-CD-IC cavities.

2. Experimental

2.1. Materials

Polycarbonate (PC) ($M_w = 28,800$ g/mol, $M_n = 17,300$ g/mol), atactic-poly(methyl methacrylate) (PMMA) ($M_w = 15,000$ g/mol), and atactic-poly(vinylacetate) (PVAc), with $M_w = 12,800$ and $167,000$ g/mol, were purchased from Aldrich Co., and used as received. Tetrahydrofuran (THF) (Aldrich, 99+ %), dioxane (Aldrich, 99+ %), methyl ethyl ketone (MEK) (Fluka, 99+ %) were used without any purification. γ-cyclodextrin (γ-CD), β-cyclodextrin (β-CD) and α-cyclodextrin (α-CD)

were obtained from Cerestar (Hammond, IN). The water used in this study was deionized (DI-H_2O).

2.2. Formation of polymer-γ-CD inclusion compounds

The formation of inclusion compounds of γ-cyclodextrin with PC, PMMA and PVAc were carried out separately. According to the literature, we assumed that one γ-CD molecule may host three repeat units of PMMA or PVAc and 0.66 repeat units of PC [1]. For the formation of inclusion compounds, a quantity of 0.480 g (1.88 mmol, repeating unit) of PC or 0.858 g (8.58 mmol, repeating unit) of PMMA or 0.7376 g (8.58 mmol, repeating unit) of PVAc was dissolved in 100 mL of dioxane at 50 °C. The γ-CD (3.712 g, 2.86 mmol) was dissolved in 10 mL of DI-H_2O at 50 °C and then added drop-wise to the polymer solution, while the stirring rate was kept at maximum and the temperature at 50 °C. As the γ-CD solution was added, a white, turbid solution was formed (Fig. 2). After stirring for 3 h at 50 °C, the white suspension was allowed to cool down to room temperature while the stirring rate was kept low for another 3 days, because, after many attempts, the time required for obtaining these polymer inclusion compounds with γ-CD in high yield was found to be 3 days. The resulting white suspension was then vacuum filtered and the collected precipitate vacuum dried at 60 °C for 24 h. The abbreviation for these polymer inclusion compounds are PC-, PMMA- and PVAc-γ-CD IC. It was found that low molecular weight PVAc ($M_w = 12,800$ g/mol) does not form an inclusion compound with γ-CD. Different solvent systems other than dioxane, like THF and MEK were
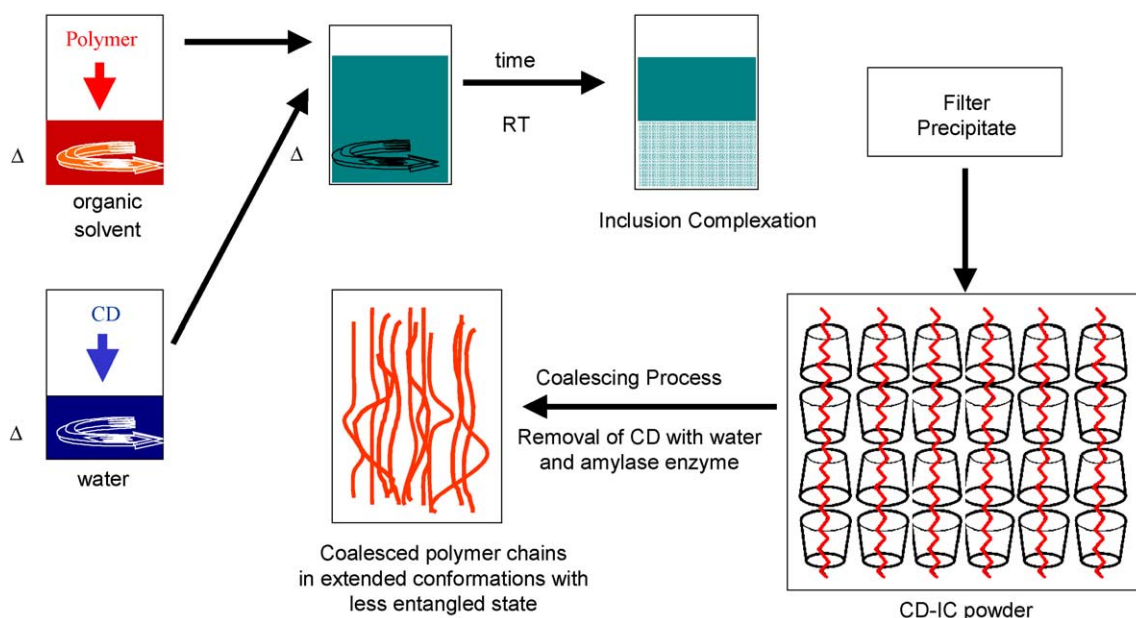
Fig. 2. Schematic representation of polymer-CD IC formation, the coalescing process and the coalesced polymer.

attempted for the formation of the the PVAc-γ-CD inclusion compound, but these failed. The host (γ-CD) was also changed to α-CD and β-CD, but neither formed an IC with the low molecular weight PVAc sample. The reason could be the branched structure of the PVAc since the CD molecules would exclude the branched chains due to their bulky size (the supplier (Aldrich) reported the branched structure for this polymer by GPC). However, we were able to obtain PVAc-γ-CD IC by using high molecular weight linear PVAc sample (M_w=167,000 g/mol).

2.3. Coalescence of PC, PMMA and PVAc from their CD-ICs

Host γ-CD was removed from the ICs by washing the white crystals with deionized water overnight at 50 °C and the α-amylase enzyme (Clarase L-4000) was used when necessary (Fig. 2). The coalesced polymers were then vacuum filtered and rinsed several times with water, and finally vacuum dried at 30–40 °C for 2 days.

The inclusion formation of PC with CD was previously reported by our research group [8]. In the present study, a 'greener' approach has been applied in the formation of polymer-CD inclusion compounds, in which the organic solvent (dimethyl sulfoxide) used previously for the CD solution is replaced by water. However, the use of organic solvents for dissolution of polymer in the formation of polymer-CD-ICs still remains, and more work needs to be done in order to achieve totally environmentally 'friendly' methods for their production. On the other hand, we observed that the coalesced polymers have characteristic properties independent of the IC preparation method.

We observed that the process of coalescing PC from its cyclodextrin inclusion compound resulted in a crystalline morphology, whereas the starting material (as-received PC) is completely amorphous. This observation can be explained by self-aggregation of extended and unentangled PC chains into a tighter and more ordered structure, which results in a crystalline phase. Solvent-induced crystallization was ruled out for the coalesced PC sample, because PC chains are segregated from neighboring polymer chains by the walls of the CD in ICs and the host γ-CD was washed out with water which is a non-solvent for PC.

The control PC sample was prepared by applying the same procedure as the formation of the PC-γ-CD inclusion compound. The same amount of PC was dissolved in dioxane and water added dropwise, instead of CD aqueous solution, into the polymer solution. The precipitation of PC was observed overnight and the powder was collected by filtration after 3 days of stirring the solution. It was observed that precipitated PC also contains a crystalline phase.

3. Characterization

3.1. Wide-angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction (WAXD) measurements were performed with a Siemens type-F X-ray diffractometer using a Ni-filtered Cu K$_\alpha$ radiation source (λ=1.54 Å). The diffraction intensities were measured every 0.1° from 2θ=5 to 30° at a rate of 2θ=3°/min. The supplied voltage and current were 30 kV and 20 mA, respectively.

3.2. Fourier transform infrared spectroscopy (FTIR)

A Nicolet 510P FTIR spectrometer was utilized to obtain the infrared spectra of samples mixed with potassium

bromide (KBr) and pressed into pellets. The spectra were taken over a range of 4000–400 cm^{-1}, with a resolution of 2 cm^{-1} obtained after 64 scans.

3.3. Modulated differential scanning calorimetry (M-DSC)

The M-DSC experiments were performed with a thermal analysis (TA) DSC Q1000 in modulated mode. Nitrogen was used as purge gas. All samples studied in this work were subjected to heating and cooling cycles consisting of: 1.0 min hold at 0 °C, ramping to target temperature at 5 °C/min, hold there for 1 min, and samples were then quenched by ramping to 0 °C at 200 °C/min. Samples were subjected to a second cycle to investigate the change in thermal behavior following the first heat.

3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analyses of the PC, PMMA, and PVAC samples were performed with a Perkin–Elmer Pyris 1 thermogravimetric analyzer (TGA). Thermal decompositions were recorded between 25 and 650 °C. The heating rate was of 20 °C/min and nitrogen was used as a purge gas.

3.5. Direct insertion probe pyrolysis mass spectrometry (DIP-MS)

The direct insertion probe pyrolysis mass spectrometry (DIP-MS) system consists of a 5973 HP quadruple mass spectrometer coupled to a JHP SIS direct insertion probe pyrolysis system. 0.01 mg samples were pyrolyzed in flared glass sample vials. The temperature was increased at a rate of 10 °C/min and the scan rate was 2 scans/s.

4. Results and discussion

4.1. Wide-angle X-ray diffraction (WAXD)

WAXD is a useful characterization technique for investigating the crystalline phase transition between the cage structure of as-received γ-CD·7H_2O (Fig. 3(a)) and the channel structure of polymer-γ-CD ICs (Fig. 4). Once the host CD molecules are threaded onto the polymer chains, it is expected that the final IC crystals adopt a channel-type structure. Complicating polymer-CD IC formation is the ability of dioxane, the polymer solvent used in this work, to precipitate γ-CD in the channel structure from its aqueous solution (Fig. 3(b)). Rusa et al. previously observed this behavior by precipitating γ-CD in the channel structure, γ-CD_{cs}, using acetone [15]. There, γ-CD_{cs} was reported to only contain water, suggesting that γ-CD channel structure can be pre-formed in solution. Subsequent vacuum drying destabilizes the channel structure, resulting in an amorphous diffraction pattern (Fig. 3(c)).

Fig. 4 shows WAXD patterns for the three polymer-γ-CD ICs. Each exhibit a pattern consistent with those presented in the literature [8,12]. To confirm the formation of polymer-γ-CD IC crystals, the precipitates resulting from the addition of the cyclodextrin solution to the polymer solutions were vacuum-dried after filtration. This destroys any γ-CD channel structure with only water included, since γ-CD_{cs} collapses into an amorphous structure upon dehydration of the crystals [15]. However, in case of the polymer-CD ICs, the included polymer chains in the γ-CD channels would preserve the channel structure. The X-ray diffraction pattern of vacuum-dried PMMA-γ-CD-IC crystals is given in Fig. 3(d). It was observed that the reflections consistent with γ-CD in the channel structure persisted after vacuum drying of PMMA-γ-CD IC. One reflection in particular occurring at $2\theta = 7.5°$ for polymer-γ-CD IC crystals is indicative of γ-CD in the channel structure and has been assigned to the 200 plane of a tetragonal lattice by Takeo and Kuge [16]. Yet, the diffraction pattern of PMMA-γ-CD-IC also indicated the existence of some amorphous structure, which is due to the presence of some γ-CD_{cs}, with only water included, that then collapsed into an amorphous structure upon vacuum drying. Diffraction patterns similar to that of PMMA-γ-CD IC were also observed for vacuum dried PC- and PVAc-γ-CD IC samples (not shown).

The presence of a peak at $2\theta = 7.5°$ represents the first evidence that γ-CD molecules formed a channel structure IC with the possible inclusion of polymer guests residing in the γ-CD cavities. FTIR (Section 4.2) and DSC studies were carried out to confirm that the polymers are included in the IC channels. DSC is a useful tool to determine whether or not the polymer chains are included inside the CD cavities: thermal transitions for polymers are observed if there is any uncomplexed polymer present in the CD ICs. None of the DSC scans of PC-, PMMA- or PVAc-γ-CD ICs (not shown) exhibited glass transitions for any of the potentially uncomplexed polymers. This result reveals that polymer chains are threaded and covered by CD molecules in the polymer-CD ICs.

4.2. Fourier transform infrared spectroscopy (FTIR)

Though not presented, the FTIR spectra of each polymer-γ-CD IC showed evidence of the presence of each polymer by virtue of C=O absorptions observed at 1730, 1739, and 1775 cm^{-1} for PMMA, PVAc, and PC, respectively. The overlayed FTIR spectra of the as-received PMMA, PVAc and PC and coalesced samples are given in Figs. 5 and 6, respectively. No heat treatment has been applied to any of the samples prior to the FTIR scans.

PMMA has an absorption band (C=O stretch) at 1730 cm^{-1} (Fig. 5(a)), whereas the C=O stretch of PVAc absorbs at 1736 cm^{-1} (Fig. 5(b)). The absorption peaks observed at 1148 and 1243 cm^{-1} (C–O–C stretching) are from PMMA and the peaks observed at 1376 and 1242 cm^{-1} are from PVAc [17].
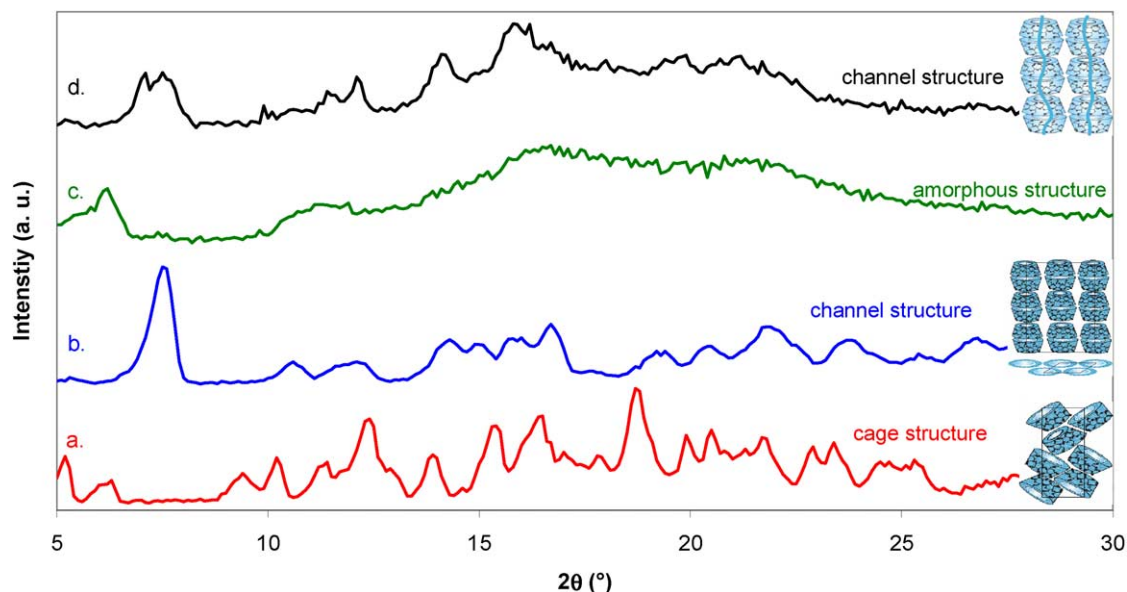
Fig. 3. X-ray diffraction patterns of (a) as-received γ-CD, (b) γ-CD columnar structure, (c) vacuum-dried γ-CD columnar structure, and (d) vacuum-dried PMMA-γ-CD IC.

It is usual to observe vibrational absorbance shifts when the interactions between or the local environments around polymer chains are different. Additionally, conformational changes can also be followed by infrared spectroscopy, since some absorption bands are conformationally sensitive. It is likely that when polymer chains are coalesced from their inclusion compounds they solidify in extended conformations that are less entangled. The infrared spectra of as-received (Fig. 5) and coalesced polymers (Fig. 6) were examined in order to identify any possible conformational differences between their constituent polymer chains.

In the PMMA polymer backbone, the absorption band at 840 cm^{-1} sensitive to *trans*, *gauche* ± backbone conformations is characteristic of random coil chains, while the absorption band at 860 cm^{-1} is characteristic for the all *trans* or close to the all *trans* conformation [18–21]. In Fig. 7(a), the as-received PMMA has an absorption band at 842 cm^{-1}, which is characteristic of random coil chains. In coalesced PMMA (Fig. 7(b)), the absorption band due to *trans*, *gauche* ± conformations is observed at 841 cm^{-1}, with a shoulder at 860 cm^{-1}, which indicates the presence of the all *trans* conformation as well, and confirms the existence of some extended chains in coalesced PMMA.

Furthermore, in the coalesced PMMA sample, some small shifts were also observed in other conformationally
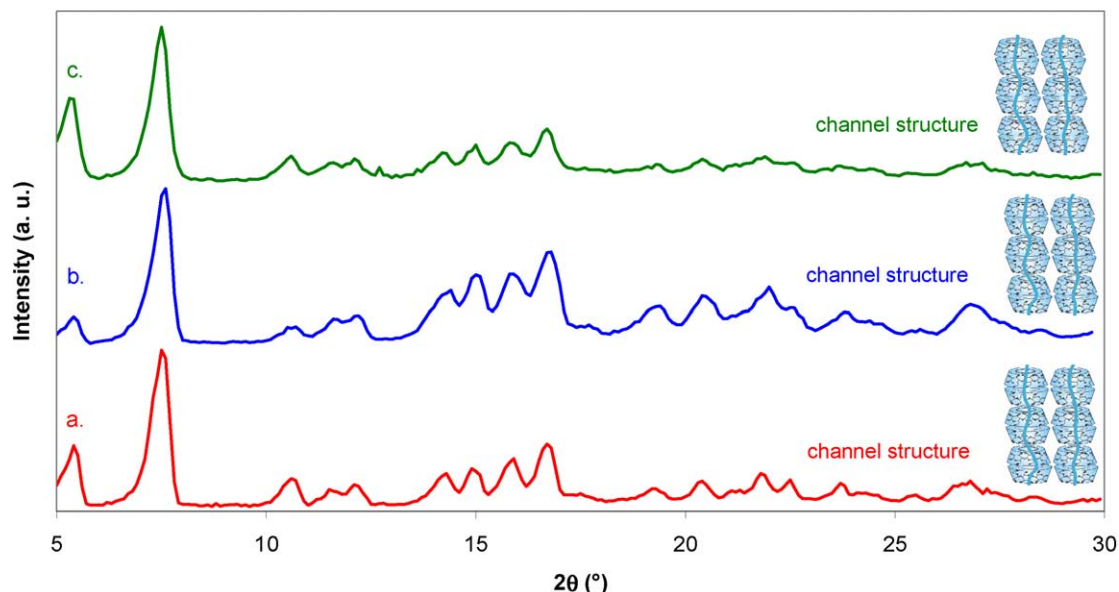

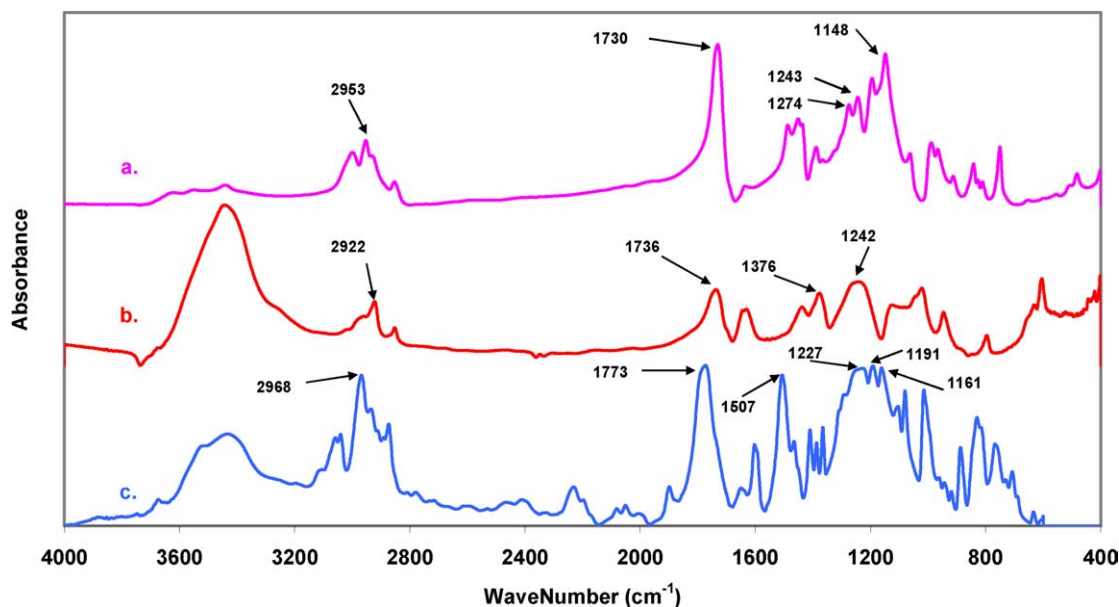Fig. 4. X-ray diffraction patterns of (a) PC-γ-CD IC, (b) PMMA-γ-CD-IC and (c) PVAc-γ-CD-IC.

Fig. 5. FTIR spectra of as-received (a) PMMA, (b) PVAc, and (c) PC.

sensitive absorption bands (1150, 1190, 1240 and 1275 cm^{-1}, which are assigned to the C–C–O vibration coupled to the C–O vibration). For instance, the peaks observed at 1148, 1244, and 1274 cm^{-1} in the as-received sample were shifted to 1150, 1241, and 1270 cm^{-1} in the coalesced sample, respectively. Similarly, in the coalesced PVAc sample, peaks at 1242 and 1376 cm^{-1} shifted to 1236 and 1378 cm^{-1}, respectively.

Additionally, the most significant difference is the much improved resolution observed in the FTIR spectra of the coalesced samples when compared to the as-received sample spectra. This improved resolution may due to the presence of less entangled and more extended chains, which

is anticipated for the coalesced polymers. Generally, broad infrared bands observed in polymer samples are due to the large variety of polymer conformations and various chain-packing environments surrounding each vibrating bond or group. In coalesced polymers, vibrating bonds or groups are subjected to smaller conformational and chain-packing variations due to their more ordered structures.

The infrared spectrum of as-received polycarbonate is given in Fig. 5(c). The absorption bands at 1161 and 1191 cm^{-1} due to carbonate C–O stretch, carbonate aryl–C–O–C(=O) stretching at 1227 cm^{-1}, para-aromatic ring stretching at 1507 and 1602 cm^{-1}, carbonate C=O stretching at 1773 cm^{-1} and CH$_3$ asymmetric stretching at
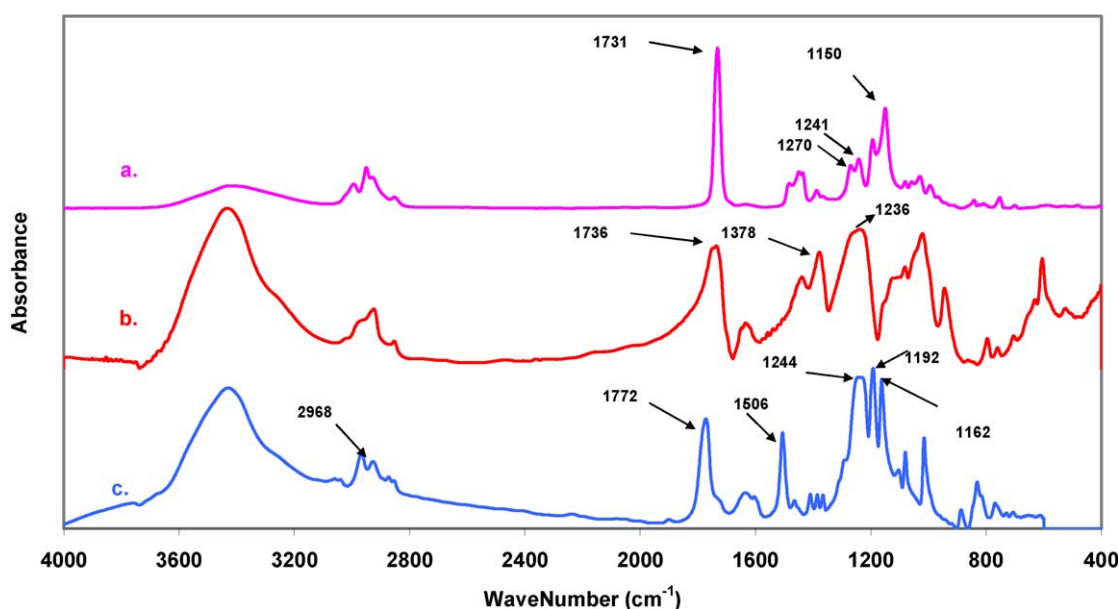

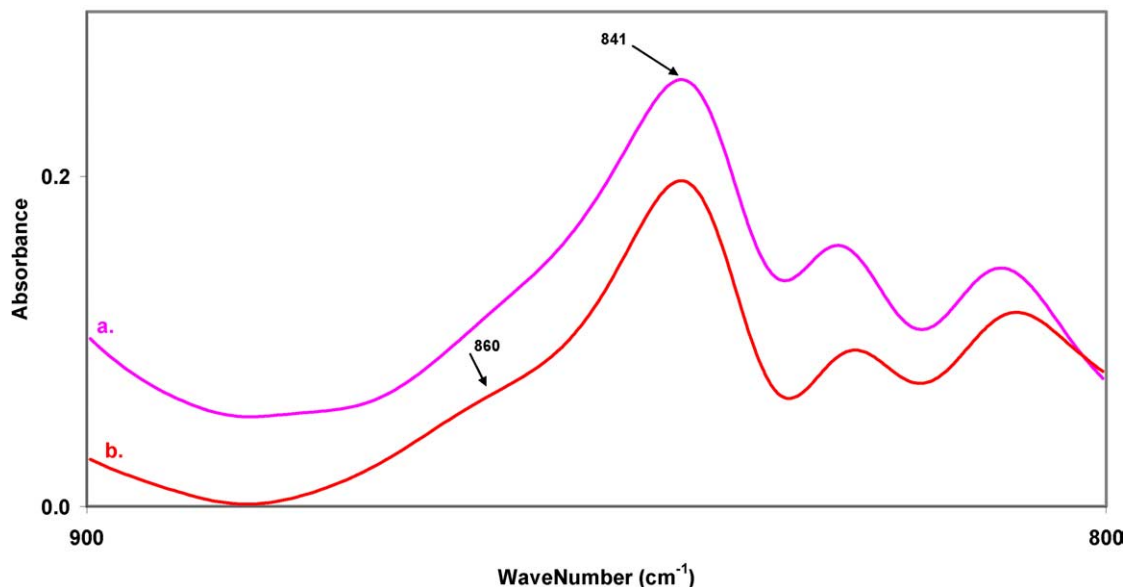Fig. 6. FTIR spectra of coalesced (a) PMMA, (b) PVAc, and (c) PC.

Fig. 7. FTIR spectra of (a) as-received PMMA and (b) coalesced PMMA.

$2968\ cm^{-1}$ are characteristic of PC [17]. Conformationally sensitive infrared bands were reported in the literature for polycarbonate [22–24]. The broad carbonyl C=O band has its maximum around $1775\ cm^{-1}$ and is subdivided into contributions from the *trans–trans* (*t–t*) conformer at $1767\ cm^{-1}$ and the *trans–cis* (*t–c*) conformer of the carbonate groups at $1785\ cm^{-1}$. The C–C aromatic in-plane stretching exhibits a doublet at $1600\ cm^{-1}$, which is divided into *t–t* and *t–c* conformational contributions at 1594 and $1604\ cm^{-1}$, respectively. The C–O–C antisymmetric vibration at $1235\ cm^{-1}$ consists of *t–t* and *t–c* conformational contributions at 1252 and $1223\ cm^{-1}$, respectively.

The conformationally sensitive regions of the FTIR spectra for PC, $1200–1800\ cm^{-1}$ are examined in detail in Fig. 8. For as-received PC, the carbonyl band was observed at $1773\ cm^{-1}$ along with a shoulder at $1785\ cm^{-1}$, which is a contribution of the *t–c* conformation. For the coalesced PC, a narrower absorption band with maximum at $1772\ cm^{-1}$ was observed and the shoulder at $1785\ cm^{-1}$ was absent. The C–C aromatic in-plane stretching was similar for both as-received and coalesced PC and the absorption bands were observed at around $1604\ cm^{-1}$, with a shoulder at $1594\ cm^{-1}$. The most noticeable difference observed between the two samples was for the C–O–C antisymmetric vibration. For as-received PC, the peak contributed by the *t–t* conformation at $1252\ cm^{-1}$ has a lower intensity than the peak at $1227\ cm^{-1}$, which is a contribution from the *t–c* conformation. In the case of coalesced PC, these absorption bands were shifted to 1244 and $1230\ cm^{-1}$. Moreover, the intensity of the $1244\ cm^{-1}$ peak is higher than that of the $1230\ cm^{-1}$ band, which indicates the

presence of a higher content of *t–t* conformation when compared to as-received PC.

To sum up, the observation of some differences in the infrared spectra of as-received and coalesced polymers indicates that the conformations and packing of polymer chains, when they are coalesced from their inclusion compounds, is different from those in the as-received bulk polymers.

4.3. Differential scanning calorimetry (DSC)

Fig. 9 displays the modulated differential scanning calorimetry (MDSC) scans recorded for as-received, precipitated and coalesced PC. The absence of a melting point (T_m) in its DSC scans indicates that as-received PC does not contain a crystalline phase, and is completely amorphous. The glass transition temperature (T_g) for this sample is observed at 145 °C. The first scan of precipitated PC shows a T_m at 239 °C, with a shoulder at 230 °C. The appearance of a shoulder prior to the $T_m = 239$ °C is possibly due to the presence of some less dense crystalline phase or imperfect crystals in the precipitated sample [8]. The sample reverts to an amorphous phase after melting and rapid cooling and shows a transition, T_g, at 143 °C as indicated in the second heating scan. The DSC thermogram of coalesced PC shows a single melting point at 240 °C, which indicates the absence of imperfect or non-uniform crystals. Moreover, the coalesced sample has a T_g at 149 °C, which is higher than those of the as-received and precipitated PCs. The presence of crystalline phases in the precipitated and coalesced samples is also confirmed by X-ray measurement The X-ray diffractograms of precipitated and coalesced PC (Fig. 10) show a similar pattern with the main diffraction peak at
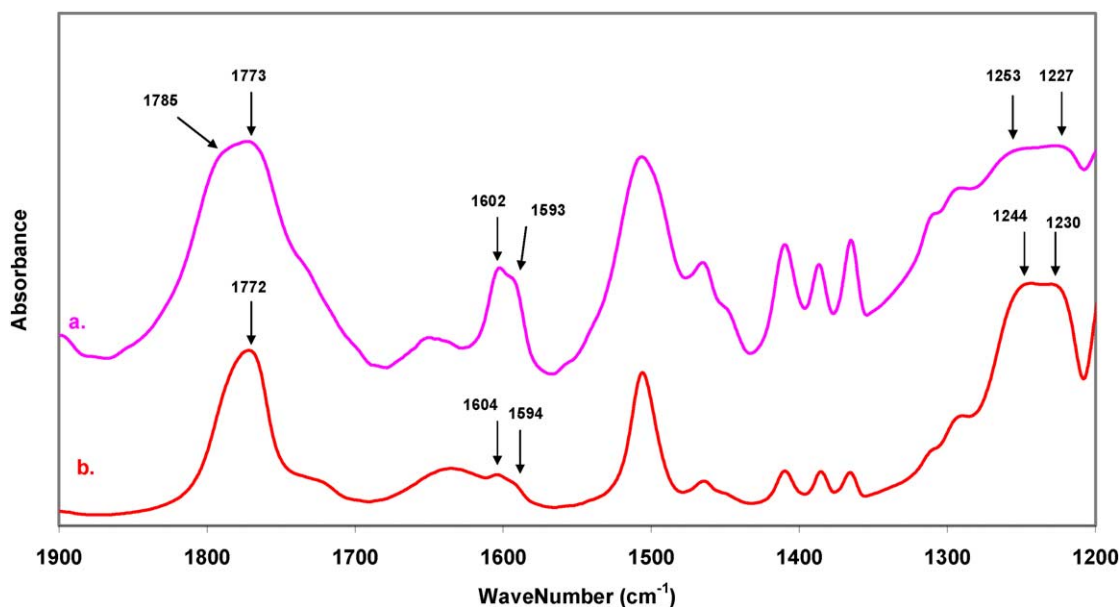
Fig. 8. FTIR spectra of (a) as-received PC and (b) coalesced PC.

$2\theta = \sim 18°$, whereas as-received, amorphous PC exhibits a broad halo in that region [8,25].

DSC scans recorded for coalesced and as-received PMMA and PVAc are given in Figs. 11 and 12, respectively. The glass transition temperature of the as-received PMMA is observed at 83 °C and is shifted to 97 °C for the coalesced PMMA sample. Similar behavior is observed for the PVAc

sample, where the T_g is shifted from 29 to 42 °C when coalesced from its inclusion compound. The increase in glass transition temperatures observed for PMMA and PVAc coalesced polymers compared to their as-received samples is significant. This behavior is commonly observed for polymers coalesced from their CD ICs [8,9] and can be explained by the less entangled and more ordered state of
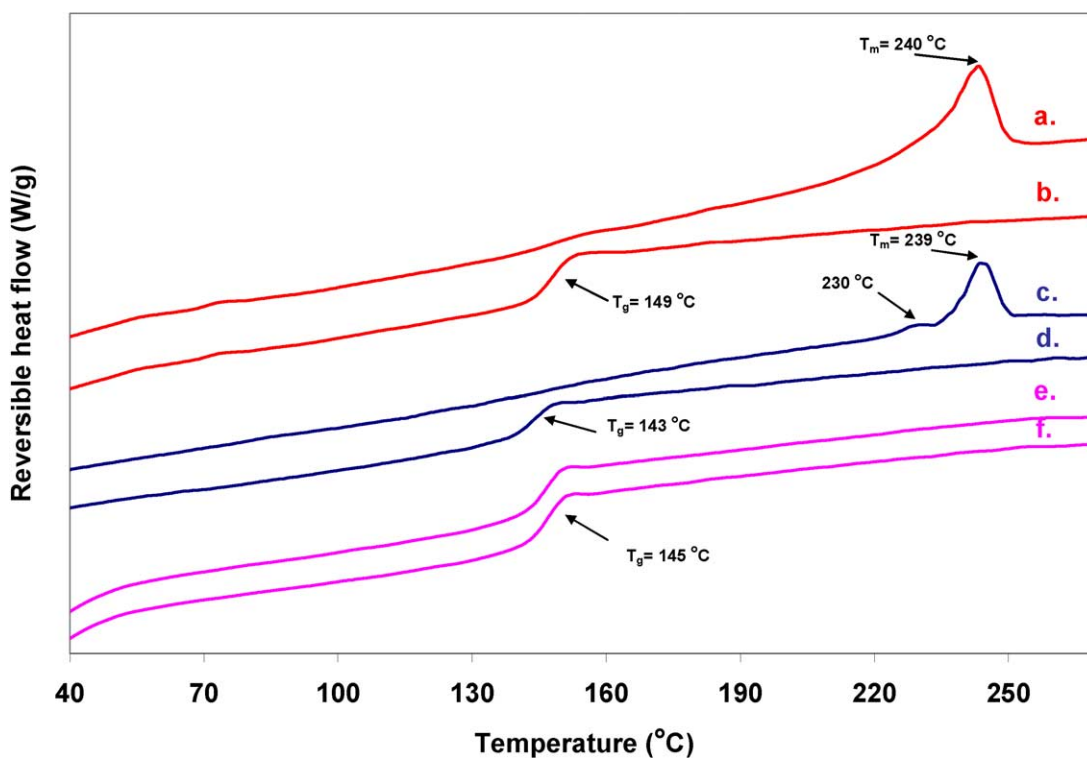

Fig. 9. Modulated DSC thermograms of (a) first heating scan of coalesced PC (b) second heating scan of coalesced PC, (c) first heating scan of precipitated PC (d) second heating scan of precipitated PC, (e) first heating scan of as-received PC (f) second heating scan of as-received PC.
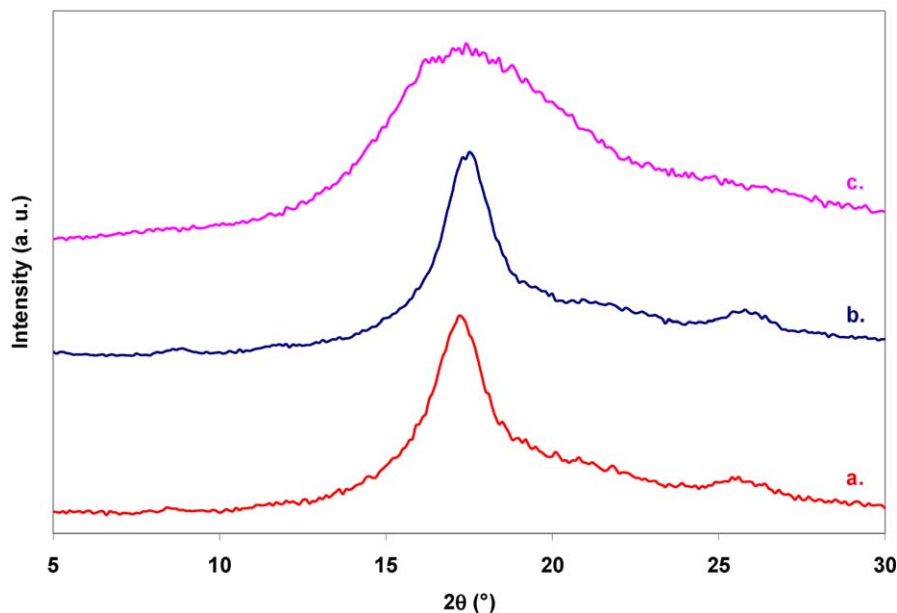
Fig. 10. X-ray diffraction patterns of (a) coalesced PC, (b) precipitated PC and (c) as-received PC.

the CD IC included chains upon their coalescence into bulk samples. Mi et al. has also observed a higher glass transition temperature for polyacrylamide (PAL) when the degree of entanglement for the polymer chains is decreased [26]. The increase in T_g value of PAL was attributed to self-aggregation of unentangled chains, where the initial extended conformation transformed to a more tightly coiled conformation upon annealing. For coalesced polymers, we also suggest the presence of extended and unentangled chains, which might form tighter and more ordered structures.

4.4. Thermogravimetric analysis (TGA)

Thermogravimetric results of pure cage γ-CD indicated two weight losses stages (Fig. 13). The first weight loss below 100 °C may be attributed to removal of water, whereas the major weight loss with a maximum at 364 °C corresponds to the main degradation of the sample.

Thermal degradation of PVAc, PMMA, and PC has been studied extensively [27–32]. Fig. 14 displays the thermal degradation of coalesced and as-received PMMA, PVAc, and PC samples. The onset weight loss value for coalesced
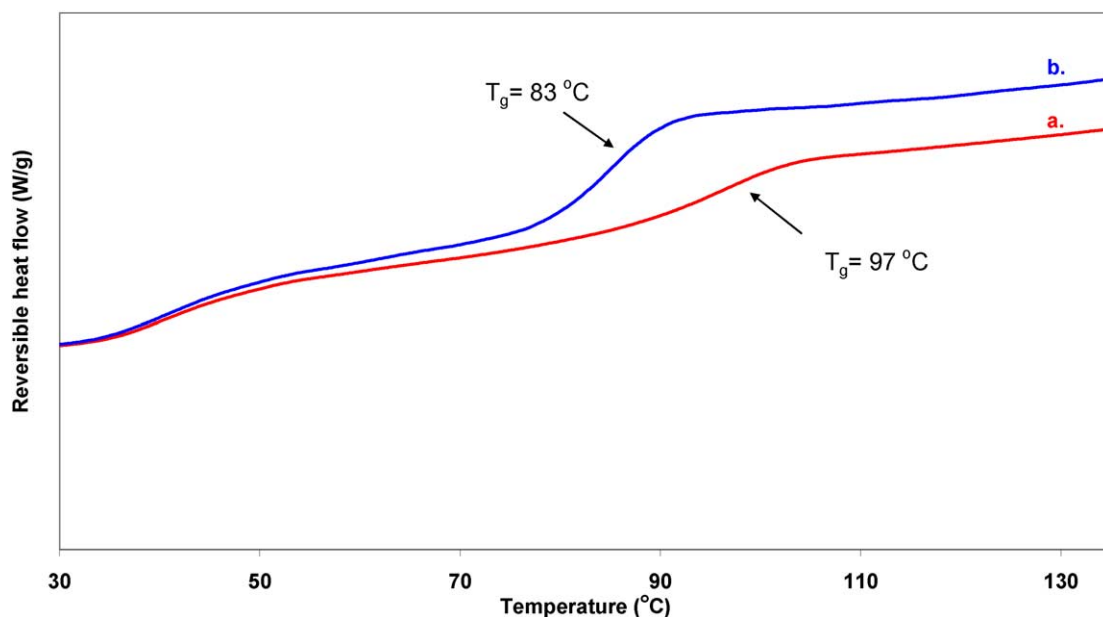

Fig. 11. Modulated DSC thermograms of (a) second heating scan of coalesced PMMA (b) second heating scan of as-received PMMA.
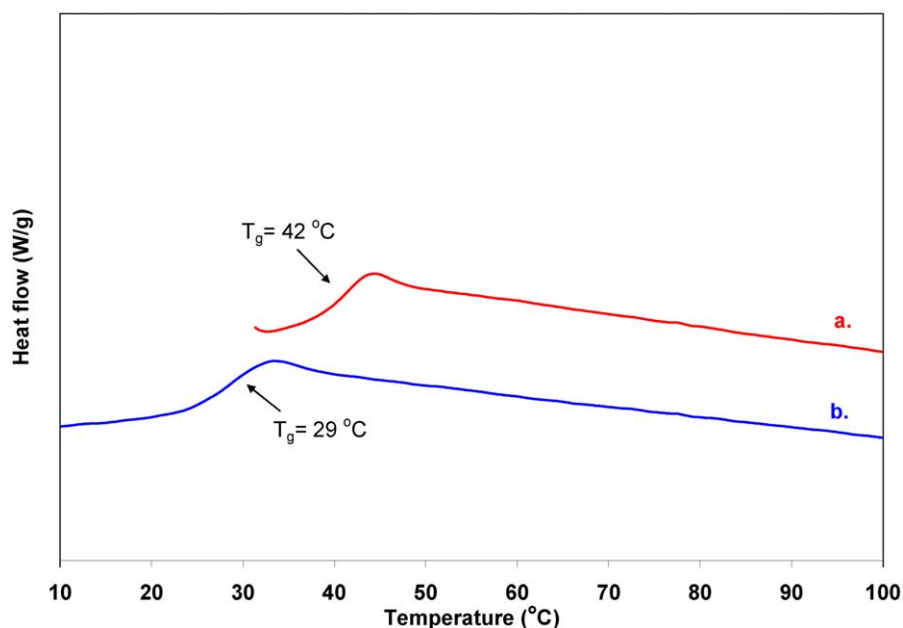
Fig. 12. DSC thermograms of (a) second heating scan of coalesced PVAc and (b) second heating scan of as-received PVAc.

PMMA is lower than that of as-received PMMA but the main degradation temperatures were shifted to higher temperature for the coalesced sample. For instance, the derivative weight loss TGA curve of as-received PMMA shows weak peaks below 300 °C and a strong peak with a maximum at 410 °C. In comparison, the TGA curve of coalesced PMMA shows two main degradation steps at 340 °C and 423 °C (higher than that of as-received sample), the second being more intense (Fig. 14(a) and (b)).

Thermal behaviors of coalesced and as-received PVAc

are shown in Fig. 14(c) and (d). The decomposition temperature, T_d, of coalesced PVAc is observed at 369 °C, whereas that of as-received PVAc is 360 °C. But, the onset weight loss value for coalesced PVAc is slightly lower than that of as-received PVAc and a shoulder around 330 °C is also present. The second degradation stages for the as-received and coalesced PVAc samples were recorded at 464 and 483 °C, respectively, indicating an increase in thermal stability for the coalesced PVAc.

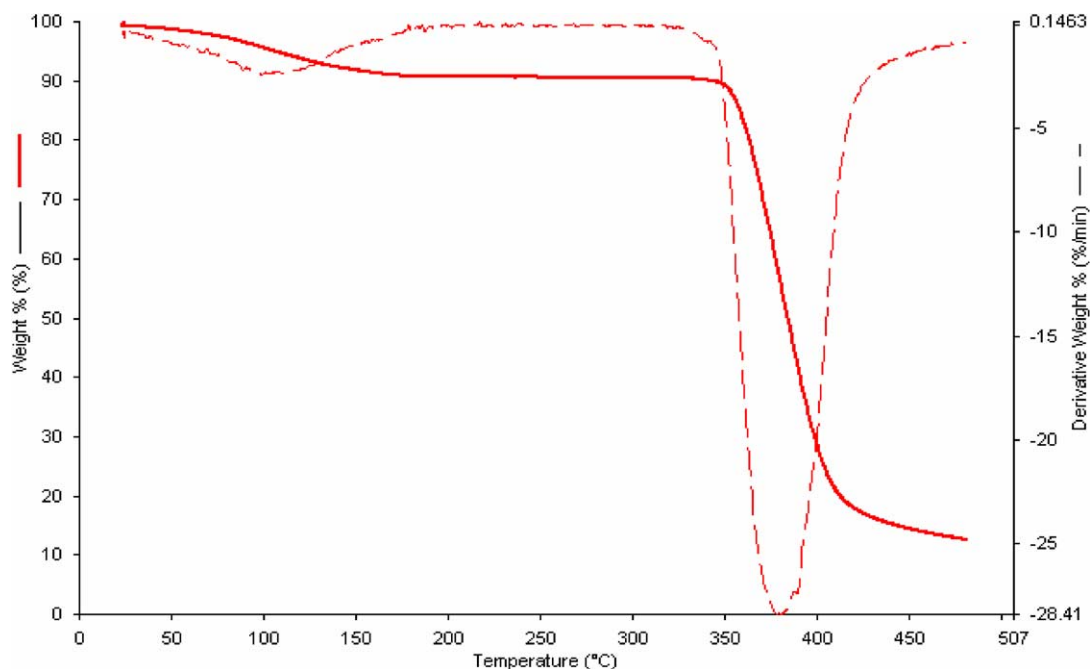TGA analysis indicated that in the case of the coalesced

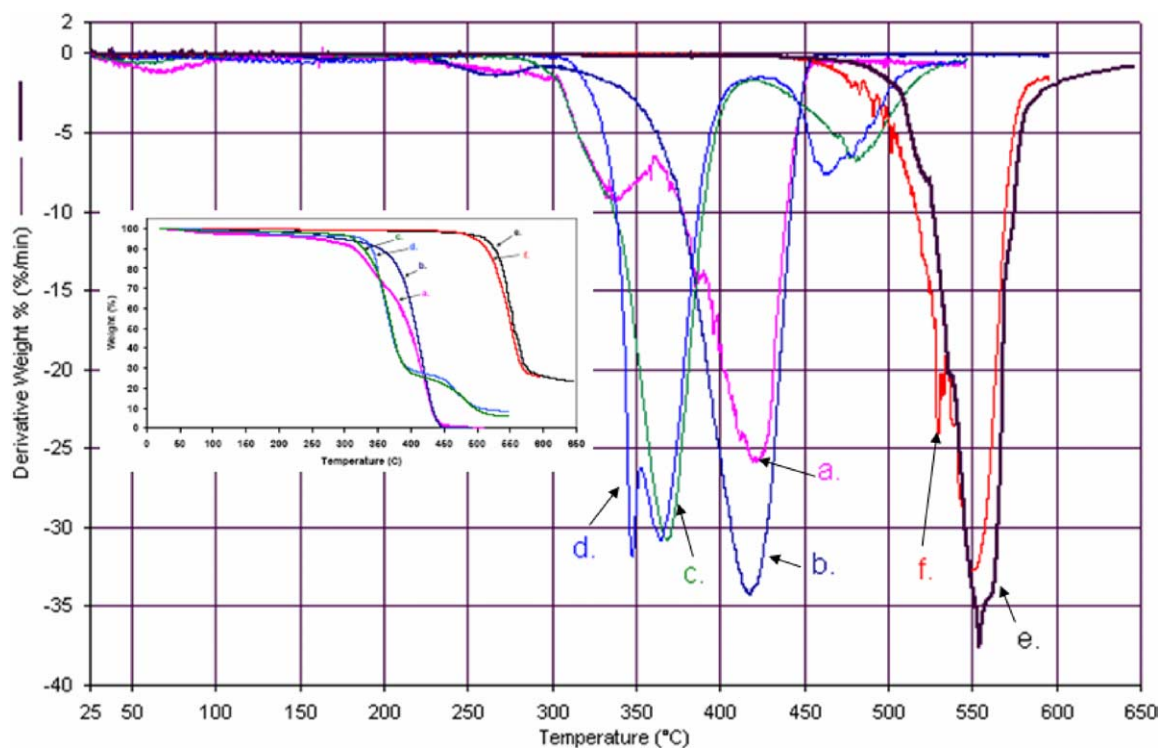Fig. 13. TGA thermograms of as-received γ-cyclodextrin.

Fig. 14. TGA thermograms of (a) coalesced and (b) as-received PMMA, (c) coalesced and (d) as-received PVAc, and (e) coalesced and (f) as-received PC.

PC sample, the T_d of PC is shifted to 554 °C, whereas as-received PC has a T_d of 549 °C (Fig. 14(e) and (f)). In general, the TGA results reveal that the thermal stabilities of coalesced samples are increased compared to the corresponding as received polymers.

4.5. Direct insertion probe pyrolysis mass spectrometry (DIP-MS)

In general, direct insertion probe pyrolysis mass spectrometry (DIP-MS) facilitates analyses of degradation mechanisms using structural information from the thermal characterization of degradation products [33–35]. However, pyrolysis mass spectra of polymers are usually very complex, as thermal degradation products further dissociate in the mass spectrometer during ionization. Furthermore, all fragments with the same mass to charge ratio make contributions to the intensities of the same peaks in the mass spectrum. Thus, in pyrolysis MS analysis, not only the detection of a peak, but also the variation of its intensity as a function of temperature, i.e. its evolution profile, is important. The trends in evolution profiles can be used to determine the source of the product, or the mechanism of thermal degradation. The direct pyrolysis mass spectrometry analysis of γ-CD, as-received polymers, polymer-CD ICs, and coalesced samples have been performed to investigate the changes in their thermal degradation behavior.

Thermal degradation of γ-CD occurs over a broad temperature range starting just above 280 °C. The variation

of total ion current (TIC) as a function of temperature shows two peaks; a sharp peak and a broad peak with a shoulder in the high temperature range having maxima at 310 and 355 °C, respectively, (Fig. 15(a)). Main degradation products are due to the cleavage of weak C–O bonds yielding intense $C_2H_4O_2$ and $C_3H_5O_2$ fragments at $m/z = 60$ and 73 Da, respectively.

The TIC curve of PVAc also shows two degradation steps, in accordance with TGA results (Fig. 15(b)). Among these peaks, with maxima at 360 and 440 °C, the low temperature one is more intense. For coalesced PVAc, the low temperature peak maximum is shifted slightly to 370 °C and the relative intensity of the second peak is noticeably diminished. Furthermore, a shoulder around 340 °C appears in the TIC curve. It is known that the thermal degradation of PVAc occurs in two stages, around 360 and 440 °C, corresponding to deacetylation and disintegration of the polyolefinic backbone, respectively, [29,30]. Analysis of our pyrolysis mass spectra also indicated loss of side groups in the first stage of thermal degradation and decomposition of the unsaturated polymer backbone formed in the second step in accordance with the literature results. In the mass spectra of the coalesced PVAc, the low temperature shoulder at ~340 °C resembles that of γ-CD pointing to the presence of some γ-CD remaining even after the long coalescence process.

A detailed study of the mass spectra recorded for coalesced PVAc around 440 °C points out an increase in H_2O evolution together with a significant decrease in olefinic product yield. These trends may be explained by
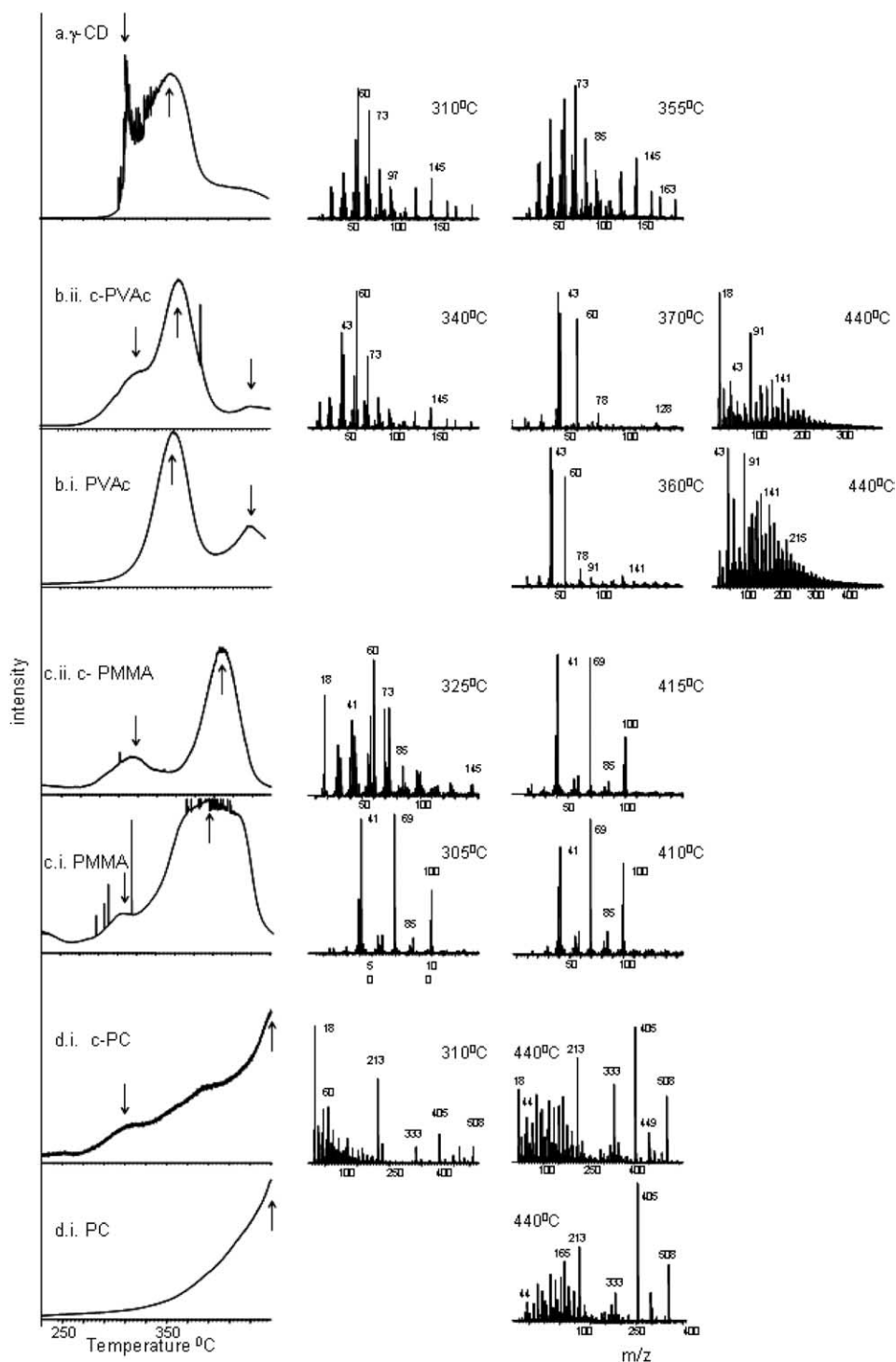
Fig. 15. TIC curves and pyrolysis mass spectra recorded at the maxima of the peaks and shoulders in the TIC curves of (a) as-received γ-CD, (b) i. as-received PVAc, ii. coalesced PVAc, (c) i. as-received PMMA, ii. coalesced PMMA, and (d) i. as-received PC ii. coalesced PC.

crosslinking of the polyolefinic backbone generated during the first thermal degradation stage, with the decomposition products of γ-CD involving two or more OH groups. Crosslinking of the polyolefinic backbone should increase thermal stability and decrease the yield of unsaturated fragments and may be a reasonable explanation for the trends observed in the TGA and TIC curves. Pyrolysis analysis were

repeated for the physical mixture of γ-CD and PVAc. The results indicated that both components degrade independetely and no support for crosslinking can be detected. Thus, it may be concluded that crosslinking is only effective when residual PVAc-γ-CD IC is present in the coalesced sample.

The thermal degradation of PMMA has been studied in detail, and it has been proposed that the degradation can be

initiated by different processes. Low temperature weight losses were attributed to scission of head-to-head linkages and loss of unsaturated end groups. At elevated temperatures (380–420 °C) initiation of weight loss was thought to be a mixture of chain end and chain scission processes, followed by depropagation to the end of the polymer chain [27,28]. Direct pyrolysis of as-received PMMA yielded a broad peak with several shoulders and two maxima at 330 and 400 °C (Fig. 15(c)). It has been proposed that in the initial stages of pyrolysis, weight losses are attributed not only to evolution of dimer and low molecular weight oligomers, but also scission of head-to-head linkages and loss of unsaturated end groups. Our pyrolysis mass spectra recorded above 300 °C show a typical fragmentation pattern for as received PMMA confirming, depolymerization.

The TIC curve of the coalesced PMMA sample is quite similar to that of the as-received sample. On the other hand, the pyrolysis mass spectra recorded around 325 °C involves peaks diagnostic for γ-CD, indicating that total removal of γ-CD was not achieved, as in the case of coalesced PVAc. Yet, the low temperature peaks are diminished and the high temperature peaks with maxima at 325 and 420 °C became sharper, indicating a decrease in polydispersity and removal of low molecular weight oligomers during the inclusion processes. It is known that cyclodextrins can include molecules selectively according to their molecular weights from their common solution and they can be used for separation/purification/fractionation purposes [36,37]. The separation/purification of PMMA from its low molecular weight oligomers may have also been attained by forming the inclusion compound with γ-CD. The selective inclusion of higher molecular weight chains of PMMA by γ-CD was also similar to that for PVAc, where only high molecular weight PVAc formed an inclusion compound with γ-CD.

Pyrolysis of PVAc- and PMMA-γ-CD ICs have also been carried out, yet, PVAc and PMMA based product yields are too low to make comparisons, because of the low stoichiometric contents of included polymers. Furthermore, no significant change was detected in the evolution profiles of γ-CD based on the decomposition of the IC products.

It has been proposed that thermal degradation studies on poly(bisphenol A carbonate) support the evolution of cyclic oligomers and CO_2 in the initial stages of degradation at about 400–500 °C. Intermolecular exchange reactions lead to formation of cyclic oligomers, whereas generation of CO_2, is explained by decarboxylation of the carbonate groups forming ether bridges and by hydrolysis reactions producing phenolic end groups [31,32]. At elevated temperatures (500–700 °C) rearrangement of carbonate groups leads to formation of condensed groups. For our direct pyrolysis system the maximum attainable temperature, 445 °C, is too low to detect the complete thermal degradation of PC. Thus, the TIC curves of as-received and coalesced PC only show the initial stages of thermal degradation as expected (Fig. 15(d)). The base peak in the pyrolysis mass spectra of as-received PC at $m/z=405$ Da is

attributed to the $C_6H_5-C(CH_3)_2-C_6H_4-O-C_6H_4-C(CH_3)_2-C_6H_4$ fragment generated by evolution of CO_2 forming ether bridges. Other intense peaks are at $m/z=213$ and 508 Da assigned to $C_6H_5-O-COO-C_6H_4$ and cyclic dimer, respectively, in accordance with the literature results [31,32]. Identical product peaks, together with peaks diagnostic for γ-CD, are identified for the coalesced sample. Yet, the evolution of degradation products shifted to lower temperatures and shoulders appear around 310 and 380 °C. Drastic differences are noted when the evolution profiles of these products from as-received and coalesced PC are compared.

To gain a better understanding of the thermal degradation of coalesced PC, PC-γ-CD IC was also studied. The TIC curve of PC-γ-CD IC shows only a single, broad peak with a maximum at 400 °C and is noticeably different from that of pure γ-CD and pure PC. Furthermore, unlike the PVAc and PMMA-γ-CD IC's, PC based product peaks are prominent. In Fig. 16, evolution profiles of some diagnostic thermal degradation products of PC and γ-CD namely $C_6H_5-C(CH_3)_2-C_6H_4-O-C_6H_4-C(CH_3)_2-C_6H_4$ ($m/z=405$ Da), $C_6H_5-O-COO-C_6H_4$ ($m/z=213$ Da), $C_3H_5O_2$ ($m/z=73$ Da), and CO_2 ($m/z=44$ Da) Da are shown. Evolution of low molecular weight PC based products shifted to lower temperatures, whereas no significant change in the evolution profiles of products generated by intermolecular exchange or rearrangement reactions are indicated. It may be thought that classical degradation pathways for PC can only be followed above 400 °C. The low temperature evolution of PC based products may be attributed to loss of polycarbonate chain ends and/or units strongly interacting with γ-CD. It is clear that both PC and γ-CD significantly affect the thermal stability of the other.

5. Conclusions

We have described a unique way of modifying the characteristics of commercial polymers through the formation of and coalescence from their inclusion compounds formed with cyclodextrins. The formation of ICs between γ-CD and polycarbonate (PC), poly(methylmethacrylate) (PMMA) and poly(vinylacetate) (PVAc) homopolymers was successfully achieved. The existence of extended chain conformations in the coalesced polymers was confirmed by FTIR findings. The chain conformations of the bulk polymers were altered when they were included inside the CD channels and partially retained their extended chain conformations when coalesced from their ICs. Significant increases in the glass transition temperatures (T_g) were observed for the coalesced polymers when compared to their as-received samples. Moreover, the thermal stabilities of the coalesced polymers increased slightly compared to the corresponding as-received polymers. It was also observed that the thermal stability and degradation products of the polymers are affected once the polymers chains are included inside the CD cavities.
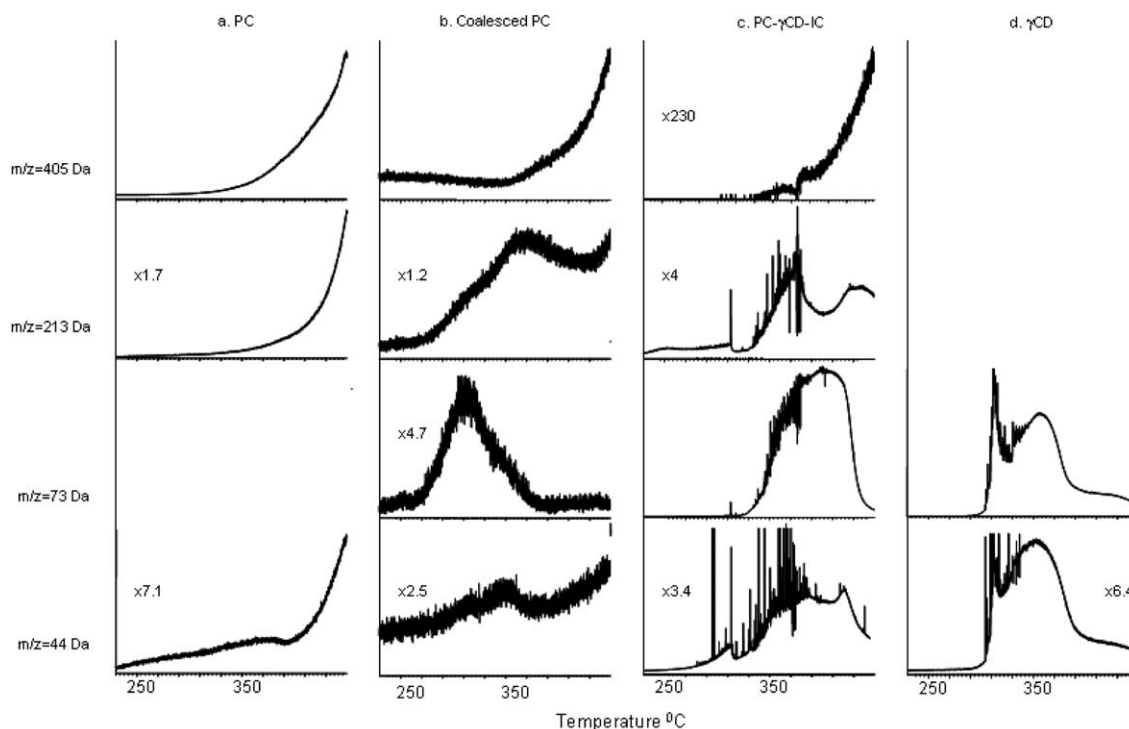
Fig. 16. Evolution profiles of CO_2 ($m/z = 44$ Da), $C_3H_5O_2$ ($m/z = 73$ Da), C_6H_5–O–COO–C_6H_4 ($m/z = 213$ Da) and C_6H_5–$C(CH_3)_2$–C_6H_4–O–C_6H_4–$C(CH_3)_2$–C_6H_4 ($m/z = 405$ Da) recorded during pyrolysis of (a) as-received PC, (b) coalesced PC, (c) PC-γ-CD-IC and (d) as-received γ-CD.

Acknowledgements

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