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INCLUSION COMPLEX FORMATION BETWEEN α-CYCLODEXTRIN AND BIODEGRADABLE COMBLIKE COPOLYMERS WITH POLY(α,β-MALIC ACID) BACKBONES AND mPEG SIDE CHAINS*

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Abstract Inclusion complexes (ICs) composed of α-cyclodextrins (α-CD) and biodegradable comblike copolymers with poly(α,β-malic acid) (PMA) backbones and methylated poly(ethylene glycol) (mPEG) side chains were prepared by the host-guest reaction. Two series of ICs with mPEG750 and mPEG2000 were prepared. The stoichiometry (EG/CD) of all the ICs in mPEG2000 series was 3.1, no matter what the graft degree was. While in mPEG750 series, the stoichiometry (EG/CD) was very different; it increased with the amount of mPEG decreasing. The decomposition temperatures of the fragments in ICs were closely related to graft degrees. The stack of α-CDs in ICs was a channel-type structure. The crystal of ICs was lamellar, and it could be reorganized to well-defined supermolecular structure.

Keywords: Inclusion complexes; α-Cyclodextrins; Comblike copolymer.

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides composed of 6 (α), 7 (β) or 8 (γ) D-glucose units linked by 1,4-α-glucosidic bonds. The average cavity diameters of α-, β- and γ-CD are 0.45 nm, 0.7 nm and 0.85 nm[1, 2], respectively. The nature of the CD cavities facilitates the ability of CDs to act as host molecules for a large number of organic molecules (guests) to form inclusion complexes (ICs) with supramolecular structure[3–10]. The driving force for ICs formation was thought to be the combination of van der Waals forces, hydrophobic interaction, hydrogen bonds and crystalline packing of host CDs[11–13]. The inclusion mechanism and process of ICs were extensively investigated[14–17]. Polyrotaxanes, which were ICs composed of CD hosts and polymer guests, were first reported in 1990[18]. Li *et al.*[19] studied the interaction between α-CDs and poly(propylene oxide)-poly(ethylene oxide)-poly(propylene oxide) (PPO-PEO-PPO) triblock copolymers and found that all the α-CDs were located in the middle PEO blocks. Lee *et al*.[20] reported that the threading/dethreading process of CDs along the polyethylenimine (PEI) chains in PEI-PEG-PEI triblock copolymers could be reversibly controlled by adjusting pH. Tonelli and Harada[21–26] studied the dynamics and crystalline behavior of polyrotaxanes with biodegradable PCL and its copolymers.

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Recently, the research of polyrotaxanes has been focused on the fabrication of polymer guests. Hyperbranched[27], star-shaped[28, 29]and comblike[30, 31] polymers were designed and applied as guests. Goh *et al*.[28] reported the self-assembly of multi-armed PEG and α, β and γ-CDs. Kwak *et al.*[32] designed four architectures of polymer guests as star-shaped, random branched, block and linear to study the reorganization of polyrotaxanes. Zhu *et al.*[27] observed juxtaposed lamellar crystal of polyrotaxane with hyperbranched polyether as guest. Polyrotaxanes are great potentially applied in biomedical engineering, for example, drug delivery. Biodegradability is an important property for polyrotaxanes in biomedical applications. Unfortunately, most polymer guests except PCL and its copolymers in polyrotaxanes reported are nondegradable, which is a limitation for biomedical applications.

In this paper, a new biodegradable polyrotaxane was reported. The polyrotaxane was composed of α-CDs and biodegradable comblike polymers with poly(α,β-malic acid) as backbones and mPEG as side chains. Two series of mPEG with molecular weight of 750 and 2000 were grafted on the carboxyl side groups in poly(α,β-malic acid). The graft degrees were controllable. The preparation, crystal structure and stoichiometry of polyrotaxane were investigated.

EXPERIMENTAL

Materials

L-malic acid, *N*,*N*′-dicyclohexylarbodiimide (DCC) and α-cyclodextrin were purchased from Aldrich and used as received. Methylated poly(ethylene glycol)s (M_n = 750 and 2000) were purchased from Aldrich and vacuum-dried before used. Tetrahydrofuran (THF), diethyl ether, acetone and dimethyl sulfoxide (DMSO) were purchased from Sinopharm chemical reagent company. THF and diethyl ether were dried by refluxing over sodium. DMSO was purified by vacuum distillation before use. Acetone was used as received.

Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-400 spectrometer, working at 400.132 MHz for ^{1}H-NMR. The solvent for ^{1}H-NMR measurements was D_2O with 0.5% tetramethylsilane (TMS) as internal standard. Fourier transform infrared (FTIR) spectra were made on a Perkin-Elmer Spectrum One FTIR spectrometer. The samples were pressed into KBr pellets, and spectra were recorded at the wave number range from 4000 cm^{-1} to 400 cm^{-1}. X-ray diffractometry (XRD) patterns of α-CD, comblike copolymers and ICs were obtained at room temperature on a Rigaku D/max-2500 X-ray diffractometer with a Cu Kα (v = 0.154 nm) radiation source, the supplied voltage and current were set to 50 kV and 100 mA, respectively. The samples were mounted on a sample holder and scanned with a step size of 0.02° from 2° to 50°. Differential scanning calorimetric (DSC) measurements were performed on a TA System Q100 under nitrogen at a flow rate of 50 mL/min. Each sample was heated from –10°C to 200°C at a heating rate of 10 K/min and scanned twice to eliminate the thermal history. Thermal gravimetric analysis (TGA) was carried out on a TA System Q500. The samples were heated from room temperature to 500°C at a heating rate of 10 K/min in a dynamic nitrogen atmosphere. The morphologies of the inclusion complexes were observed with scanning electron microscopy (SEM) (JEM-2100F at 10 kV).

Synthesis of PMA

The synthesis of PMA was prepared as the same method described in reference[33]. In brief, 50 g of L-malic acid was added in a 150 mL bottom-rounded flask with a magnetic stirrer. The polycondensation was carried out under 13.3 Pa vacuum at 110°C for 72 h. The white products were dissolved in anhydrous THF and precipitated in a large amount of anhydrous diethyl ether. The diethyl ether was removed and the remaining white precipitate was vacuum-dried at room temperature for 24 h. The M_n of PMA was 2280 and the M_w/M_n = 1.97 (GPC result) .

Preparation of Comblike Copolymers

A typical procedure was as following: prescribed amounts of mPEG and PMA were added in a 150 mL bottom-rounded flask with anhydrous THF. DCC (the mole ratio of DCC and mPEG was 3:1) was dissolved in

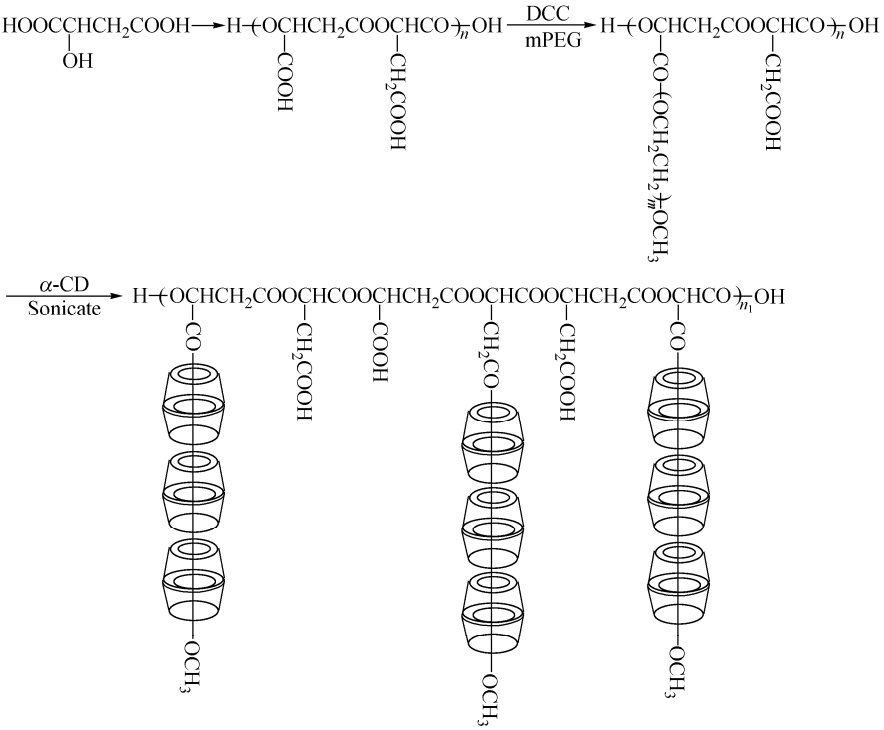
anhydrous THF and added in the mixture dropwise. The mixture was magnetically stirred at 0°C for 24 h, and white precipitate appeared in the mixture. The mixture was filtrated. The filtrate was condensed and precipitated in distilled water. The mixture was centrifuged to remove the white precipitate and the solution was dried by lyophilization. The obtained white powder was vacuum-dried at room temperature for 48 h.

Formation of Inclusion Complexes

α-CD was dissolved in distilled water (1.016 g in 7 mL H_2O) at room temperature. The comblike copolymer was dissolved in DMSO (0.300 g in 4 mL DMSO). The solutions were mixed together and sonicated for 30 min. The mixture was kept at 4°C overnight, and white precipitate appeared in the bottom. The precipitate was collected by centrifugation and repeatedly washed with acetone and water to remove the free copolymer and α-CD. The recovered ICs were vacuum-dried at 60°C for 48 h. The yield of IC was determined from the weight of comblike copolymer and CD used: yield = weight of complex/(weight of comblike copolymer + weight of CD).

RESULTS AND DISCUSSION

The poly(α,β-malic acid) backbones were synthesized by the polycondensation of L-malic acid. There were two types of α and β-carboxyl groups on the poly(α,β-malic acid) backbones, and the ratio of the two types was nearly 1:1[33]. mPEGs with different molecular weights were grafted to the pendant carboxyl groups in the presence of DCC as catalyst, and the graft degrees were designed as 20%, 40% and 100%. The 20% graft degree meant that 20% pendant carboxyl groups were grafted with mPEG chains. α-CDs were threaded onto the mPEG chains to form inclusion complexes. The possible structure of the ICs was presented in Scheme 1.



Scheme 1 Synthetic route for the comblike polymers and the structure of the IC

The prepared inclusion complexes are shown in Table 1. Two series of comblike copolymers with mPEG2000 and mPEG750 side chains were synthesized. It was clear that the graft degrees were nearly the same as feeding doses. The yield of IC in the two series decreased with increasing graft degree. The IC yield in mPEG2000 series was 51.8%, 45.8% and 38.7% when the graft degree was 20%, 40% and 100%, and that in

mPEG750 series was 55.2%, 50.3% and 40.8%. The yield of IC was lower than that of ICs composed of free PEG chains and α-CDs[34]. The mole ratio between the repeated units in mPEG chains and α-CDs (EG/α-CD) was an important factor to study the structure of ICs. Many researchers reported that the mole ratio of EG/α-CD in ICs with free PEG chains was around 2.0[10, 34], and the thickness of α-CD was about the length of two repeated EG units. An interesting result was found in our studies, in the series of mPEG2000, the mole ratios of EG/α-CD in ICs were nearly the same around 3.0, no matter what the graft degree was, while in the series of mPEG750, the ratio varied with graft degree. The ratio was 3.1, 2.5 and 2.0 when the graft degree was 20%, 40% and 100%. The low yield and variation of EG/α-CD in the two series of ICs could be explained from the structure of comblike copolymers and the length of mPEG side chains. In the comblike copolymers, the mPEG chains were immobilized on the pendant carboxyl groups of PMA backbones, the mobility of the immobilized mPEG chains was much lower than that of free PEG chains, so α-CDs were harder to thread on the mPEG chains, and this led to the higher EG/α-CD ratio in ICs with comblike copolymer guests. Some researchers found that the molecular weight of PEG chains was important in the formation of ICs, if the chain length of PEG was too short, the ICs could not form because α-CDs would slide down from PEG chains[31, 34]. There were about 45 repeated EG units in mPEG2000 chains and 17 repeated EG units in mPEG750 chains, the flexibility of the mPEG2000 chains was relatively higher than that of mPEG750 chains. A single mPEG2000 chain was more like a random coil in solution, and the threaded α-CDs were hard to slide down from mPEG2000 chains. That was why the mole ratios of EG/CD in ICs series of mPEG2000 were stable around 3.0. The chain of mPEG750 was short, and α-CDs were easily threaded on it. The distance between mPEG750 chains in comblike copolymers with 100% graft degree was short, and the threaded α-CDs were easily to form crystal subsequently provide strong interaction to stabilize ICs, thus rare α-CDs slid down from mPEG750, so the mole ratio of EG/α-CD was close to that in ICs with free PEG chains. In the ICs with 20% and 40% graft degree, the interactions were weak for the long distance between mPEG750 chains, the α-CDs were easily slid down from mPEG750 chains, which led to higher EG/CD ratios.

Table 1. Inclusion complexes of α-CD and comblike copolymers

Entry	mPEG (M_n)	Graft degree (%)		IC yield (%)	Mole ratio[a] (EG/α-CD)
		Feeding	^{1}H-NMR		
1	2000	20	19	51.8	3.1
2	2000	40	40	45.8	3.0
3	2000	100	99	38.7	3.1
4	750	20	21	55.2	3.1
5	750	40	41	50.3	2.5
6	750	100	99	40.8	2.0

[a] Calculated from ^{1}H-NMR spectra

The ^{1}H-NMR spectra of PMA, comblike copolymer and inclusion complex are presented in Fig. 1. The multi-peaks at δ = 3.0–3.2 were assigned to the protons of C$\underline{H}_2$ (b) in both α and β-type units in poly(α,β-malic acid), the doublets at δ = 5.5 and 5.6 were attributed to the protons of C$\underline{H}$ (a) in poy(α,β-malic acid). The chemical environment of the random aggregated α and β-type of the repeated units in PMA backbones was in little difference and thus led to the signals split into multipeaks. Figure 1(B) shows the ^{1}H-NMR spectrum of comblike copolymer. In comparison with the spectrum in Fig. 1(A), the peaks at δ = 3.4 and 3.6–3.8 were attributed to the protons of mPEG as OC$\underline{H}_3$ (d) and OC$\underline{H}_2$C$\underline{H}_2$ (c). From the intensity ratios between C$\underline{H}_3$ (d) in mPEG and C$\underline{H}$ (a) in poly(α,β-malic acid) backbones, the graft degree was calculated, and it was consistent with the feeding dose.

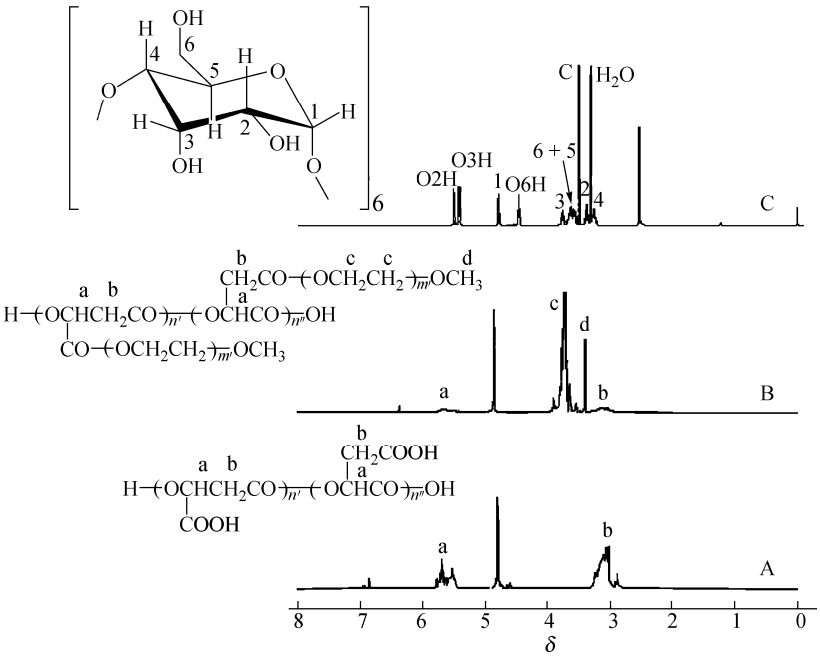


Fig. 1 ^{1}H-NMR spectra of PMA (A), comblike copolymer (mPEG2000 with 40% graft degree) (B), and IC (entry 2) (C)

The ^{1}H-MNR spectrum of IC is presented in Fig. 1(C). According to the assignments of the protons in ICs reported in previous studies[34], the sharp peak at $\delta = 3.3$ was attributed to the protons in water. Because both α-CDs and comblike copolymers were very hydrophilic, it was hard to get rid of the water completely. The signal at $\delta = 3.5$ was the protons of O$\underline{\text{C}}\underline{\text{H}}_2\text{C}\underline{\text{H}}_2$ in mPEG, it shifted from $\delta = 3.75$ (in Fig. 1B) to $\delta = 3.5$. The mole ratio of EG/α-CD was calculated from the integrities of O$\underline{\text{C}}\underline{\text{H}}_2\text{C}\underline{\text{H}}_2$ (c) in mPEG and C$\underline{\text{H}}$ (1) in α-CDs.

The FTIR spectra of comblike copolymer, α-CD, and corresponding IC are shown in Fig. 2. The strong band at 1749 cm^{-1} was attributed to the carbonyl stretching vibration ($\nu_{c=o}$) in the poly(α,β-malic acid) backbones, and the band at 1158 cm^{-1} was due to the asymmetric stretching vibration of the C—O—C glycosidic bridge. The bands at 1026 and 1079 cm^{-1} were the stretching vibrations of coupled C—C/C—O. With the comparison of all the three spectra, it could be found that the spectrum of IC was very similar to that of α-CD in the fingerprint region, which indicated that the α-CDs were threaded onto the mPEG side chains. An additional vibration band appeared at 1632 cm^{-1} in all the three FTIR spectra, it was attributed to the vibration of water absorbed, which was mentioned in the former ^{1}H-NMR spectrum.

In order to determine the structure of ICs, the XRD measurements were carried out, and the spectra are presented in Fig. 3. As for all the three comblike copolymers with mPEG750 side chains were viscous liquid at room temperature, the XRD spectrum of comblike copolymer with mPEG2000 was selected as a control. In Fig. 3(a), the pattern of α-CD crystal represented a cage-type structure[17]. The prominent peaks of mPEG crystal was appeared at $2\theta = 19.3°$ and 23.4°. In the spectra of IC, a very strong peak at $2\theta = 19.7°$ was presented in the diffraction patterns, it was the characteristic peak associated with a channel-type crystalline structure by virtue of the polymeric nature of the guest molecules[16–19, 35]. The α-CD rings were threaded onto mPEG side chains and stacked on to produce necklace-like polyrotaxanes.

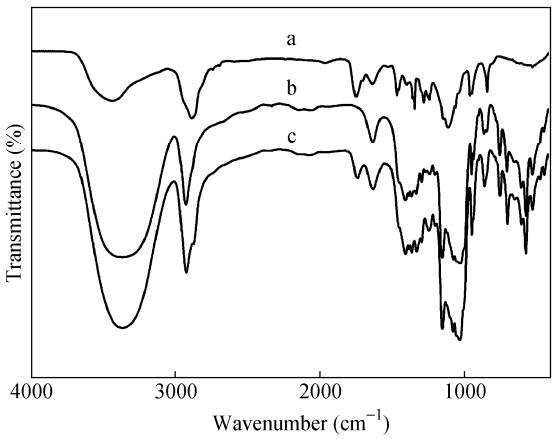


Fig. 2 FTIR spectra of comblike copolymer (mPEG2000 with 40% graft degree) (a), α-CD (b), and IC (entry 2) (c)

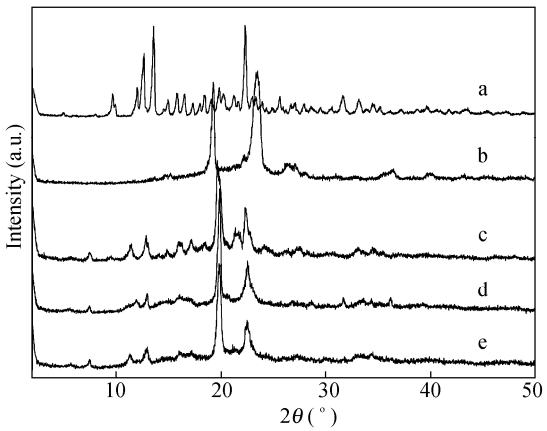


Fig. 3 XRD spectra of α-CD (a), comblike copolymer (mPEG2000 with 40% graft degree) (b) and ICs of series mPEG750 with graft degree: 20% (entry 4) (c), 40% (entry 5) (d), 100% (entry 6) (e)

The thermal properties of ICs were characterized by DSC and TGA. The DSC curves of PMA, comblike copolymer and IC are shown in Fig. 4. The curve of PMA (Fig. 4a) was a straight line without any endothermic or exothermic peaks in the testing temperature ranged from −10°C to 80°C. An obvious strong endothermic peak appeared at about 47.8°C in the curve of comblike copolymer (Fig. 4c), indicating the melting of mPEG crystals. The endothermic mPEG-melting peak vanished in the curve of IC (Fig. 4b). Upon formation of IC, the temperature range did not show any thermal events corresponding to the fusion of crystalline comblike copolymer. The results of DSC measurements showed convincing evidences that the crystallization of mPEG was remarkably suppressed in the α-CD cavity, and the original crystal properties of comblike polymer was lost owing to the formation of inclusion complexes. The results were consistent with the XRD analysis.

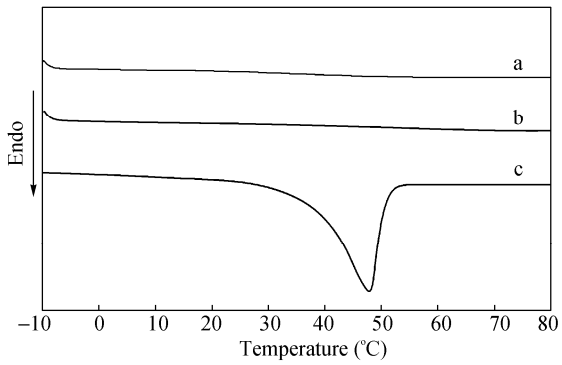


Fig. 4 DSC curves of PMA (a), IC (entry 2) (b) and comblike copolymer (mPEG 2000 with 40% graft degree) (c)

The weight loss of PMA, comblike copolymer, α-CD and IC in thermal gravimetric analysis is presented in Fig. 5. As shown in Fig. 5(b), the comblike copolymer showed two distinct decomposition transitions, the first step was attributed mainly to the decomposition of the PMA backbones, and the second step was the decomposition of mPEG side chains. The IC also underwent an obviously two-step weight loss, the first one was attributed to the decomposition of threaded α-CDs, and the second one was due to the side mPEG chains. As for the low concentration of PMA backbones in IC, the decomposition step of PMA was very weak. There was

about 10% weight loss happened in the curve of α-CD (Fig. 5c) below 100°C, which was the water absorbed in α-CDs. Both PMA and the comblike copolymer were decomposed completely with the weight remaining reached to zero. In the case of α-CDs and ICs, nearly 10% weight was left.

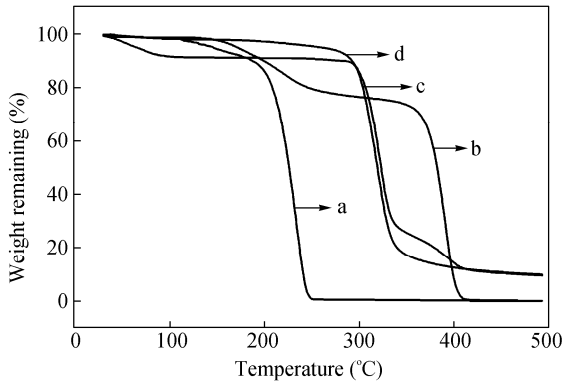


Fig. 5 TGA curves of PMA (a), comblike copolymer (mPEG2000 with 40% graft degree) (b), α-CD (c) and IC (entry 5) (d)

TGA was an effective method to study the interaction in inclusion complexes[19, 36]. The TGA curves of mPEG750 ICs series are shown in Fig. 6, and the decomposition temperatures of the segments in ICs are presented in Table 2. The decomposition temperature of free PMA was 213°C and that of PMA backbones in comblike copolymer was 170°C, which was much lower than that of free PMA. This was because that the interaction in PMA backbones was weakened for the mPEG graft. The decomposition temperatures of free mPEG and mPEG side chains were 374°C and 371°C, respectively. The decomposition temperature of free α-CD was 302°C, and those of α-CD in ICs with 20%, 40% and 100% graft degree were 295°C, 319°C and 321°C. This could be explained by the molecular interactions, for the low value of EG/α-CD ratio, the interaction among α-CDs in IC with 100% graft degree was the strongest, so the corresponding decomposition temperature of α-CD was the highest. The ratios of EG/α-CD in ICs calculated from TGA curves are also presented in Table 2. Although the ratios were not as accurate as the results in ^{1}H-NMR, they were quite in agreement with those calculated from ^{1}H-NMR spectra.

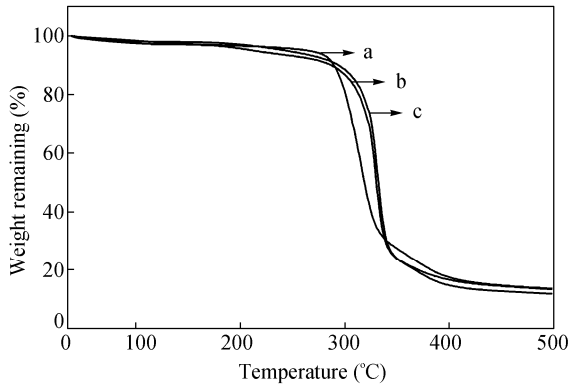


Fig. 6 TGA curves of mPEG750 ICs series, graft degree: 20% (a), 40% (b) and 100% (c)

Table 2. The decomposition temperatures of the segments in mPEG750 ICs series

Graft degree (%)	T_d (free) (°C)				T_d (IC) (°C)			EG/α-CD	
	PMA	PMA[a]	MPEG[a]	α-CD	PMA	mPEG	α-CD	^{1}H-NMR	TGA
20	213	170	374	302	–	371	295	3.1	3.5
40	213	170	374	302	–	370	319	2.5	2.7
100	213	170	374	302	–	371	321	2.0	2.1

[a] The decomposition temperatures of comblike copolymer with 40% mPEG graft degree;
– Not available

The crystal structure of ICs composed of α-CD and polymers was lamellar[17, 30, 37]. Recently, Kwak *et al*.[32] reported a method to reorganize ICs with well-defined supramolecular architectures. The morphology of ICs was closely related to the treatments (Fig. 7). The original IC under SEM was powder with multi-layer lamellar crystals (Fig. 7a), and the lamellar crystal became large and thick after recrystallization subsequently treated with acetone (Fig. 7b). The morphology of IC crystals changed greatly and the crystal was reorganized to form regular well-defined structure after treated with ethanol (Fig. 7c). From the micrograph of Fig. 7(d), it could be found that the IC crystals showed connected multi-wall structure.

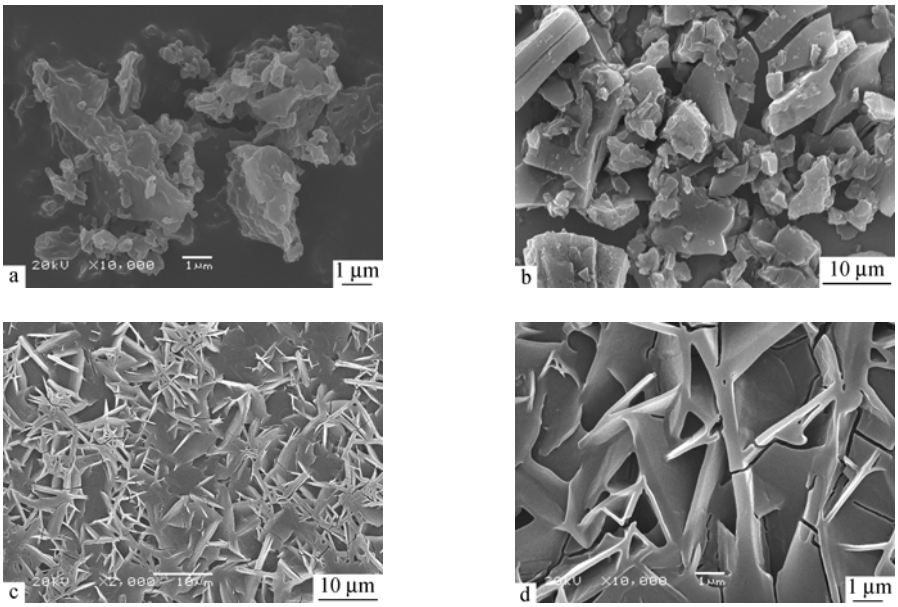


Fig. 7 SEM images of ICs: original (a), treated with acetone (b), treated with ethanol (c) and enlarged c (d)

CONCLUSIONS

The inclusion complexes of comblike biodegradable polymers with poly(α,β-malic acid) backbones and mPEG side chains and α-cyclodextrin were prepared. The α-CDs in ICs were channel-type stacks. In the series of ICs with mPEG750 side chains, the amount of α-CDs threaded on mPEG750 increased with graft degree increasing, while in the series of ICs with mPEG2000 side chains, the amount of threaded α-CDs was stable, and the ratio of EG/α-CD was around 3.0. The decomposition temperature of the segments in ICs varied with mPEG graft degrees. The crystal of ICs could be reorganized to well-defined supramolecular structure. With the mechanism of IC formation, it is potentially applicable in biomedical engineering. The research of biodegradable ICs in drug delivery is under exploring and will be reported in following papers.

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