Using Hydroxypropyl-β-cyclodextrin for the Preparation of Hydrophobic Poly(ketoethyl methacrylate) in Aqueous Medium

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ABSTRACT: This work was committed to the polymerization of hydrophobic ketoethyl methacrylate monomer in aqueous medium in the presence of cyclodextrin, instead of polymerizing the monomer in toxic and volatile organic solvents. For this purpose, a new ketoethyl methacrylate monomer, *p*-methylphenacylmethacrylate (MPMA), was synthesized from the reaction of *p*-methylphenacylbromide with sodium methacrylate in the presence of triethylbenzylammonium chloride. The monomer was identified with FTIR, ^{1}H and ^{13}C-NMR spectroscopies. Hydroxypropyl-β-cyclodextrin (HPCD) was used to form a water-soluble host/guest inclusion complex (MPMA/HPCD) with the hydrophobic monomer. The complex was identified with FTIR and NMR techniques and polymerized in aqueous medium using potassium persulfate as initiator. During polymerization the resulting hydrophobic methacrylate polymer precipitated out with a majority of HPCD left in solution and a minority of HPCD bonded on the resulting polymer. The thus-prepared polymer exhibited little difference from the counterparts obtained in organic solvent in number average molecular weight (M_n), polydispersity (M_w/M_n) and yield. The investigation provides a novel strategy for preparing hydrophobic ketoethyl methacrylate polymer in aqueous medium by using a monomer/HPCD inclusion complex. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2933–2939, 2010

Key words: *p*-methylphenacylmethacrylate; polymerization; inclusion complex; hydroxypropyl-β-cyclodextrin; host-guest systems

INTRODUCTION

Cyclodextrins (CDs), as cyclic oligosaccharides consisting of 6 (α), 7 (β), or 8 (γ) glucopyranose units linked by 1,4-α-glucosidic bonds,[1–3] are well-known to form inclusion complexes with suitable organic molecule guests due to CDs' polar hydrophilic outer shell and relatively hydrophobic cavity.[4–8] The occurrence of inclusion complex leads to a drastic change in the solubilities and reactivities of guest molecules. For instance, by forming inclusion complex with CDs, hydrophobic monomers become water-soluble and their polymerizations can therefore be performed in aqueous medium instead of toxic organic solvents. Accordingly, CDs can be utilized in organic chemistry for example as microvessels[9] or as catalysts in organic syntheses.[10,11] In particular, CDs are widely used in polymer chemistry by many researchers. Ritter and coworkers[12–14] have prepared a series of methacrylate monomer/methylated-β-cyclodextrin inclusion complexes and polymerized them in aqueous solution. Rimmer and Tattersall[15] have examined the emulsion polymerization of dodecyl and octadecyl methacrylate using a conventional water-soluble initiator and sulphonate surfactant in the presence of CD. They have also investigated the emulsion polymerization of butyl methacrylate with β-cyclodextrin instead of usual surfactant.[16] Additionally, many reports have been focused on polyrotaxanes formed by threading a polymer chain or a long molecule through many CD rings.[17–19]

Over the past several decades, thermal degradation and thermal stability of polymethacrylates have been of considerable interest.[20] Polymethacrylates

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bearing suitable side groups exhibited thermal stability and thermal decomposition properties. Soykan and coworkers[21–25] synthesized a series of polymethacrylates containing different side groups, and the thermal degradation mechanism[26,27] of these polymers was investigated in detail. Madison and Long[28] polymerized several methacrylate monomers in aqueous media by using methylated-β-cyclodextrin additives. However, this type of polymers is generally prepared in organic solvents, and up to now no reports have been found to focus on the use of CDs to perform polymerizations of ketoethyl methacrylate monomers in aqueous media, from which an important class of degradable polymers can be prepared.

In our group, we have succeeded in preparing polymers from hydrophobic monomers via radical polymerization in water.[29,30] We have also reported a novel and facile method for performing catalytic polymerization of hydrophobic substituted acetylenes in an aqueous medium by using a monomer/HPCD inclusion complex.[31] We attempt in the present article to polymerize a new hydrophobic ketoethyl methacrylate monomer in aqueous medium by using the monomer/HPCD inclusion complex in the presence of a water-soluble radical initiator. Interestingly, polymerization of the inclusion complex was readily carried out providing the corresponding polymer. The thus-prepared polymer exhibited no pronounced difference in number average molecular weight (M_n), polydispersity (M_w/M_n) and yield, when compared with the counterpart prepared in organic solvent. To our knowledge, this novel strategy for preparing ketoethyl polymers has not yet been reported. It is worthwhile to point out that the aqueous polymerization technique is superior in terms of environmental protection to the traditional polymerizations in organic solvents. We believe that the present investigation will not only provide an environmentally friendly route to preparing polymers, but extensively widen the uses of CDs and their derivatives also.

EXPERIMENTAL

Materials

Hydroxypropyl-β-cyclodextrin (HPCD) was purchased from ACROS, with an average degree of substitution about 1.0 per glucose unit mainly in 2-position. Water was freshly deionized before use. THF was purified by distilling under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform into methanol. *p*-Methylphenacylbromide (Alfa Aesar), sodium methacrylate, triethylbenzylammonium chloride (TEBAC), hydroquinone, potassium persulfate, sodium hydroxide and other chemicals were used as received.

Instrumentation

^{1}H and ^{13}C-NMR spectra were obtained on a Bruker AV600 spectrometer at room temperature. For HPCD and monomer/HPCD complex, the NMR spectra were recorded in D_2O; for monomer, $CDCl_3$ was used as solvent. FTIR spectra were recorded on Nicolet NEXUS 670 spectrophotometer. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were determined by GPC (Waters 515-2410 system) calibrated by using polystyrenes as standards and THF as eluent. TGA was performed on a NETZSCH TG 209 instrument on powder samples at a heating rate of 10°C/min under nitrogen atmosphere from 25 to 500°C.

Synthesis of *p*-methylphenacylmethacrylate (MPMA)

MPMA was synthesized by the reaction of *p*-methylphenacylbromide and sodium methacrylate using TEBAC as a phase transfer catalyst according to the literature.[23] The typical preparation procedure is as follows: *p*-methylphenacylbromide (0.1 mol), sodium methacrylate (0.1 mol), TEBAC (0.01 mol), KI (0.01 mol) as catalyst and hydroquinone (100 ppm) as inhibitor were sequentially added in a 100 mL flask containing 50 mL acetonitrile and stirred at 75°C for 24 h. KOH aqueous solution (5 wt %) was added to the mixture until it was neutralized. The organic layer was washed several times with water and extracted with diethyl ether. The acetonitrile layer and diethyl ether layer were collected and dried over anhydrous $MgSO_4$ overnight. Acetonitrile and diethyl ether were then removed using a rotorevaporator. The residue was recrystallized from chloroform into *n*-hexane to provide the product.

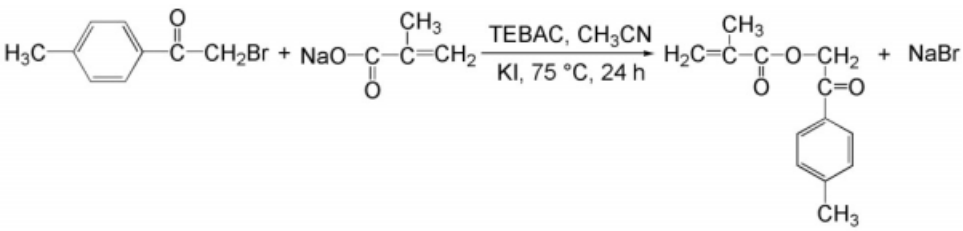
Characteristic FTIR bands (see the figure later): 1721 and 1700 cm^{-1} (C=O of ester and ketonic groups), 1636 cm^{-1} (C=C stretching of the vinyl), 1608 and 1428 cm^{-1} (C=C stretching of the aromatic ring), 2954 cm^{-1} (C—H stretching of the methylene and methyl group), 1168 cm^{-1} (C(=O)—O—C stretch and C—O—C asymmetric stretch).

^{1}H-NMR (δ ppm): 7.9–7.2 (4H, H-9; H-10), 6.3–5.6 (2H, H-1), 5.3 (2H, H-5), 2.4 (3H, H-7), 1.9 (3H, H-3).

^{13}C-NMR (δ ppm): 191 (C-6), 167 (C-4), 135, 126 (C-1; C-2), 144, 131, 129, 127 (C-8; C-9; C-10; C-11), 66 (C-5), 21 (C-7), 18 (C-3).

Preparation of MPMA/HPCD inclusion complex

HPCD (3.174 g, 2.3 mmol) was dissolved in 10 mL of deionized water. MPMA (0.5 g, 2.3 mmol) was



Scheme 1 The main procedure for synthesis of *p*-methylphenacylmethacrylate.

dissolved in 0.2 mL THF and then added into the above solution. The mixture was stirred at 50°C for 24 h to obtain a clear solution. Water was then removed using a rotorevaporator and the complex was dried under vacuum at 50°C for 24 h.

Characteristic FTIR bands (see the figure later): 1721 and 1700 cm^{-1} (C═O of ester and ketonic groups of MPMA), 1168 cm^{-1} (C(═O)─O─C stretch and C─O─C asymmetric stretch), 3419 cm^{-1} (─OH of HPCD), 1154–1037 cm^{-1} (C─O─C of HPCD).

Aqueous polymerization of MPMA/HPCD inclusion complex

A predetermined amount of HPCD was added into 10 mL water and stirred to obtain a clear solution. A solution of MPMA (0.11 g, 0.52 mmol) in THF (0.1 ml) was added and the mixture was stirred at 50°C for 24 h, in which $K_2S_2O_8$ (0.0014 g, 0.0052 mmol) was added then. The polymerization reactor was sealed and polymerization was carried out at 70°C for ~ 24 h. The entire procedure was conducted under N_2 atmosphere. The precipitated polymer (PMPMA/HPCD) was filtered and then dried in vacuum at room temperature for 24 h.

Polymerization of MPMA in THF

A solution of MPMA (0.5 g, 2.34 mmol) in 2 mL THF was added in a 10 mL reactor tube and AIBN (0.0038 g, 0.0234 mmol) was added in this solution. The polymerization reactor was then sealed under nitrogen and heated to 60°C for about 24 h. The product was cooled and PMPMA was precipitated from THF into methanol.

RESULTS AND DISCUSSION

Synthesis and characterization of MPMA

The preparation of monomer MPMA has not yet been reported in literature. As described in Scheme 1, MPMA was synthesized from *p*-methylphenacylbromide with sodium methacrylate according to the usual method.[23] The yield of the monomer in Scheme 1 was 72%. The ^{1}H-NMR and ^{13}C-NMR spectra of the monomer were recorded, as shown in Figure 1. The attributions are also presented in the figure, demonstrating the exact structure and high purity of the monomer.

Formation and characterization of MPMA/HPCD inclusion complex

To improve the solubility and reactivity of hydrophobic monomers in aqueous medium, CDs are widely used to form an inclusion complex with the hydrophobic monomer.[1,16,17] In literature, the

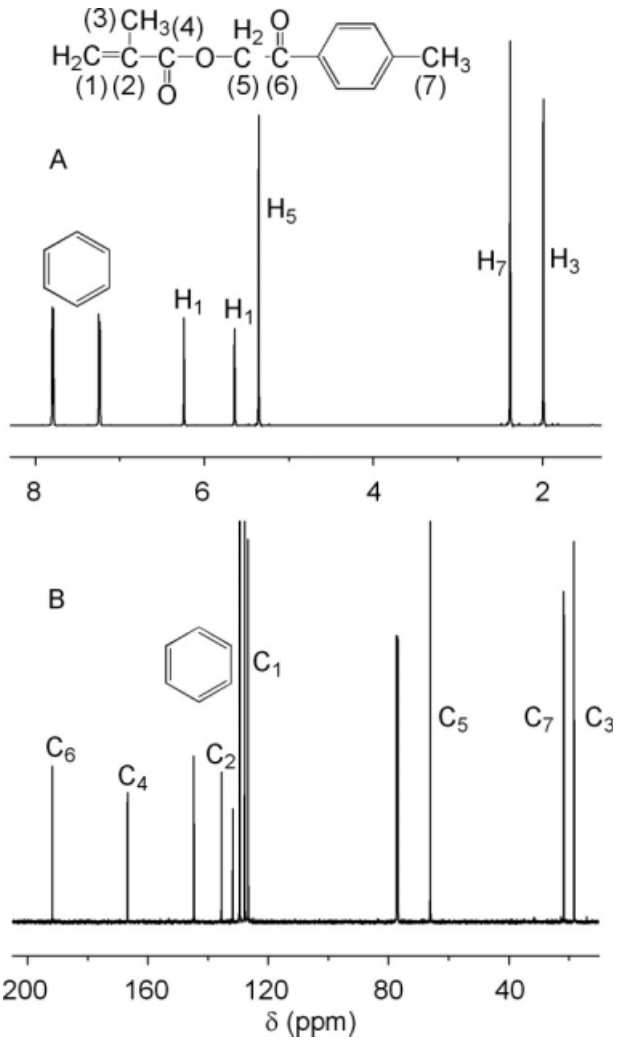
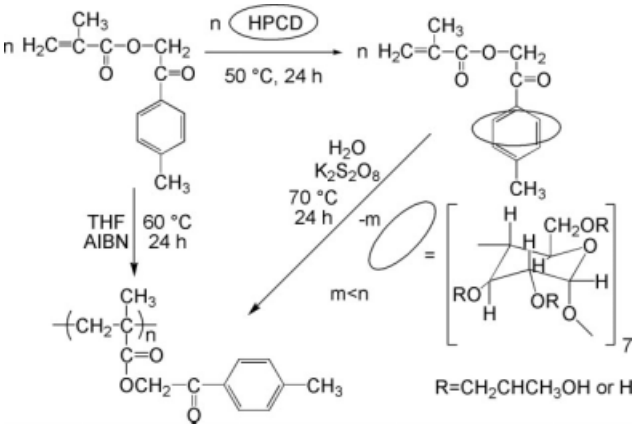


Figure 1 (A) ^{1}H-NMR and (B) ^{13}C-NMR spectra of MPMA.



Scheme 2 Preparation and polymerization of MPMA/HPCD inclusion complex in water in comparison to polymerization of uncomplexed MPMA in THF.

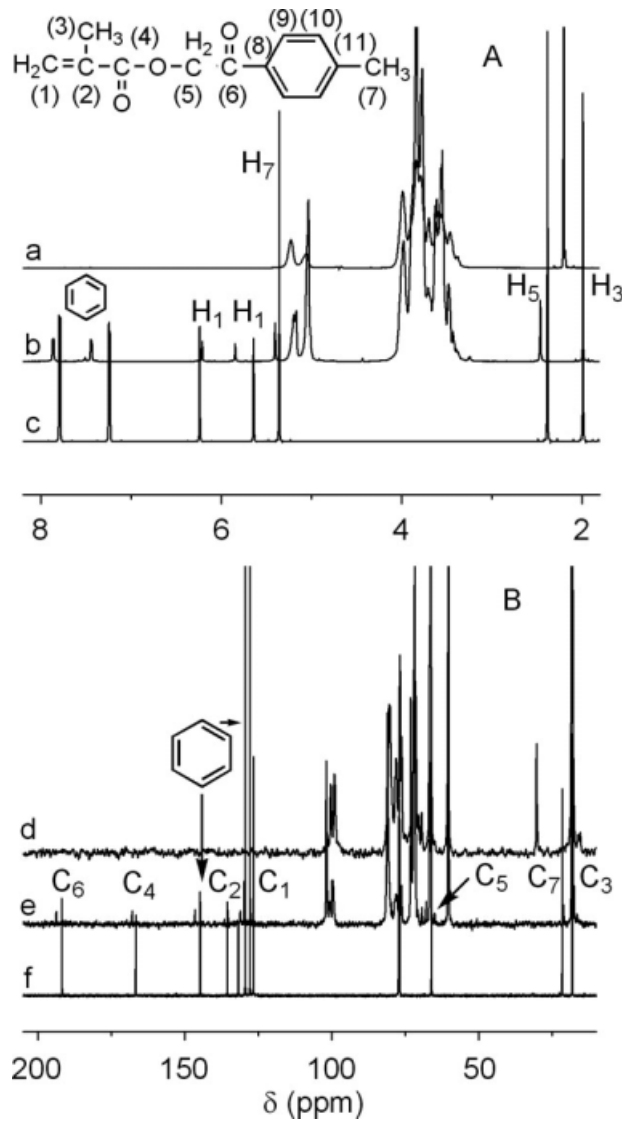


Figure 2 (A) ^{1}H-NMR spectra of a: HPCD; b: MPMA/HPCD inclusion complex; and c: MPMA. (B) ^{13}C-NMR spectra of d: HPCD; e: MPMA/HPCD inclusion complex; and f: MPMA.

inclusion complex of ketoethyl methacrylate monomer and HPCD has not yet been found up to now.

Water-soluble MPMA/HPCD inclusion complex was easily prepared in solution (Scheme 2). An equimolar amount of MPMA was added into the aqueous solution of HPCD. The monomer dispersed in the system immediately. After stirred at 50°C for $\sim$ 24 h, no solid monomer was observed and a clear, homogenous solution of the guest monomer was obtained. The change in the appearance of the solution preliminarily confirmed the formation of inclusion complex. For a further attesting to the occurrence of the inclusion, NMR and FTIR spectroscopy techniques were employed according to the previous reports.[29–33] The relevant results are presented in Figures 2 and 3.

Figure 2(A) illustrates the ^{1}H-NMR spectra of MPMA, HPCD and their inclusion complex. The detailed data are summarized in Table I, where the chemical shifts for the protons of MPMA both in the absence and presence of HPCD are presented together. As can be seen in the Table, obvious upfield or downfield chemical shifts were observed in the inclusion complex because of the influence of HPCD on the monomer. Furthermore, no new peaks were observed and only chemical shifts occurred to the protons, suggesting that the complexation was formed by a physical process rather than by chemical reactions. Hence, the chemical shifts offered evidence for the conclusion that MPMA molecules were included in the cavity of HPCD.

The formation of MPMA/HPCD inclusion complex was further verified by ^{13}C-NMR spectra [Fig. 2(B)], for which the detailed data are listed in Table II. In comparison to the free monomer, significantly

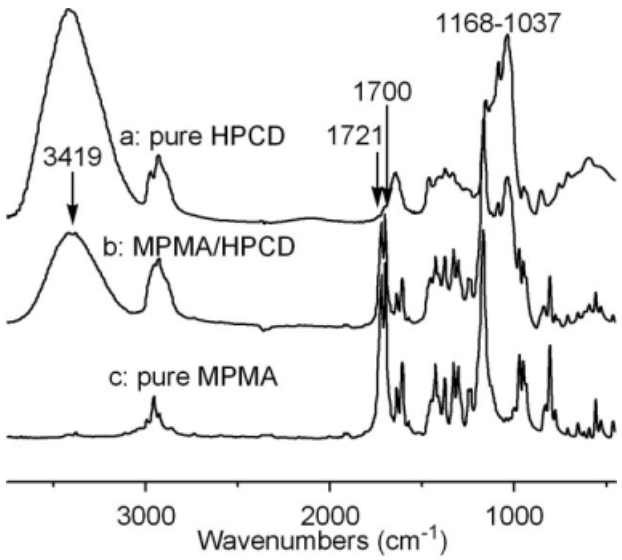


Figure 3 FTIR spectra of a: pure HPCD; b: the inclusion complex of MPMA/HPCD; and c: pure MPMA.

TABLE I
^{1}H Chemical shifts in MPMA in the Absence and Presence of HPCD ($\Delta\delta = \delta_{complex} - \delta_{free}$)[a]

Proton	δ_{free}	$\delta_{complex}$	$\Delta\delta$
H-1	5.642	5.847	+0.205
H-1	6.242	6.214	−0.028
H-3	1.987	1.987	0.000
H-5	5.358	5.404	+0.046
H-7	2.381	2.460	+0.079
H-9	7.789	7.874	+0.085
H-10	7.238	7.451	+0.213

[a] The data were based on Figure 2(A) in the text. Only part of the protons was presented here for the sake of clarity.

TABLE II
^{13}C Chemical Shifts in MPMA in the Absence and Presence of HPCD ($\Delta\delta = \delta_{complex} - \delta_{free}$)[a]

Carbon	δ_{free}	$\delta_{complex}$	$\Delta\delta$
C-1	126.62	127.58	+0.96
C-3	18.29	17.66	−0.63
C-4	166.73	167.93	+1.20
C-5	66.13	66.44	+0.31
C-6	191.75	193.67	+1.92
C-7	21.70	21.20	−0.50
C-10	129.49	129.76	+0.27
C-11	144.75	146.53	+1.78

[a] The data were based on Figure 2(B) in the text. Only part of the carbons was presented here for the sake of clarity.

obvious chemical shifts can be observed in the carbons of the host/guest complex. The phenomena are similar to the observations in the ^{1}H-NMR spectra discussed above, also indicating that the HPCD formed an inclusion complex with MPMA. Accordingly, on the basis of ^{1}H and ^{13}C-NMR spectroscopies, it may be concluded that the MPMA molecules are included inside the hydrophobic cavity of HPCD.

Besides NMR spectroscopies, the inclusion complex was also confirmed by FTIR spectra (see Fig. 3). When compared with the spectra of pure HPCD (spectrum a in Fig. 3), the characteristic bands of the MPMA monomer at 1721, 1700, 1636, and 1608 cm^{-1} appeared in the spectrum of the MPMA/HPCD inclusion complex (spectrum b in Fig. 3) and the characteristic peaks of HPCD at 3419, 2930, and 1037 cm^{-1} were also observed, demonstrating the formation of the expected inclusion complex.

Polymerization of the MPMA/HPCD inclusion complex

As shown in Scheme 2, the polymerizations of MPMA/HPCD complex were carried out in water in the presence of $K_2S_2O_8$ as a radical initiator. The corresponding polymerization results are listed in Table III. For entry 1 to 6, the monomer/HPCD inclusion complexes with different amounts of HPCD were polymerized using $K_2S_2O_8$ as initiator. All the systems were homogenous and apparently clear before the initiator addition, but immediately after the initiator addition, they became heterogeneous and obviously turbid. Polymerizations took place at a fast speed and rapid precipitation of the corresponding water-insoluble polymers was observed. With further polymerization, the systems became colorless and transparent again but the yellow polymers gathered at the bottom of the reactor. In the appearance of the precipitated polymers, little difference can be observed when compared to their counterparts obtained in organic solvent (entry 7 in Table III). For entry 8 and 9, no polymerization occurred due to the insolubility of MPMA itself (entry 8) or the initiator (entry 9) in aqueous medium.

The resultant polymers were isolated by filtration and washed with deionized water to remove the free HPCD which was unthreaded from the polymer. After reprecipitation from THF into *n*-hexane, the obtained polymers were then characterized by GPC and the relevant results are presented in Table III. Compared with the corresponding polymer prepared in organic solvent (entry 7), no pronounced difference

TABLE III
Results for Polymerization of MPMA/HPCD Inclusion Complex in Water

Entry	Solvent	MPMA (mmol)	HPCD (mmol)	Initiator	M_n[a]	M_w/M_n[a]	Yield (%)
1	H_2O	0.52	1.30	$K_2S_2O_8$	76,000	4.71	90.7
2	H_2O	0.52	1.04	$K_2S_2O_8$	75,000	3.86	94.7
3	H_2O	0.52	0.78	$K_2S_2O_8$	81,000	1.96	96.1
4	H_2O	0.52	0.52	$K_2S_2O_8$	84,000	4.76	97.2
5	H_2O	0.52	0.26	$K_2S_2O_8$	73,000	3.31	92.0
6	H_2O	0.52	0.13	$K_2S_2O_8$	77,000	1.07	92.4
7	THF	0.52	0.00	AIBN	79,000	3.74	97.4
8	H_2O	0.52	0.00	$K_2S_2O_8$	/[b]	/	/
9	H_2O	0.52	0.52	AIBN	/	/	/

The concentration of monomer was 50 mmol L^{-1}; the concentration of the catalyst was 0.5 mmol L^{-1} and the polymerization time was 24 h.
[a] Determined by GPC, with polystyrene as the standard and THF as eluent.
[b] No polymerization occurred.

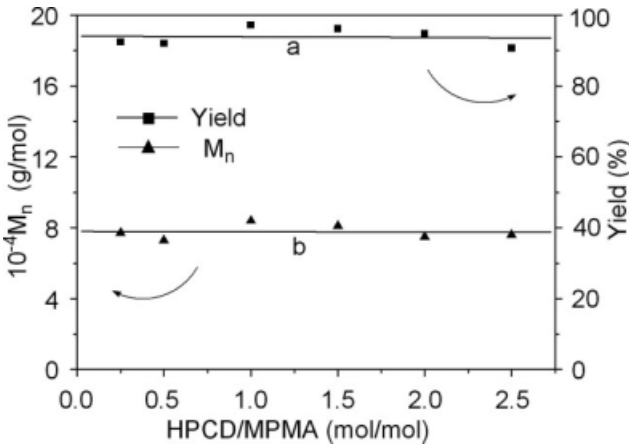


Figure 4 The influence of different molar ratios of HPCD/MPMA on the aqueous polymerization of the MPMA/HPCD inclusion complex. a: yield and b: M_n. The data were based on Table III in the text.

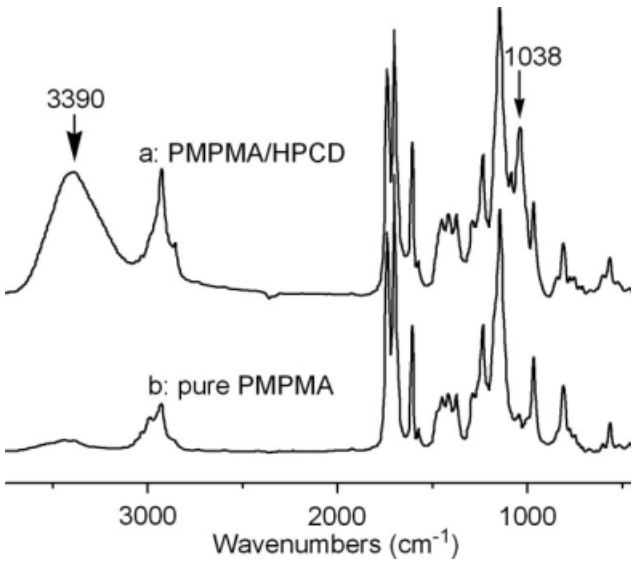


Figure 5 FTIR spectra of a: PMPMA/HPCD and b: pure PMPMA; for the polymerization conditions, cf. Table III, a: entry 4, b: entry 7.

was observed in number average molecular weights (M_n), polydispersity (M_w/M_n) and yield. More interestingly, we found that when the concentration of HPCD varied, there was no obvious difference in M_n and yield of the polymer. This phenomenon can be easily seen in Figure 4. It shows that both the yield and the number average molecular weight (M_n) kept nearly constant regardless of the HPCD/MPMA molar ratios. The yields of the aqueous polymerizations were all over 90%, and the number average molecular weights were all about 80,000. Even in the cases where the amount of the HPCD was largely lower than that of MPMA (entry 5 and 6 in Table III), the polymerization still took place with little difference from the other entries. That is to say, HPCD was not enough to form inclusion complex with all the monomer used in the first stage, but the final polymer yield was not reduced. This indicates that the HPCD unthreaded from the polymer can form inclusion complex again with free monomer molecules. Namely, HPCD can be used repeatedly for the formation of inclusion complex with monomer and thus the polymerization proceeded continuously until all the monomer was consumed. It should be pointed out that, one MPMA molecule is assumed to form inclusion complex with one HPCD molecule, according to the previous reports from us[30] and others.[12–14]

The resulting polymer obtained via aqueous polymerization was further subjected to FTIR spectroscopy after the complete removal of the free HPCD from the polymer by washing it with water. The FTIR spectrum of PMPMA/HPCD from entry 4 in Table III is shown in Figure 5, together with that of PMPMA (entry 7 in Table III) for a comparison. As seen in Figure 5, the FTIR band at 1635 cm^{-1} (C=C) of MPMA disappeared after the polymerization, just as to be expected. PMPMA/HPCD was identified according to the characteristic peaks at 1700 cm^{-1} for ketonic carbonyl group and at 1721, 1168 cm^{-1} for the ether group. Compared with the curve of PMPMA, two peaks are observed at 3490 cm^{-1} and 1038 cm^{-1} in the spectrum of PMPMA/HPCD. It should be pointed out that before the measurement of FTIR spectrum, the free HPCD was entirely excluded, so the peaks at 3490 cm^{-1} and 1038 cm^{-1} strongly indicate the existence of HPCD bonded on the resulting polymer. Nevertheless, taking into account the good solubility of the obtained PMPMA in THF, it is assumed that the amount of HPCD bonded in the polymer was quite small.

According to the Refs. [26,27] ketoethyl methacrylate polymers can degrade under heating. We therefore

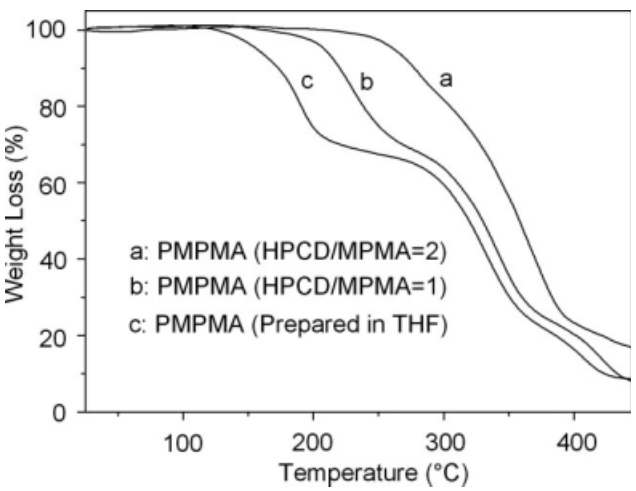


Figure 6 Thermogravametric analysis of a, b: PMPMA/HPCD and c: PMPMA; for the polymerization conditions, cf. Table III, a: entry 2; b: entry 4; c: entry 7.

investigated the thermal stability of the polymers obtained in water and in organic solvent by TGA in a nitrogen stream with a heating rate of 10°C/min. The results are shown in Figure 6, where the curves of PMPMA/HPCD (entry 2, 4 in Table III) and PMPMA (entry 7 in Table III) are shown together for a comparison. It is interesting that the onset decomposition temperature of the polymer obtained via aqueous polymerization increased drastically due to the existence of HPCD. Although the majority of the HPCD used in the polymerization unthreaded from the polymer, there was still a small bit of HPCD on the polymer according to the aforementioned FTIR spectroscopy (Fig. 5). Owing to the existence of HPCD, the onset decomposition temperature of the polymer enhanced compared to the counterpart obtained in organic solvent.

CONCLUSION

It is concluded that the new monomer, MPMA, was successfully included into the cavity of HPCD and an inclusion complex was formed. Polymerization of the complex was readily carried out providing high-yield hydrophobic ketoethyl methacrylate polymer. The thus-prepared polymer exhibited no significant difference from their counterparts obtained in organic solvent in number average molecular weight, polydispersity and yield. A small bit of HPCD was threaded in the resulting polymer, which may be helpful to enhance the thermal durability of the polymer. This novel technique based on monomer/HPCD inclusion complex is of interest for the preparation of methacrylate polymers, especially those thermal degradable polymers, and may have great impact on environmental protection owing to the advantages of aqueous polymerization.

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