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ORIGINAL PAPER

Soap-free emulsion polymerization of *n*-butyl acrylate in aqueous solution in the presence of α- and methylated β-cyclodextrin

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Abstract Butyl acrylate, a relative hydrophobic monomer, was found to become completely water soluble simply by mixing with either α-cyclodextrin or methyl-β-cyclodextrin. The both cyclodextrins were found to form 1:1 host–guest complexes with butyl acrylate. The complexes formed exhibited similar supramolecular structures, i.e., butyl group of butyl acrylate included in the cavity of cyclodextrins, but the double bond of the monomer locating outside of the cavity. Association constant values for α-cyclodextrin and methyl-β-cyclodextrin were determined to be 407.3 and 45.8 L/mol, respectively, indicating the better fitting of butyl acrylate with α-cyclodextrin than with methyl-β-cyclodextrin. It was found that the addition of either α-cyclodextrin or methyl-β-cyclodextrin, even at very low concentration, could markedly improve the reaction rate, reduce the amount of coagulum, and narrow the molecular weight distribution and particle-size distribution, in which α-cyclodextrin exhibited a better effect on polymerizations because of its stronger interaction with the monomer.

Keywords Cyclodextrins · Butyl acrylate · Supramolecular structure · Soap-free emulsion polymerization

Introduction

Cyclodextrins (CDs) are a group of structurally related cyclic oligosaccharides, which consist of 6(α), 7(β), 8(γ) units of 1,4-linked glucose. Because of their unique conical, tube-like shape, which forms a hydrophobic cavity and hydrophilic outer shell, CDs are able to form host–guest complexes with many kinds of hydrophobic molecules [1–3]. The formation of these complexes results in significant changes of

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the solubility and reactivity of the guest molecules, but without any chemical modification on them. Thus, water insoluble organic monomers may become water soluble simply by mixing with aqueous solutions of CDs, and it has been turned out that the complexed hydrophobic monomers can be successfully polymerized in water [4–7]. This kind of CD-mediated polymerization has been thought to be a “green” method for polymer synthesis, thus aroused great interests of many researches in the recent decade [8, 9].

For example, monomers with long-alkyl chains, like octadecyl methacrylate (OM) and dodecyl methacrylate (DM), can not be polymerized in aqueous media using traditional emulsion polymerization as their water solubility are too low. However, in the presence of β-CD, these monomers can be successfully polymerized by emulsion polymerizations that do not involve the use of excessive levels of surfactant [10, 11]. Up to now, lots of important monomers used in polymer synthesis, such as styrene, methacrylates and acrylates, and fluorinated monomers, have been polymerized with this new CD-mediated strategy, in which many valued studies were reported by Prof. Ritter’s group [12–14]. They pointed out that during the free-radical polymerization of the complexed hydrophobic monomers, the CD ring would slip off step by step from the monomer during chain propagation and the polymer precipitates, which is consistent with the results from Leyrer et al. and Tonelli et al. [11, 15]. Our previous studies [16–19] also indicated that in the presence of CD, both the reaction rate and the monomer conversion would be markedly elevated. It is believed that there are important effects of the supramolecular structure of the host–guest inclusion complexes on the polymerization.

However, most published reports related to the polymerization in the presence of CD used β-CD or its derivatives, because of the price consideration. As the solubility of native β-CD is not satisfactory, randomly methylated β-CD (RAMEB) was usually utilized in most cases. But with the development of CDs synthesizing technology, α-CD with good solubility is readily available now, whose price is even lower than RAMEB. Very recently, Rimmer and co-workers [20] described the emulsion copolymerization of butadiene with butyl methacrylate in the presence of α-CD and β-CD. It was found that α-CD would facilitate more butadiene incorporated into the copolymer than β-CD.

Considering the different cavity sizes of α- and β-CD, the supramolecular structure of α-CD/monomer complex and its influence on the polymerization may be different from those of β-CD. So, in this paper, basing on the analysis of the supramolecular structure of host–guest complexes formed, we wish to report the soap-free emulsion polymerization of *n*-butyl acrylate in aqueous solution in the presence of α-CD, and its comparison with RAMEB-mediated polymerization.

Experimental part

Materials

n-butyl acrylate (BA) and potassium persulfate were purchased from Sinopharm Chemical Reagent Co. Ltd (China); α-CD and RAMEB were obtained from

Kunshan Ruisike Chemical Reagent Co. Ltd (China). Butyl acrylate was washed twice with the aqueous 2 % sodium hydroxide solution, followed by two equal portions of distilled water. This washed butyl acrylate was then distilled under reduced pressure prior to use. The water utilized in this study was deionized water.

Measurements

UV–Visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer with a 1 cm quartz cell.

The ^{1}H NMR spectra of samples were recorded on a Brucker Avance AM 400 spectrometer at 30 °C in D_2O. The δ scale relative to TMS was calibrated by the deuterium signal of the solvent as internal standard.

Average molecular weights were measured by size exclusion chromatography (SEC) using an apparatus with a HPLC pump (LC-20AD) and a DRI detector (RID-10A). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. The calibration was carried out with narrowly distributed polystyrene standards. Sample concentrations were approximately 2 mg/mL.

The average particle size and particle-size distribution were determined by a laser diffraction particle-size analyzer (BI-9000, Brookhaven Instruments Corporation, USA).

For kinetic measurements, a sample was removed from the reaction mixture at a given time with a syringe, which was then cooled in ice water at once. The conversion of monomer at the given time was determined by gravimetry [21]. All experiments were repeated at least three times.

Amounts of coagulum in the latexes were determined by filtrating the latex through filter paper, drying the residue in a vacuum at 70 °C for 12 h and weighing.

Complexation of monomer with α-CD and RAMEB

To obtain host–guest inclusion complex solution, a given amount of α-CD (or RAMEB) and BA were dissolved in water. The mixture was sonificated at ambient temperature for 10 min, yielding clear colorless solution of the complexed monomer. The solid complex of monomer with CD could be gotten by evaporating to remove water, and then dried for 24 h at 40 °C in a vacuum.

Polymerization of BA in the presence of α-CD and RAMEB

The soap-free emulsion polymerization experiments were carried out in a four-necked glass reactor equipped with a mechanical stirrer, condenser, temperature control, and a nitrogen inlet. Fifty millilitre deionized water, 5.12 g (40 mmol) BA and different amount of α-CD or RAMEB (0.08, 0.2, 0.4, 0.6, 0.8 mmol) were introduced into the reactor. The mixture was sonificated for 10 min and stirred under nitrogen for 30 min. Then the solution was heated to 70 °C and 0.2 mmol $K_2S_2O_8$ added. The reaction mixture was kept at 80 °C for 8 h to get final product.

Results and discussion

Complexation of BA with α-CD and RAMEB

Figure 1 shows the UV spectra of BA dispersed in water in the presence of different amount of α-CD. When 0.25 mmol BA was dispersed in 10 mL water, lots of monomer droplets were observed because of its poor solubility. With the addition of α-CD, it was observed clearly that organic droplets tended to solve in the aqueous solution. After 10 min sonification and 24 h on standing of the mixture, 1 mL subnatant was diluted to 100 mL and detected by the UV spectrometer, just as shown in Fig. 1. It is indicated that the UV absorbance around 196 nm gradually increases with the increasing of α-CD concentration until the molar ratio of CD/BA beyond 0.9 (0.22/0.25 mmol), which demonstrates the complexation of BA with α-CD, inducing more BA molecules dissolved in water. Further increasing the amount of α-CD to 0.28 mmol, no change of UV absorbance is observed. It is shown that all BA molecules has formed inclusion complexes with α-CD and solved in water. The UV spectra of BA dispersion solution in the presence of RAMEB are almost the same with Fig. 1, so it is not presented here. Thus, water insoluble monomer BA becomes completely water soluble simply by mixing with either α-CD or RAMEB.

The structures of the inclusion complexes of BA with CDs were characterized by ^{1}H NMR. It is known that NMR spectroscopy gives one of the most powerful evidence for the study of host–guest chemistry in solution, and the information of the chemical shifts has been used to establish inclusion modes [22]. Chemical shift variations of selected host and guest protons reflect the formation of a complex between them. Figure 2 illustrates ^{1}H NMR spectra of the α-CD/BA complex in deuterium oxide (D_2O), in comparison with free BA and CD molecules. It is found that the inner α-CD protons, C3-H and C5-H, shift toward the higher field when complex with BA, which indicates the formation of the inclusion complex between guest molecule and α-CD. On the other hand, the δ of C1-H, C2-H, C3-H, and C4-H protons in BA molecule shift toward the lower field for 0.164, 0.128, 0.161, and 0.039 ppm, respectively; however, the δ of C5-H and C6-H protons shift to the higher field for −0.002, and −0.005 ppm. It is indicated that C1, C2, C3, and C4 in

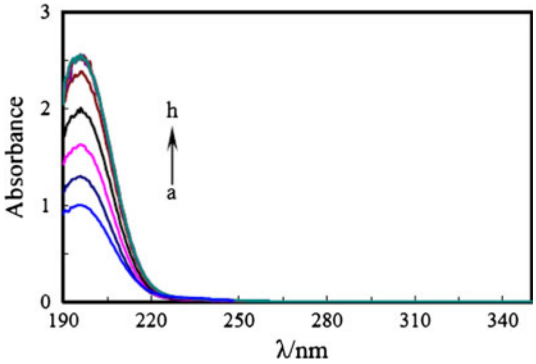

Fig. 1 UV spectra of 0.25 mmol BA dispersed in 10 mL water in the presence of different amount of α-CD, *a* 0, *b* 0.05, *c* 0.1, *d* 0.15, *e* 0.2, *f* 0.22, *g* 0.25, *h* 0.28 mmol. The mixture was sonificated for 10 min and on standing for 24 h, and then 1 mL subnatant was diluted to 100 mL to detect by UV spectrometer

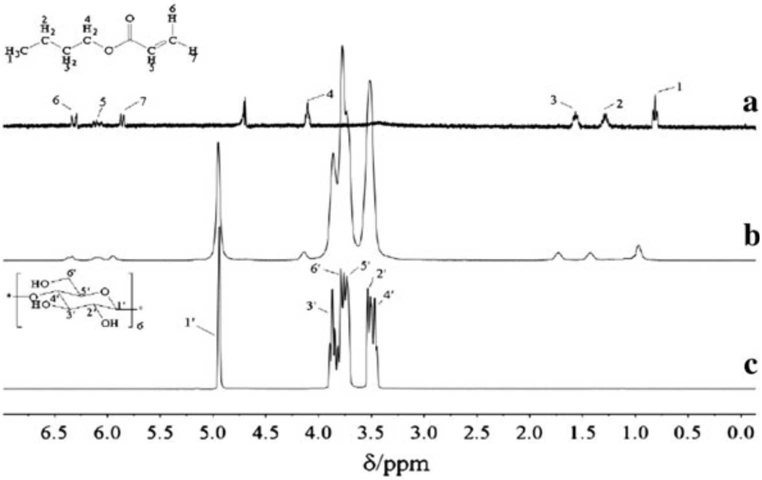

Fig. 2 ^{1}HNMR spectra of BA (*a*), α-CD/BA (*b*) inclusion complex and α-CD (*c*) in D_2O

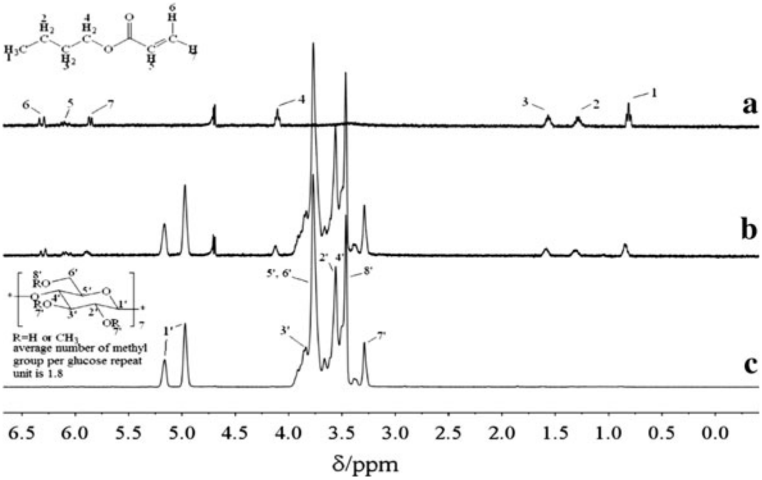

Fig. 3 ^{1}HNMR spectra of BA (*a*), RAMEB/BA inclusion complex (*b*), and RAMEB (*c*) in D_2O

BA locate within the cavity of α-CD, nevertheless the double bond lying outside of the cavity.

For RAMEB/BA complex, it can be seen from Fig. 3 that the δ of C1-H, C2-H, C3-H, and C4-H protons in BA molecule shifted toward the lower field for 0.038, 0.03, 0.014, and 0.014 ppm, respectively; but the δ of C5-H and C6-H protons shift to the higher field for −0.005, and −0.004 ppm, respectively. It is demonstrated that when complexes with RAMEB, C1, C2, C3, and C4 in BA molecule also locate within the cavity of α-CD, and double bond outside of the cavity.

Figure 4 shows the formation of inclusion complexes of BA with α-CD and RAMEB, basing on the NMR analysis above mentioned. The molecular sizes of BA

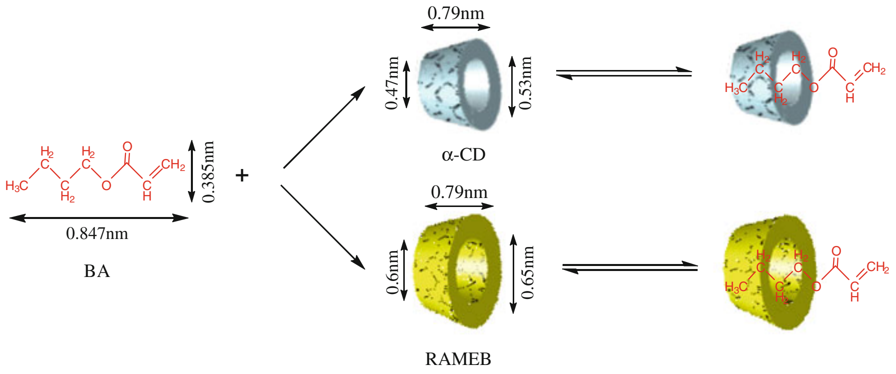

Fig. 4 Schematic representation of the formation of inclusion complexes of BA with α-CD and RAMEB

and CDs are obtained from literatures or calculated through MM2 simulation by CS Chem3D Pro. Software [23, 24]. Although both complexes exhibit similar supramolecular structure, it seems that α-CD fits BA better than RAMEB according to the molecular sizes of them. The cavity of RAMEB is a little too big for BA, which is supported by the fact that the values of δ shift for C1-H, C2-H, C3-H, and C4-H protons in BA are much smaller when complexed with RAMEB than withα-CD. That is to say that α-CD is much easier to form complex with BA than RAMEB.

To evaluate the tendency of complexation and the stability of complexes quantitatively, the association constants are estimated. Figure 5I, II shows the ^{1}H NMR spectra of BA in the presence of varying concentrations (C_{CD}) of α-CD and RAMEB, respectively. As C_{CD} increased, obvious down-field shifts of the signals ascribable to the C3-H protons in BA are observed for both cases. Using the ^{1}H NMR spectra, the reciprocals of the peak shifts for the signal due to the proton (C3-H) in BA ($1/\Delta\delta$) are calculated and plotted against the reciprocals of the CD concentration ($1/C_{\alpha\text{-CD}}$ and $1/C_{\mathrm{RAMEB}}$). As shown in Fig. 5III ,IV, both of them show good linear relationships, indicating 1:1 stoichiometry for both α-CD/BA and RAMEB/BA complexes. From the intercept and the slope of the straight line, the K values for α-CD and RAMEB are determined to be 407.3 and 45.8 L/mol, respectively, by the following Benesi–Hildebrand equation:

$$\frac{1}{\Delta\delta} = \frac{1}{K\Delta\delta_{\mathrm{eq}}}\frac{1}{C_{\mathrm{CD}}} + \frac{1}{\Delta\delta_{\mathrm{eq}}} \tag{1}$$

where $\Delta\delta_{\mathrm{eq}}$ is the difference between the observed chemical shift for the one-to-one inclusion complex and the chemical shift in the absence of α-CD. The K value of α-CD with BA is as almost nine times as that of RAMEB, which indicates much stronger interaction between α-CD and BA than that between RAMEB and BA, and much better stability of α-CD/BA complex than RAMEB/BA.

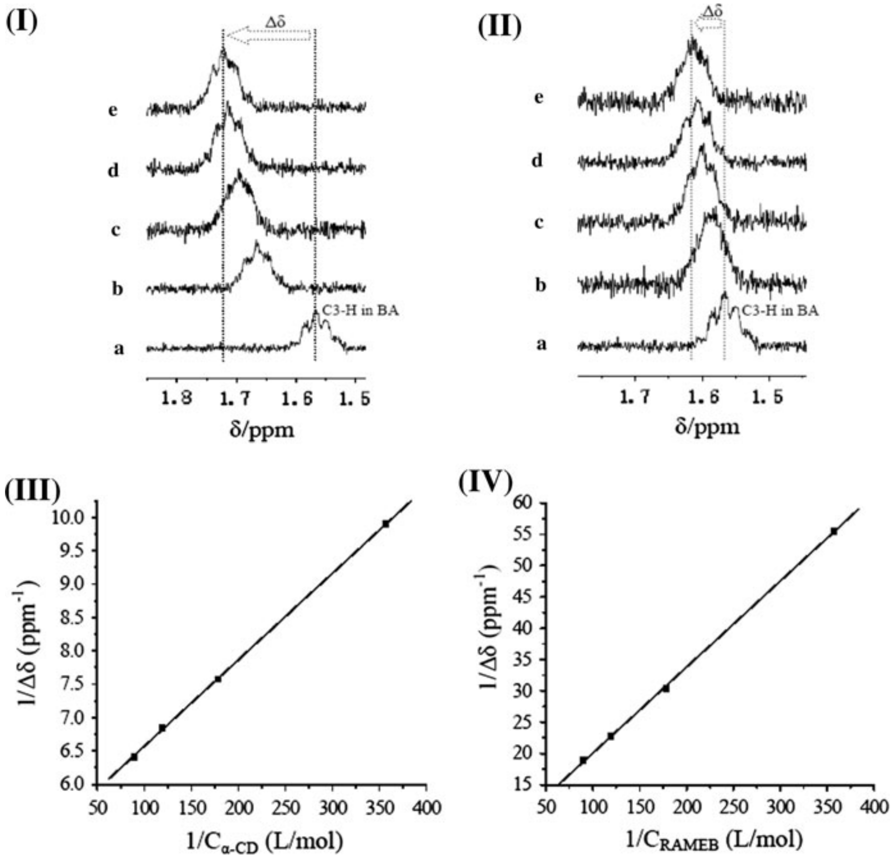

Fig. 5 ^{1}HNMR Spectra of 1.4 mmol/L BA in the presence of various concentrations (C_{CD}) of α-CD (**I**) or RAMEB (**II**) measured in D_2O, C_{CD}: 0 (*a*), 2.8 (*b*), 5.6 (*c*), 8.4 (*d*), 11.2 (*e*) (mmol/L). Benesi–Hildebrand plots of $1/\Delta\delta$ against $1/C_{CD}$ for BA with α-CD (**III**) or RAMEB (**IV**)

Polymerization of BA in aqueous solution in the presence of α-CD and RAMEB

The effects of CDs on soap-free emulsion polymerization of BA were examined by a series of reactions. In an aqueous solution with 5.12 g (40 mmol) BA dissolved in 50 mL water, different amount of α-CD or RAMEB (0–1.6×10^{-2} mol/L) were introduced. As shown in Fig. 6, both CDs even at very low concentration could markedly improve the reaction rate and final conversion of the monomer. In polymerizations containing 1.6×10^{-2} mol/L of either CDs, conversions after 60 min were beyond 90 %, and progressed to almost 100 % after 120 min. However, the conversion in the absence of CD was only 51.7 % after 1 h, and the final conversion was determined just near 90 % even after 8 h.

In addition, it was found that the polymerization rate in early stage in the presence of α-CD was much higher than that in the presence of RAMEB. In the polymerization containing 1.6×10^{-3} mol/L α-CD, the conversion reached to 49 % after 30 min, 20 % higher than that in the presence of RAMEB. When the

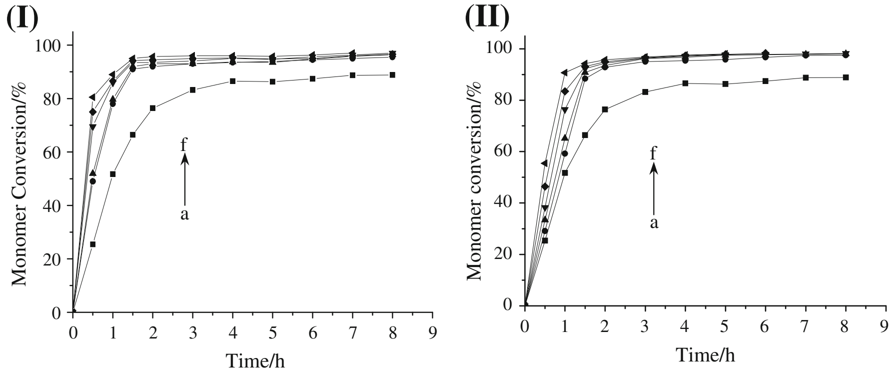

Fig. 6 Monomer conversion as a function of time in the presence of different amount of α-CD (**I**) and RAMEB (**II**): 0 (*a*), 1.6 (*b*), 4 (*c*), 8 (*d*), 12 (*e*), 16 (*f*) ($\times 10^{-3}$ mol/L)

concentration of α-CD increased to 1.6×10^{-2} mol/L, the monomer conversion after 30 min was even up to 80 %.

It is thought from a kinetical viewpoint that the monomer transporting resistance between interfaces, including at the water/polymer particle interface and at the monomer droplet/water interface, are of importance for the polymerization rate consideration. Nomura et al. [25] demonstrated quantitatively that in a polymerization, the monomer concentration decrease in the polymer particle was due to mainly to the resistance to mass transfer at the interfaces. The formation of water soluble monomer complexes with CDs, as discussed above through UV spectra, reduces the kinetical barrier for the BA migration through the monomer droplet/water interface, and the water/polymerizing center interface. This will increase the rate of propagation, and thus the overall rate of polymerization. Compared with RAMEB, stronger interaction of α-CD with BA facilitates the formation of complex with higher stability. It improves the ability of α-CD to take the BA molecule acrossing the interfaces, so inducing a higher polymerization rate. Results from Ritter [26] also indicated that a monomer with higher hydrophobicity, thus exhibiting stronger interaction with methylated *β*-CD, would be polymerized in a higher initial reaction rate when complexed with methylated *β*-CD.

In a control polymerization containing neither α-CD nor RAMEB, it was found that the reaction coagulated at an early stage, and produced a little large amount of coagulum (13.7 %) when the polymerization finished. As can be seen from the data in Table 1, the addition of α-CD has a beneficial effect on the colloidal stability of products. When the concentration of α-CD increased to 0.008 mmol/L, coagulum produced in polymerization decreases to only 1.2 %. However, it is found that the further increase of α-CD concentration from 0.008 to 0.016 mmol/L is disadvantage for the decrease of coagulum, in which the coagulum content increased to 7.8 %.

As shown in Table 1, it seems that there is no obvious change in molecular weight with increasing of α-CD concentration. However, the molecular weight distributions of the poly(butyl acrylate) latexes prepared in the presence of α-CD are narrower than that prepared without α-CD. The average particle sizes increased with

Table 1 Results from the polymerizations of BA in the presence of different amounts of α-CD or RAMEB

CD	C_{CD} (mol/L)	M_n (g/mol)	M_w/M_n	Particle size (nm)	PSD	Coagulum (wt%)
None	–	38,000	3.2	128 ± 2.1	0.27	13.7
α-CD	0.0016	42,000	2.8	149 ± 2.4	0.25	5.3
α-CD	0.004	39,000	2.0	160 ± 1.9	0.13	1.6
α-CD	0.008	45,000	2.1	238 ± 2.1	0.10	1.2
α-CD	0.012	47,000	1.9	300 ± 2.7	1.15	2.7
α-CD	0.016	43,000	2.5	343 ± 3.2	0.20	7.8
RAMEB	0.0016	37,000	2.6	137 ± 2.5	0.24	2.3
RAMEB	0.004	43,000	2.4	170 ± 2.1	0.16	2.0
RAMEB	0.008	41,000	2.7	212 ± 2.4	0.12	1.2
RAMEB	0.012	44,000	2.2	312 ± 2.3	0.10	2.0
RAMEB	0.016	39,000	2.5	358 ± 3.3	0.17	3.3

PSD particle-size distribution

increasing α-CD concentration from 0.0016 (149) to 0.016 mmol/L (323 nm). The main point is, however, that the polymer particles prepared in the presence of α-CD show a narrower particle-size distribution in contrast to sample synthesized without CD. Since the monomer conversion are quantitative in those polymerizations in the presence of α-CD, the final particle size can be adjusted conveniently by the variation of the α-CD contents without changing other reaction parameters.

From the analysis of the supramolecular structure of CD/BA complexes mentioned above, the complexed monomer is thought to be not so active in free-radical reaction because of the steric hindrance of the big CD ring. α-CD is proposed to mainly act as an effective transfer agent, which results in a fast and uniform delivery of the monomer molecules from monomer droplets to reaction loci. The increased propagation rate of the polymer chain in the presence of α-CD induces a shortened particle formation period. Thus, less but bigger particles with narrower particle-size distributions are formed during the polymerization process.

As can be seen from Table 1, no obvious difference is observed among data obtained from polymerizations of BA in the presence of RAMEB or α-CD. In general, with the addition of either RAMEB or α-CD, the amount of coagulum is decreased, particle size increased, and molecular weight distribution and particle-size distribution narrowed. It seems that the interaction difference of BA with α-CD and with RAMEB does not exert obvious effects on those polymer properties, which may be because of the relative low concentration of CDs.

Conclusion

From the above-described experiments it can be concluded that BA, a hydrophobic monomer, becomes completely water soluble simply by mixing with either α-CD or

RAMEB. It is found that when mixed with CDs in water, BA forms 1:1 host–guest complexes with α-CD and RAMEB. Furthermore, the both complexes exhibit a similar supramolecular structure, i.e., butyl group of BA included in the cavity of CD, but the double bond of the monomer locating outside of the cavity. The association constant values of BA with α-CD and RAMEB are determined to be 407.3 and 45.8 L/mol, respectively, which indicates the stronger interaction of BA with α-CD than with RAMEB. Polymerization kinetical analysis shows that although both α-CD and RAMEB can improve the reaction rate, α-CD exhibits a better effect on the increasing of the polymerization rate than RAMEB. From the characteristics of polymers prepared, it is demonstrated that with the addition of either α-CD or RAMEB, the amount of coagulum is decreased, particle size increased, and molecular weight and particle-size distribution narrowed. It seems that the interaction difference of BA with α-CD and with RAMEB does not exert obvious effects on those polymer properties.

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