



## Temperature-structure Dependence of Poly(1-octene-*co-t*-butyl Acrylate) Prepared by Conventional Free Radical Polymerization

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### ABSTRACT

A series of poly(1-octene-*co-t*-butyl acrylate) were prepared by conventional free radical polymerization under mild conditions. The influence of different high-temperature decomposition initiators (e.g., *t*-butyl peroxybenzoate, di-*t*-butyl peroxide) on copolymer composition was above all investigated. Subsequently, poly(1-octene-*co-t*-butyl acrylate) was hydrolyzed to form amphiphilic poly(1-octene-*co*-acrylic acid). Thermal behaviours of poly(1-octene-*co-t*-butyl acrylate) and poly(1-octene-*co*-acrylic acid) and micellar behaviours of poly(1-octene-*co*-acrylic acid) in water were investigated. By using high-temperature initiators the copolymerization temperature can be increased which results in incremental incorporation of 1-octene and monomer conversion. 1-Octene incorporation can be regulated in the range of 0~37.1 mol%. Meanwhile, molecular weights of these copolymers decreased as copolymerization temperature increased. The reactivity ratios of 1-octene ( $r_1$ ) and *t*-butyl acrylate ( $r_2$ ) were figured out as  $r_1 = 0.005 \pm 0.001$  and  $r_2 = 9.016 \pm 0.035$ . CMC Value of poly(1-octene-*co*-acrylic acid) in water increased as their molecular weight and 1-octene incorporation were lowered. However, the mean hydrodynamic radius decreased as molecular weight increased or 1-octene incorporation dropped. Although  $T_g$  value of poly(1-octene-*co*-acrylic acid) is much higher than that of poly(1-octene-*co-t*-butyl acrylate), they all drop with the lowering of molecular weight or the increased 1-octene incorporation.

### Key Words:

hydrophilic polymers;  
radical polymerization;  
micelles;  
olefin;  
acrylate.

### INTRODUCTION

The incorporation of polar groups into polymers leads to significant modifications and improvements in their properties [1-3]. Indeed, important properties such as toughness, adhesion, surface properties (paintability, printability, etc.), solvent resistance, solubility, miscibility and rheological are dramatically affected by the presence of these groups in the polymer [3,4]. Incorporation of polar functional groups to conven-

tional polyolefins is an extremely attractive subject because it would add values to inexpensive and readily available polyolefins. Since the discovery of Ziegler-Natta [5,6], there has been an important interest in coordination polymerization catalyzed by transition metals due to the possibility to control the microstructures of polymers and therefore their properties. In the last two decades, the introduction of metallocenes [7] and non-

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metallocenes [8] has led to exceptional control and improved properties of common polymers such as polyethylene or polypropylene. However, these excellent results obtained by early-transition metals have not been able to be extrapolated to polymerization of polar monomers. Although protecting groups have been very often used to allow the complex formation of polar monomer to metal by  $\pi$ -C=C coordination to take place [4], these routes require, inevitably, additional steps such as deprotection mechanism and therefore increase of the final price of the polymer and wastes generation. Furthermore, these catalysts are not applicable to random copolymerization of polar monomers with non-polar monomers. Recently, some catalysts based on palladium and nickel complexes have been developed for polymerization of polar monomers [9-11]. Although significant advances have been reported in the last decade, there are still several problems to be overcome in the polymerization of polar vinyl monomers. It is highly desirable to have a perfect control in the incorporation of polar monomer in all ranges, from homopolymerization (100% incorporation) to lower degrees of incorporation. The present incorporation ratio in coordination polymerization does not exceed 20% which is much lower than the value observed for radical polymerization (up to 50% in the case of methyl methacrylate) [12]. Furthermore, the low activity is a routine behaviour. The activity is highly dependent on the incorporation ratio of the polar monomer into the polymer chain: high incorporation leads to a significant loss of activity in polymerization and vice versa. Additionally, copolymerization with other important polar monomers such as methyl methacrylate or vinyl acetate is still not achieved.

Free radical polymerization which has been an important technological area for seventy years is naturally a candidate to obtain such copolymers. A major virtue of radical polymerizations is that they can often be carried out under relatively undemanding conditions. In marked contrast to ionic or coordination polymerizations, they exhibit a tolerance of trace impurities. It is this apparent simplicity of radical polymerization that has led to the technique being widely adopted for both industrial and laboratory [13]. In radical polymerizations,

acrylates can be readily polymerized while the reactivity of the non-polar olefins is extremely low due to the less reactive unconjugated double bond and the less stable alkyl radical species [14]. The conventional radical copolymerization of the two monomers thus generally results in polyacrylates containing a small amount of non-polar olefin units. One of the most effective methods for increasing the copolymerizability of non-polar olefins with polar monomers is to add strong Lewis acids [15], although it usually needs strict anhydrous conditions, low temperatures, large excess of the olefin monomers, etc. As we all know, increasing temperature can help reactants to overcome the energy barrier and then allow chemical reactions to occur. The research work of Iino et al. on radical terpolymerization of sulphur dioxide, 1-hexene and methyl acrylate or methyl methacrylate indicated that increasing temperature from 0°C to 50°C resulted in increased incorporation of 1-hexene from 5.2 mol% to 31.1 mol% [16]. In other words, the copolymerizability of non-polar olefins with polar monomers can be improved by just increasing polymerization temperature which is a simple and convenient method. Venkatesh et al. investigated the atom transfer radical copolymerization of methyl methacrylate with 1-octene using 2,2,2-trichloroethanol and *p*-toluenesulphonyl chloride as initiator at 90°C [17]. However, the resulting copolymers constituted no more than 20 mol% of 1-octene. So far, there is no report about the influence of temperature on the copolymerization of alkene and polar monomer with traditional radical polymerization. Hence, in this paper three kinds of relatively high-temperature initiators, *t*-butyl peroxybenzoate (TBPB), di-*t*-butyl peroxide (DTBP) and azodiisobutyronitrile (AIBN), were used to initiate the copolymerization of 1-octene and *t*-butyl acrylate (*t*-BA) in the temperature range of 50~165°C. Under proper conditions copolymers containing 37.1 mol% of 1-octene were obtained. The influence of copolymerization conditions, such as temperature, consumption of initiator and so on, on the incorporation of 1-octene, conversion of monomers and molecular weight of copolymers was investigated. Subsequently amphiphilic copolymers of poly(1-octene-*co*-acrylic acid) were prepared by hydrolysis. The micellar behaviour of these

hydrolyzates was observed, because of their potential application in making water-in-oil emulsion.

## EXPERIMENTAL

### Materials

*t*-Butyl acrylate (Alfa Aesar, 99%, *t*-BA) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over CaCl<sub>2</sub> and distilled twice over CaH<sub>2</sub> under reduced pressure just before use. 1-Octene (Acros, +99%, abbreviated as Oc) was distilled and stored over molecular sieves. *t*-Butyl peroxybenzoate (Alfa Aesar, TBPB), di-*t*-butyl peroxide (J&K Chem, DTBP) and trifluoroacetic acid (Alfa Aesar, 99%) were used as received. Azodiisobutyronitrile (Fluka, +98%, AIBN) was recrystallized twice from methanol before use. Toluene and tetrahydrofuran (THF) as solvents were distilled over sodium/benzophenone ketyl under dry N<sub>2</sub> atmosphere prior to use.

### Preparation of Poly(1-octene-*co-t*-BA)

A typical copolymerization was carried out in a 100-mL round-bottomed flask connected to a standard Schlenk line and equipped with a magnetic stirrer. The flask was evacuated and filled with nitrogen three times. The flask was immersed in a thermostated oil bath maintained at the designated temperature and stirred vigorously. Toluene (20 mL), 1-octene and *t*-BA were accurately weighed and transferred to the flask. The free radical initiators (AIBN, TBPB and DTBP) were added slowly via a degassed syringe. The reactions were carried out under nitrogen atmosphere for the designated time. Then the polymerization was terminated by the addition of HCl acidified isopropyl alcohol. The resulting polymer was dissolved in *n*-hexane and precipitated in isopropyl alcohol for three times to remove homopoly(*t*-BA), free *t*-BA and 1-octene. Finally, the polymer was dried in vacuum at 50°C overnight.

### Hydrolysis of Poly(1-octene-*co-t*-BA)

*t*-BA units in poly(1-octene-*co-t*-BA) could be hydrolyzed to form acrylic acid (AA) units. An amount of 2 g poly(1-octene-*co-t*-BA) was dissolved in 60 mL anhydrous THF and then a 5-fold molar

excess (with respect to the ester groups in the copolymers) of trifluoroacetic acid (TFA) was added. The mixture was heated to boiling temperature and reflux for 48 h. Finally, solvent and TFA were removed by rotary evaporator. Traces of TFA in the copolymers were removed by drying in vacuum at 50°C overnight.

### Measurements

The conversion of the copolymerization was determined gravimetrically. Molecular weight and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) on a PL-GPC220 instrument (Polymer Laboratories, Ltd.) at room temperature with THF as eluant with a 1.0 mL.min<sup>-1</sup> flow rate. Three PL gels (10 μm) mixed B columns (7.5 mm × 300 mm) were used. The system was calibrated with narrow dispersity polystyrene standards. <sup>1</sup>H NMR Spectra of all copolymers were recorded on a Bruker AMX-500 spectrometer in chloroform-*d* for poly(1-octene-*co-t*-BA) and methanol-*d* for poly(1-octene-*co*-AA) at room temperature. The 1-octene content in the copolymers can be determined from the integrated intensity ratio between the peaks at 0.8 ppm (corresponding to the methyl protons of 1-octene units) and the peaks in the region from 2.2 ppm to 2.3 ppm (corresponding to the methine protons of *t*-BA or AA units).

FTIR Spectra were performed on a Bruker Vector 22 Spectrometer. Steady-state fluorescent spectra were measured using a Fluoromax 2 Spectrometer (Jobin-Yvon) with a slit width of 0.5 mm (Band-pass 2.125 nm) for both excitation and emission spectra. For fluorescence emission spectra, ex (peak excitation wavelength) was 333 nm, and for excitation spectra, em (peak emission wavelength) was 390 nm. Spectra were accumulated with an integration time of 0.1 s. Samples with a pyrene concentration of 6 × 10<sup>-7</sup> mol.L<sup>-1</sup> were prepared according to literature [18]. The hydrodynamic diameter and size distribution of micelles were determined by dynamic light scattering (DLS) using a Brookhaven 90 Plus particle size analyzer. The scattered light of a vertically polarized He-Ne laser (632.8 nm) was measured at an angle of 90° and was collected on an autocorrelator. Each analysis lasted for 3 min and performed at 25°C. Prior to the light scattering measurements the sample

solutions were filtered using Millipore Teflon filter with a pore size of 0.45  $\mu\text{m}$ . A field emission scanning electron microscope (SEM) (Jeol JSM 6700F) was used to observe the morphology of the particle of poly(1-octene-*co*-AA) from micelle by dialysis on isinglass. Differential scanning calorimeter (DSC) measurements were carried out under a nitrogen flow with a Perkin-Elmer DSC7 (heating rate: 10°C/min). The  $T_g$  was estimated as the midpoint of the corresponding stage in the exothermic heat-flow curves.

#### Calculation of Reactivity Ratio in 1-Octene/*t*-BA Copolymerization by Computer Programming

A common individual computer was used and the programming was performed in MATLAB 7.5.0 software to calculate the reactivity ratio in 1-octene/*t*-BA copolymerization. In order to calculate the most accurate  $r_1$  and  $r_2$ , which are qualified in all the equations based on different entries rather than each equation (each equation was possible to bear deviation), the sum of the deviations was searched to find the minimum and the checking step length was 0.001 to acquire as many as possible computer reading times. A typical experiment was performed by 70,000 times of computer reading and operating for about 5 min. The step length of 0.001 was considered to be the optimal because small variation would greatly enhance the time for calculation, in which case the error bar for the calculation of  $r_1$  and  $r_2$  was 0.001.

#### Preparation of Micelles

The modified dialysis method of Zhang et al. [19] was used in this work to prepare micelle solutions. Typically, the amphiphilic copolymers were first dissolved in THF to obtain homogeneous solutions. Subsequently, de-ionized water was added to polymer/THF solutions at a rate of 1 drop every 10 s with vigorous stirring. The addition of water was continued until the water content reached 20-30 wt% depending on the composition of the copolymer. The resulting solutions were transferred to dialysis tubes (MWCO = 1200) and dialyzed against de-ionized water for 48 h to remove the organic solvent. After dialysis, the solutions were transferred to volumetric flasks and then a certain volume of de-ionized water

was used to wash the dialysis bags and added to the flasks to make the final concentration of micelle solutions at  $1 \times 10^{-4}$  g.mL<sup>-1</sup>.

#### Determination of Critical Micelle Concentration

Sample solutions for fluorescence investigation were prepared as described previously [20]. Briefly, a known amount of pyrene in acetone was added to each of a series of empty 10 mL flask, and the acetone evaporated under a flow of N<sub>2</sub> gas. A total of 10 mL of various concentrations (from  $4 \times 10^{-6}$  g.mL<sup>-1</sup> to  $3 \times 10^{-4}$  g.mL<sup>-1</sup>) of copolymer aqueous solutions were added to each flask. The final concentration of pyrene was  $6 \times 10^{-7}$  g.mL<sup>-1</sup>, slightly below the saturation concentration of pyrene in water (2-3  $\mu\text{M}$ ). The flasks were heated with stirring overnight to equilibrate the pyrene and micelle, and left to cool to room temperature.

## RESULTS AND DISCUSSION

#### Different Free Radical Initiators in Relation to Copolymerization of 1-Octene and *t*-Butyl Acrylate

Our previous research work [21] indicates that 1-octene/*t*-BA copolymer initiated by AIBN is a random copolymer that 1-octene units distribute randomly among *t*-BA units. In this paper, the influence of different free radical initiators, namely polymerization temperature, on the copolymerization is emphasized.

The copolymerization results are summarized in Table 1. These copolymers, except Entry 1, contained more than 20 mol% of 1-octene. It indicated increasing temperature was a simple but efficient strategy to improve the incorporation of alkenes in the traditional radical copolymerization. According to Entry 1~4 (AIBN as initiator) or Entry 5~8 (TBPB as initiator) or Entry 9~12 (DTBP as initiator) we can see that polymerization temperature plays an efficient role on 1-octene incorporation and the monomer conversion. The approximate temperature for decomposition half-lives of 10 h ( $t_{1/2} = 10$  h) of AIBN, TBPB and DTBP is 64°C, 105°C and 126°C, in the order given. When the polymerization temperature is lower than the decomposition

**Table 1.** Influence of different free radical initiators on copolymerization of 1-octene and *t*-butyl acrylate.

Entry	Temperature (°C)	Initiator	Conversion (%)	Octene incorporated (mol%)	$\bar{M}_n \times 10^{-3}$ (g.mol <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1	50	AIBN	12.1	16.3	26.0	1.79
2	70	AIBN	27.1	25.1	8.7	2.15
3	80	AIBN	28.6	25.2	7.5	2.20
4	90	AIBN	26.2	26.7	2.1	2.08
5	85	TBPB	4.3	21.0	8.7	1.79
6	105	TBPB	32.3	27.1	4.0	1.99
7	125	TBPB	35.8	29.1	3.1	1.99
8	145	TBPB	33.1	30.7	3.0	1.89
9	105	DTBP	13.7	26.1	6.2	1.92
10	125	DTBP	37.3	26.4	3.4	1.90
11	145	DTBP	36.1	28.9	3.2	1.85
12	165	DTBP	33.7	27.6	3.2	1.86

(\*) Copolymerization conditions: toluene 20 mL, 1-octene 48.7 mmol, *t*-BA 16.2 mmol, [initiator]  $4.06 \times 10^{-3}$  mol.L<sup>-1</sup>, copolymerization time 19 h.

temperature ( $t_{1/2} = 10$  h) of any initiator, the monomer conversion and 1-octene incorporation are much lower than those at higher temperatures. While the polymerization temperature is higher than the decomposition temperature ( $t_{1/2} = 10$  h) of every initiator, the monomer conversion and 1-octene incorporation almost equal to each other at different temperatures for every initiator. On the one hand, at lower temperature, less initiator can decompose. Thus less primary radicals can initiate monomers to

propagate. On the other hand, at lower temperature less probability of the colliding of 1-octene and *t*-BA to capture one another to form copolymer. Meanwhile, less 1-octene can overcome the energy barrier to incorporate into the copolymer.

According to Table 1, the monomer conversion and 1-octene incorporation increase in the following order: AIBN < TBPB  $\approx$  DTBP. The highest monomer conversion and the highest 1-octene incorporation are 37.3% and 30.7 mol%, respectively. The decom-

**Table 2.** Influence of feeding mode of TBPB on the copolymerization of 1-octene and *t*-BA<sup>a</sup>.

Entry	TBPB (mmol)	Conversion (%)	Octene incorporated (mol%)	$\bar{M}_n \times 10^{-3}$ (g.mol <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1 <sup>b</sup>	0.12	32.3	27.1	4.0	1.99
2 <sup>c</sup>	0.04×3	34.3	26.9	4.1	2.15
3 <sup>d</sup>	0.12 (dripping)	35.3	25.8	7.6	2.16
4 <sup>b</sup>	0.36	36.0	26.7	2.3	1.77
5 <sup>c</sup>	0.12×3	37.6	28.4	3.6	2.26
6 <sup>e</sup>	0.06×6	38.0	27.7	3.9	2.44
7 <sup>f</sup>	0.03×12	39.1	28.4	4.4	2.53
8 <sup>d</sup>	0.36 (dripping)	40.2	30.3	4.8	2.59

(<sup>a</sup>) Copolymerization conditions: toluene 20 mL, 1-octene 48.7 mmol, *t*-BA 16.2 mmol, copolymerization time 19 h, copolymerization temperature 105°C; (<sup>b</sup>) TBPB was added once at the time beginning of the copolymerization; (<sup>c</sup>) TBPB was divided into 3 parts equally and added into the reactor at 19/3 h interval; (<sup>d</sup>) TBPB was added into the reactor by dripping over the course of the entire copolymerization; (<sup>e</sup>) TBPB was divided into 6 parts equally and added into the reactor at 19/6 h interval; (<sup>f</sup>) TBPB was divided into 12 parts equally and added into the reactor at 19/12 h interval.

**Table 3.** Influence of consumption of TBPB on the copolymerization of 1-octene and *t*-BA.

Entry	TBPB (mmol)	Conversion (%)	Octene incorporated (mol%)	$\bar{M}_n \times 10^{-3}$ (g.mol <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1	0.12	32.34	27.12	4.0	1.99
2	0.24	35.00	27.62	4.0	2.04
3	0.36	36.00	26.70	2.3	1.77
4	0.48	37.21	29.24	3.2	2.00

(\*) Copolymerization conditions: toluene 20 mL, 1-octene 48.7 mmol, *t*-BA 16.2 mmol, copolymerization time 19 h, copolymerization temperature 105°C.

position temperature ( $t_{1/2} = 10$  h) of TBPB and DTPB is much higher than that of AIBN. Therefore, at higher temperature, the concentration of TBPB and DTPB can be kept at higher level and maintain longer time than that of AIBN. Hence more monomer can be initiated and copolymerized with each other to produce more copolymer. At the same time, as polymerization temperature increases, molecular weight gradually decreases which has no relationship with the type of initiator. The polydispersity indices (PDI) are not much different from each other.

To further improve the monomer conversion and 1-octene incorporation, the concentration of initiator and feeding mode of initiator were changed (Table 2). To some extent, increasing the concentration of initiator can increase the monomer conversion and 1-octene incorporation. The higher concentration of initiator, more monomer molecules can be initiated and then copolymerized to form the corresponding copolymer. At lower concentration, changing feeding mode of initiator does not influence the monomer conversion and 1-octene incorporation much. At higher concentration of initiator, however, from Entry 4 to Entry 8, adding initiator by dripping over the course of the entire copolymerization can obviously increase both monomer conversion and 1-octene incorporation. As under these conditions, the concentration of initiator in the reactor is very low over the course of the entire copolymerization. Thus the concentration of primary radicals, primary propagating radicals and propagating radicals is very low in the reactor that results in low probability of side reactions, such as combination and disproportionation of all kinds of radicals and chain transfer to initiator, monomer, polymer and solvent. Therefore, the initiator added

into the reactor can be used efficiently and give rise to more copolymer molecules. Under these conditions, since the molecular weight of polymer is positively proportional to the ratio of [monomer]/[initiator]<sup>1/2</sup> [14], poly(1-octene-*co-t*-BA) with higher molecular weight but slightly broader PDI can be prepared.

The influence of TBPB consumption on the copolymerization of 1-octene and *t*-BA is shown in Table 3. As the consumption of TBPB increases, the monomer conversion and 1-octene incorporation increase to some extent. Transfer to initiator is of greatest importance for polymerizations taken to high conversion or when the ratio of initiator to monomer is high. It introduces a new end group into the polymer, lowers the molecular weight of the polymer, reduces the initiator efficiency and increases the rate of initiator disappearance [13]; therefore, as the consumption of TBPB increases the molecular weights of these copolymers tend to decrease.

To further increase the monomer conversion and 1-octene incorporation, more initiator and longer copolymerization time were adopted. The results are shown in Table 4. In Entry 1, 0.12 mmol TBPB was added into the reactor at the beginning of the copolymerization, and then the copolymerization was carried out for 19 h. In Entry 2, 0.24 mmol TBPB was divided into 2 parts equally (0.12×2 mmol) and added into the reactor at the interval of 19 h. In Entry 3, 0.12×3 mmol TBPB was added into the reactor at the interval of 19 h. In Entry 4, 0.12×6 mmol TBPB was added into the reactor at the interval of 19 h. According to these experiments, the monomer conversion and 1-octene incorporation increase as the consumption of initiator and copolymerization time

**Table 4.** Influence of consumption of initiator and copolymerization time on the copolymerization of 1-octene and *t*-BA<sup>a</sup>.

Entry	Time (h)	TBPB (mmol)	Conversion (%)	Octene incorporated (mol%)	$\bar{M}_n \times 10^{-3}$ (g.mol <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1 <sup>b</sup>	19	0.12×1	32.3	27.1	4.0	1.99
2 <sup>c</sup>	38	0.12×2	35.7	31.7	3.3	2.15
3 <sup>d</sup>	57	0.12×3	37.0	35.2	3.9	2.05
4 <sup>e</sup>	114	0.12×6	41.1	37.1	3.0	2.56

(<sup>a</sup>) Copolymerization conditions: initiator TBPB, toluene 20 mL, 1-octene 48.7 mmol, *t*-BA 16.2 mmol, copolymerization temperature 105°C; (<sup>b</sup>) 0.12 mmol TBPB was added into the reactor at the beginning of the copolymerization; (<sup>c</sup>) 0.12×2 mmol TBPB was added into the reactor at 19 h interval; (<sup>d</sup>) 0.12×3 mmol TBPB was added into the reactor at 19 h interval; (<sup>e</sup>) 0.12×6 mmol TBPB was added into the reactor at 19 h interval.

increase. The 1-octene incorporation can be enhanced as high as 37.1 mol%. At the same time, the monomer conversion is as high as 41.1%.

#### Determination and Validation of Reactivity Ratio in 1-Octene/*t*-BA Copolymerization

Reactivity ratio plays the most important role in copolymerization, provides great incentives for revealing the copolymerization mechanism, copolymer components, relationship between feed ratio and conversion and sequence-length distributions of copolymer. To determine the reactivity ratio, copolymerization in low conversion (<10%) was carried out and the results are shown in Table 5. As the consumption of 1-octene increases, the 1-octene incorporation in the copolymers increases. Meanwhile, molecular weight of these copolymers decreases which may arise from high termination

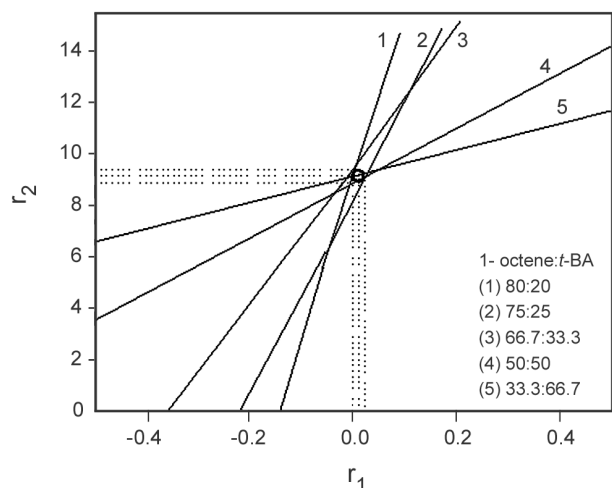
probability once the end of a copolymer chain is occupied by a 1-octene unit. To calculate reactivity ratio of 1-octene ( $r_1$ ) and *t*-BA ( $r_2$ ), Mayo-Lewis equation [22] and Mayo-Lewis integral equation [23] were adopted. Trial and error method has been used to determine the range of reactivity ratio as shown in Figure 1a. The calculation results are  $0.001 < r_1 < 0.019$  and  $8.776 < r_2 < 9.401$ . Since  $r_1 < 1$ ,  $r_2 > 1$  and  $r_1.r_2 < 1$ , copolymerization of 1-octene and *t*-BA belongs to non-ideal copolymerization.

Traditionally, Mayo-Lewis integral method cannot gain an accurate result because of the randomness for individual to draw a circle to cover the densest district, and the calculation turns out to be heavy and complex. To gain a relative, accurate and reliable  $r_1$  and  $r_2$ , computer programming method has been introduced. Eqn (1) was derived from Mayo-Lewis integral equation as follows:

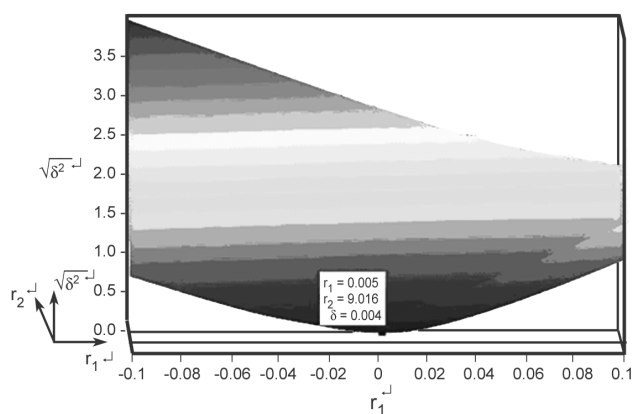
**Table 5.** Influence of feed ratio of 1-octene/*t*-BA on the copolymerization of 1-octene and *t*-BA.

Entry	1-Octene (mmol)	<i>t</i> -BA (mmol)	Time (h)	AIBN (mmol)	Conversion (%)	Octene incorporated (mol%)	$\bar{M}_n \times 10^{-3}$ (g.mol <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1	64.8	16.2	4	0.12	8.82	25.37	5.81	2.34
2	48.7	16.2	1	0.12	5.64	22.23	6.74	2.12
3	32.4	16.2	0.5	0.12	8.72	15.93	9.34	2.30
4	16.2	16.2	1/12	0.12	8.81	9.81	18.09	2.06
5	16.2	8.1	1/12	0.12	9.07	5.23	43.05	1.96
6	16.2	5.4	1/30	0.12	7.58	4.46	55.68	3.11
7	16.2	4.1	1/30	0.12	8.14	3.89	72.84	2.20

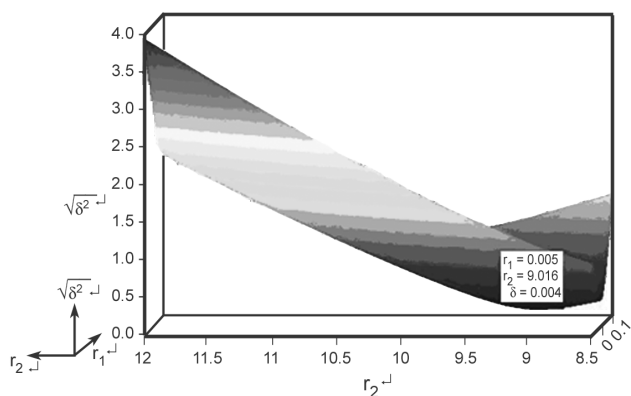
(\*) Copolymerization conditions: AIBN as initiator, toluene 20 mL, copolymerization temperature 80°C.



(a)



(b)



(c)

**Figure 1.** Determination and validation of reactivity ratios of 1-octene ( $r_1$ ) and  $t$ -BA ( $r_2$ ): (a)  $r_2$  as a function of  $r_1$  for copolymerization of 1-octene and  $t$ -BA estimated from  $^1\text{H}$  NMR by Mayo-Lewis integral equation; and surface of  $\sqrt{\delta^2}$  as functions of: (b)  $r_1$  and (c)  $r_2$  in MATLAB 7.5.0.

$$\delta(r_1, r_2) = r_2 - \frac{\lg \frac{[M_2]_0}{[M_2]} - Q \lg \left( \frac{Q - \frac{[M_1]}{[M_2]}}{Q - \frac{[M_1]_0}{[M_2]_0}} \right)}{\lg \frac{[M_1]_0}{[M_1]} + \lg \left( \frac{Q - \frac{[M_1]}{[M_2]}}{Q - \frac{[M_1]_0}{[M_2]_0}} \right)} \quad (1)$$

where  $Q = r_2 - 1/r_1 - 1$ ,  $[M_1]_0$  and  $[M_2]_0$  are the original concentration of 1-octene and  $t$ -BA, respectively;  $[M_1]$  and  $[M_2]$  are the concentrations of 1-octene and  $t$ -BA at the end of copolymerization, respectively.  $\delta^2$  is defined as:

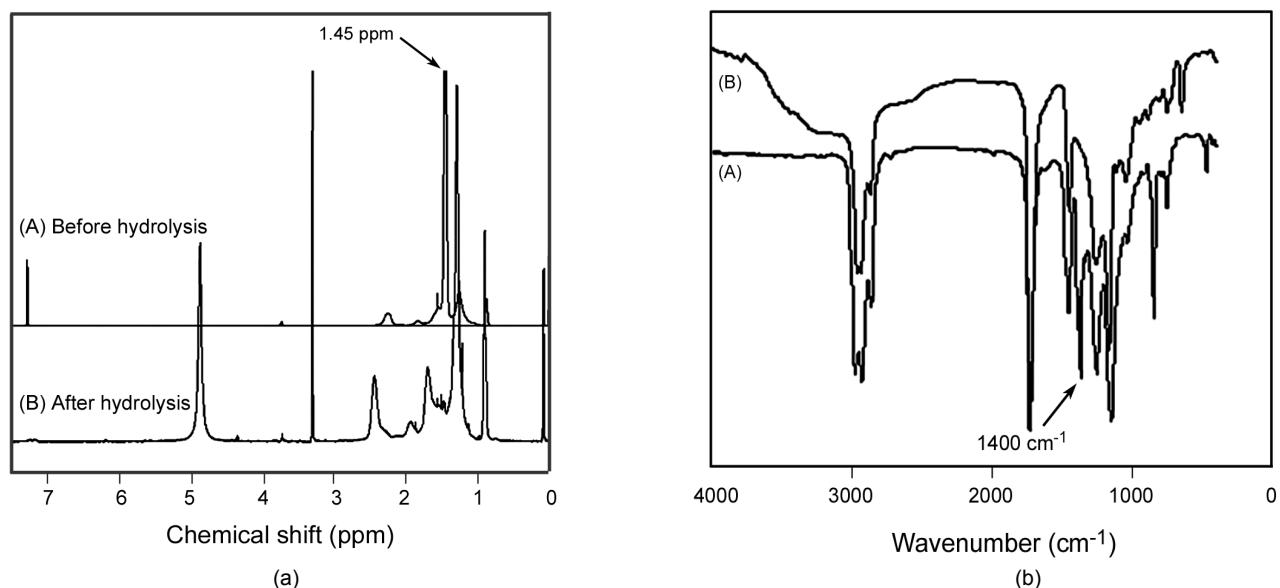
$$\delta^2 = \sum_{\substack{a < r_1 < b \\ c < r_2 < d}}^n \delta_{i,r_1,r_2}^2, n = 5 \quad (2)$$

$\delta_{i,r_1,r_2}$  is the  $\delta$  value at the experiment  $i$  at any value from  $a < r_1 < b$ ,  $c < r_2 < d$ . The  $\delta_{\text{Min}}^2$  is gained by programming in MATLAB 7.5.0 by checking  $-0.1 < r_1 < 0.1$ ,  $8.5 < r_2 < 12$  (referring to the range gained above by drawing). The calculation results are  $r_1 = 0.005 \pm 0.001$ ,  $r_2 = 9.016 \pm 0.001$  (Figures 1b and 1c), by which the sequence-length distributions of 1-octene/ $t$ -BA copolymer was calculated. The theoretical calculation indicates that these copolymers are random copolymers that 1-octene units distribute randomly among  $t$ -BA units as confirmed by  $^{13}\text{C}$  NMR spectrum of our previous work [21].

### Hydrolysis of Poly(1-octene-co- $t$ -BA)

Amphiphilic poly(1-octene-co-AA) can be easily obtained by hydrolyzing poly(1-octene-co- $t$ -BA) with trifluoroacetic acid (TFA).  $^1\text{H}$  NMR Spectra and FTIR of the hydrolyzate of poly(1-octene-co- $t$ -BA) are shown in Figure 2. As shown in Figure 2a, there is no resonance at 1.45 ppm (arising from methyl group of  $t$ -BA unit) on spectrum (b) indicates that  $t$ -BA units in poly(1-octene-co- $t$ -BA) are completely transformed into AA units. Furthermore, as shown in Figure 2b, there is no signal of deformation vibration of  $t$ -butyl group at  $1400 \text{ cm}^{-1}$  on spectrum (b) but the





**Figure 2.** Comparison of copolymers before and after hydrolysis by (a)  $^1\text{H}$  NMR: (A) poly(1-octene-*co-t*-BA) in  $\text{CDCl}_3$  and (B) poly(1-octene-*co-AA*) in  $\text{CD}_3\text{OD}$ ; and (b) FTIR: (A) poly(1-octene-*co-t*-BA) and (B) poly(1-octene-*co-AA*).

signal of  $-\text{OH}$  at  $3500\text{--}3000\text{ cm}^{-1}$  appears. This indicates that *t*-BA units are completely hydrolyzed by TFA.

#### Micellar Behaviours of Poly(1-octene-*co-AA*)

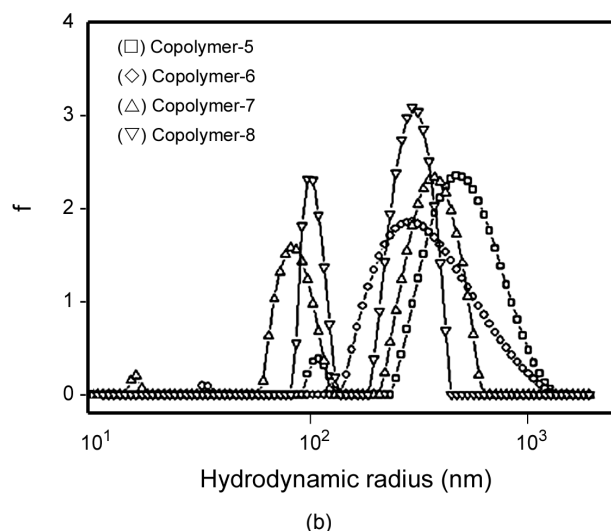
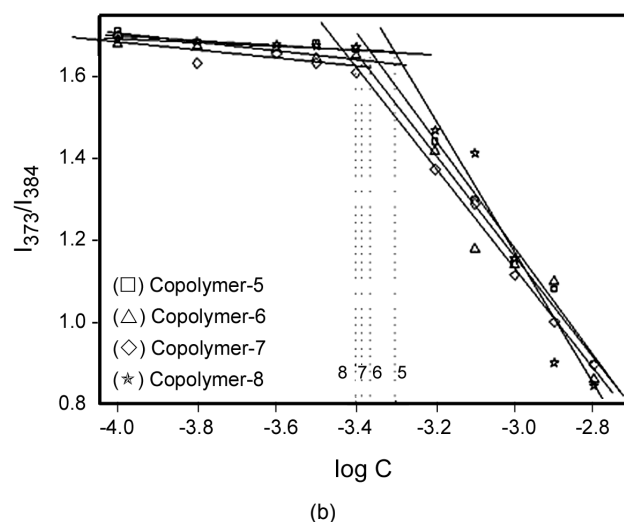
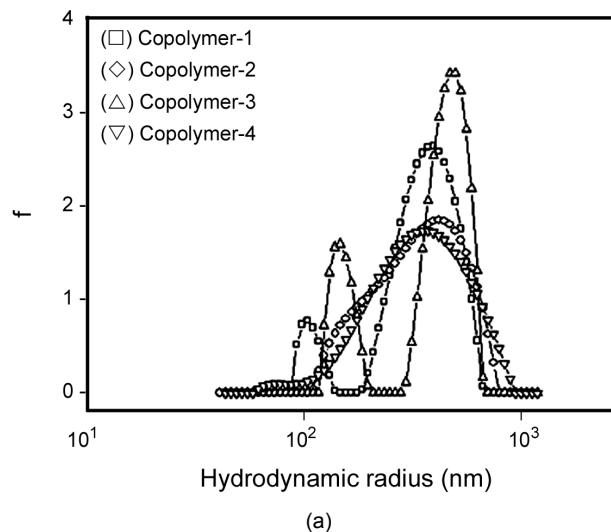
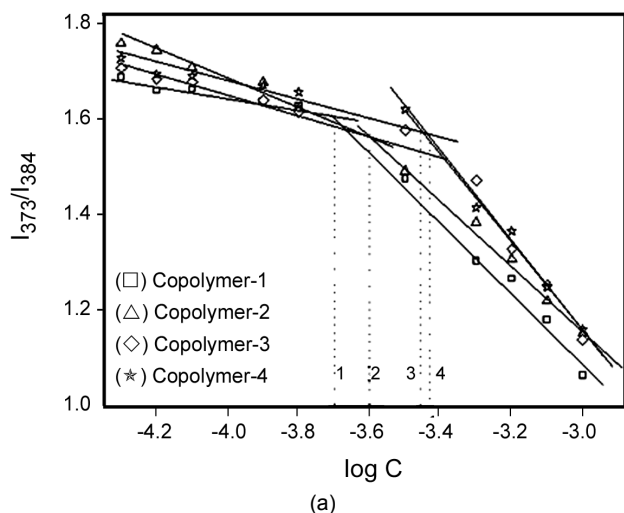
Critical micelle concentration (CMC) values of poly(1-octene-*co-AA*) provide vital reference to the application of this kind of material. Eight poly(1-octene-*co-AA*) listed in Table 6 were studied by fluorescence probe method with pyrene as the fluorescence probe. High content of AA units in the chains makes these polymers dissolve in water. Pyrene is a non-polar fluorescence probe, insoluble in

water and greatly sensitive to surrounding micro-change of polarity. Therefore, when in low concentration of polymers where there is no micelle formed, pyrene is in polar water circumstance which leads to a high  $I_{373}/I_{384}$ , while as the increase of concentration of polymers where micelles are largely formed, pyrene enters the micelle and the micro-change of polarity surrounding pyrene will lead to an obviously decline of  $I_{373}/I_{384}$ , by which the CMC values can be determined. The fluorescence spectrum of a series of sequential concentration of aqueous solutions of poly(1-octene-*co-AA*) was determined and  $I_{373}/I_{384}$  values were plotted on concentration logarithm ( $\log C$ )

**Table 6.** The characteristic data of poly(1-octene-*co-AA*) in water at  $25^\circ\text{C}$ .

Copolymer	Octene incorporated (wt%)	$\bar{M}_n \times 10^{-3}$ ( $\text{g}\cdot\text{mol}^{-1}$ )	PDI	$R_h$ (nm)	$\text{CMC}^* \times 10^4$ ( $\text{g}\cdot\text{mL}^{-1}$ )
1	34.2	6.789	2.19	301	1.98
2	35.4	5.623	1.90	308	2.54
3	36.7	3.622	2.20	328	3.43
4	36.1	3.265	2.14	330	3.72
5	48.0	2.569	1.81	410	4.00
6	40.7	2.412	2.24	323	4.17
7	38.9	2.400	2.07	267	4.30
8	35.9	2.777	2.44	218	4.68

(\*) CMC: critical micellar concentration;  $R_h$ : mean hydrodynamics radius.



**Figure 3.** Plots of  $I_{373}/I_{384}$  versus  $\log C$  of: (a) copolymers 1~4 with different molecular weights and (b) copolymers 5~8 with various 1-octene incorporations.

**Figure 4.** The distribution of hydrodynamic radius of poly(1-octene-*co*-AA) in water measured by DLS ( $\theta = 90^\circ$ ).

as shown in Figure 3. CMC Values were gained by the intersection of two simulated lines and summarized in Table 6 as well as other characteristic data.

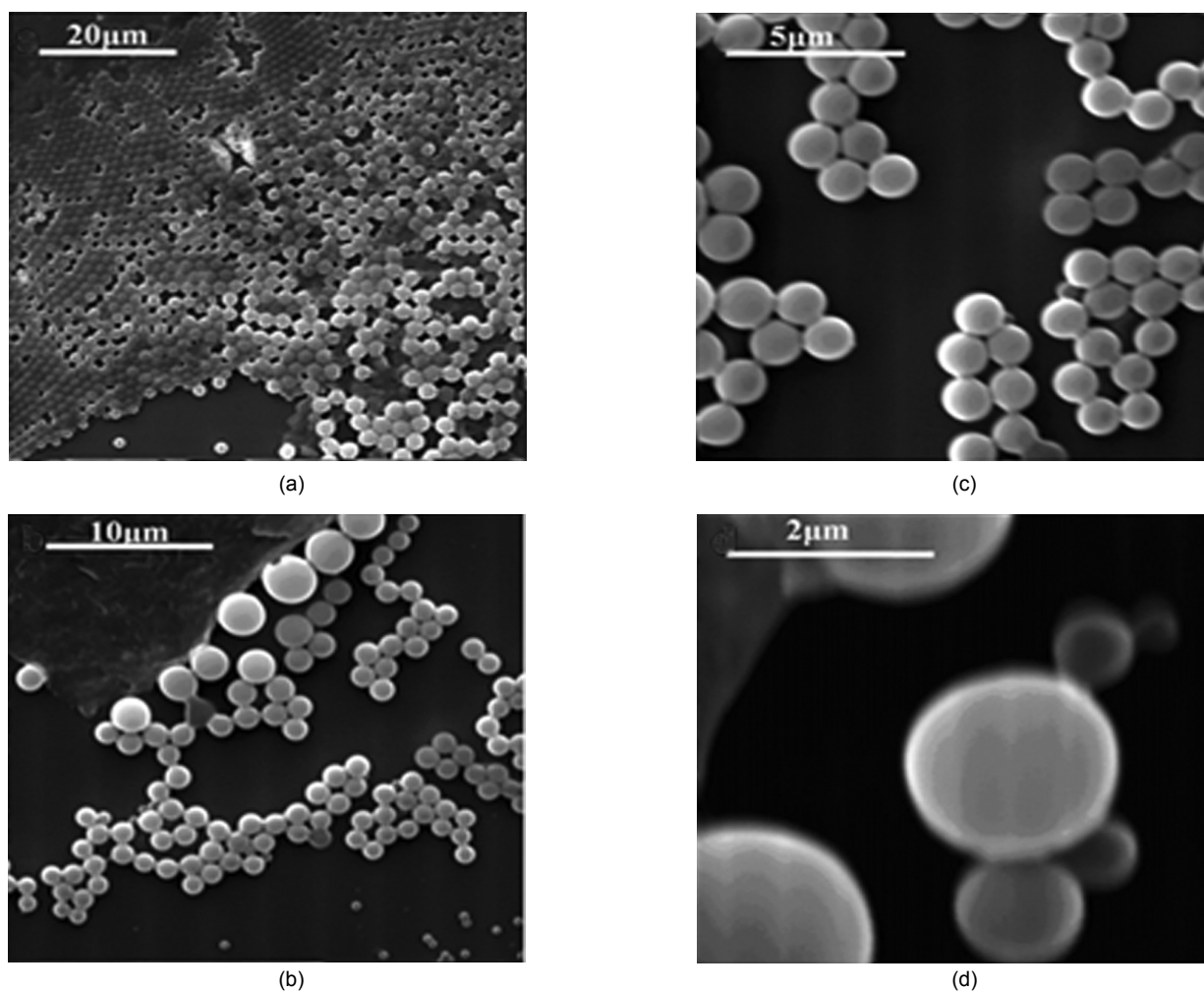
As shown in Table 6, in case of copolymers 1~4 whose contents of AA units are almost similar to each other, CMC values increase with decreased molecular weights. In case of copolymers 5~8 whose molecular weights and their polydispersity indices are almost similar to each other, CMC values decrease as 1-octene incorporation is increased.

As shown in Figure 4, hydrodynamic radius of poly(1-octene-*co*-AA) micelles in water has a broad distribution ranging from 87 nm to 1338 nm which can also be clearly observed by SEM (as shown in

Figure 5). The mean hydrodynamic radius ( $R_h$ ) of these micelles was determined by DLS and shown in Table 6.  $R_h$  Values of copolymers 1~4 increase as the molecular weights of these copolymers decrease due to longer chain is more likely to reach stability by intra-molecular interaction [24]. Meanwhile,  $R_h$  values of copolymers 5~8 increase as the 1-octene incorporation increases. This may be due to more hydrophobic units which would be more difficult for hydrophilic units to stabilize the micelles.

**Thermal Behaviours of Poly(1-octene-*co*-*t*-BA) and its Hydrolyzates**

In association to a significant reference to these copolymers processing and application conditions,  $T_g$



**Figure 5.** SEM Images of poly(1-octene-co-AA) micelle-particles deposited on isinglass plates.

values and its influential factors were studied by DSC. As shown in Table 7, every poly(1-octene-co-*t*-BA) has one unique glass-transition.  $T_g$  Values increase with the increase of molecular weight and the decline of 1-octene incorporation.  $T_g$  Values of poly(1-octene) and poly(*t*-butyl acrylate) are  $-65^\circ\text{C}$  and  $107^\circ\text{C}$ , respectively [25]. So incorporation of

1-octene lowers  $T_g$  values of these copolymers.

As shown in Table 8,  $T_g$  values of poly(1-octene-co-AA) increase with increases in molecular weight and decreases in 1-octene incorporation. Universally,  $T_g$  value of poly(1-octene-co-AA) is much higher than that of poly(1-octene-co-*t*-BA) even while poly(1-octene-co-AA) contains more 1-octene units

**Table 7.** DSC Results of poly(1-octene-co-*t*-BA).

Copolymer	Octene incorporated (mol%)	$\bar{M}_n \times 10^{-3}$ (g.mol $^{-1}$ )	PDI	$T_g$ ( $^\circ\text{C}$ )
1	15.9	9.34	2.30	8.4
2	9.8	18.09	2.06	24.8
3	5.2	43.05	1.96	28.6
4	4.5	55.68	3.11	32.8
5	3.9	72.84	2.20	37.2

**Table 8.** DSC Results of poly(1-octene-co-AA).

Copolymer	Octene incorporated (mol%)	$\bar{M}_n \times 10^{-3}$ (g.mol <sup>-1</sup> )	PDI	T <sub>g</sub> (°C)
1	25.1	6.789	2.19	106.3
2	26.1	5.623	1.90	105.2
3	27.1	3.622	2.20	100.5
4	26.7	3.265	2.14	62.0
5	37.3	2.569	1.81	39.2
6	30.7	2.412	2.24	42.1
7	29.1	2.400	2.07	54.4
8	26.4	2.777	2.44	57.8

and has lower molecular weight than poly(1-octene-co-*t*-BA). This may arise from the strong hydrogen bonding among AA units.

## CONCLUSION

1-Octene and *t*-butyl acrylate can be copolymerized by conventional free radical polymerization under mild conditions. The 1-octene incorporation can be regulated in the range of 0~37.1 mol%. Using high-temperature decomposition initiators, such as *t*-butyl peroxybenzoate and di-*t*-butyl peroxide, copolymerization temperature can be increased which results in incremental 1-octene incorporation and monomer conversion. Meanwhile, molecular weights of these copolymers decrease as copolymerization temperature increases. By combining Mayo-Lewis differential equation with computer programming, the reactivity ratios of 1-octene ( $r_1$ ) and *t*-butyl acrylate ( $r_2$ ) were figured out as  $r_1 = 0.005$  and  $r_2 = 9.016$ . Amphiphilic poly(1-octene-co-acrylic acid) can be easily obtained by hydrolyzing poly(1-octene-co-*t*-butyl acrylate). CMC Values of these amphiphilic copolymers in water increase as their molecular weight and 1-octene incorporation decrease. However, the mean hydrodynamic radius decreases as molecular weight increases or 1-octene incorporation decreases. Although T<sub>g</sub> value of poly(1-octene-co-acrylic acid) is much higher than that of poly(1-octene-co-*t*-butyl acrylate), they all decrease with the lowered molecular weight or increases 1-octene incorporation.

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