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ORIGINAL PAPER

Synthesis and assessment of the effect of monomer feed ratio and Lewis acids on copolymerization of butyl methacrylate/1-octene

Mohammad Reza Jozaghkar, Seyed Mehrdad Jalilian*, Farshid Ziaee

Department of Polymer Science, Iran Polymer and Petrochemical Institute, P. O. Box: 14965/115, Tehran, Iran

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ABSTRACT

This study was designed to investigate the effect of molar ratio of 1-octene and type as well as concentration of Lewis acids on the free radical copolymerization of butyl methacrylate (BMA) with 1-octene. The synthesized copolymers have been substantially described by FTIR, ^{1}H NMR, GPC and DSC. The quantitative ^{1}H NMR and GPC demonstrated that by increase in the molar ratio of 1-octene and Lewis acids to BMA, the incorporation of 1-octene in the copolymer backbone enhanced, M_n reduced and polydispersity became narrower. The maximum incorporation of 1-octene (13.7%) was observed for sample CSC7 having [1-octene/BMA] of 3 mol% and [$AlCl_3$/BMA] of 1.5 mol%. The DSC results confirmed the NMR and GPC outcomes, suggesting a decrease in T_g by increasing 1-octene in the copolymer backbone. Moreover, it is found that temperature has a remarkable influence on the copolymerization behavior. The results also showed that by substituting the acrylate monomer from butyl methacrylate to butyl acrylate, the incorporation of 1-octene increased. **Polyolefins J (2022) 9: 85-91**

Keywords: Copolymerization; butyl methacrylate; 1-octene; monomer incorporation; Lewis acid.

INTRODUCTION

In the last few decades, copolymerization of non-polar and polar monomers with a variety of compositions and architectures has received great research interests. Recent studies have demonstrated that the major properties of the aforementioned copolymers can be controlled by the choice of monomer and catalyst as well as feeding ratio, which could make them desired materials for many industrial applications [1-3].

Among these copolymers, the copolymers of α-olefin and acrylates could own substantial chemical resistance and barrier characteristics. Also, these copolymers have defined functionalities, which are important for adhesion to substrates and further modification as well [4, 5]. Previous studies are full of interesting outcomes related to the synthesis of α-olefin/acrylates copolymers. However, the synthesis of α-olefin/acrylates copolymers with controlled composition and molecular weight is still demanding. It has been demonstrated that α-olefin/acrylates copolymers could be synthesized either via late transition metal-mediated

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*Corresponding Author - E-mail: M.djalilian@ippi.ac.ir polymerization or via free radical polymerization [6, 7]. The copolymers synthesized by free radical polymerization often are rich in acrylates due to the higher reactivity of acrylate monomers than α-olefin ones. Therefore, for the synthesis of these copolymers with higher incorporation of α-olefin at lower polymerization temperature and pressure, the addition of Lewis and Brønsted acids to the aforementioned system has been suggested [8, 9].

Lutz and coworkers [10] studied the alternating copolymer by CRP in the presence of Lewis acids. According to their finding, the Lewis acids could coordinate with the carbonyl group of meth (acrylate) monomer. They could decrease the density of electron of the conjugated double bond and increase the acrylate radical reactivity. Variety of Lewis acids such as $AlCl_3$, Al_2O_3 and scandium triflate have been reported to enhance α-olefin mole fraction [11-13]. Nagel et al. [14] reported that both reaction rate and incorporation of 1-hexene were improved by addition of scandium triflate to AIBN-initiated copolymerization of methyl acrylate and methyl methacrylate.

Recently, several literatures have been published on the copolymerization of acrylate and 1-alkene using controlled radical polymerization. Venkatesh and coworkers [15, 16] investigated the copolymerization of 1-octene with methyl acrylate and methyl methacrylate using ATRP. They reported that the copolymers having 20 mol% of 1-octene were attained. Also, by increasing the more fraction of 1-octene, the incorporation of this α-olefinic monomer enhanced. However, in the presence of higher mole fraction of 1-octene the copolymerization became more difficult to control. Carlson et al. [17] reported that presence of scandium triflate in the free radical copolymerization of 1-hexene with acrylamide could increase the alkene incorporation in the copolymer chain.

To the best of our knowledge, Lewis acid-mediated copolymerization of butyl meth acrylate with 1-octene has not been studied so far. Butyl methacrylate is a polar monomer that offers extraordinary properties such as adhesion, printability, paint ability, surface property, etc. in copolymerization with 1-octene. Therefore, in this particular study, free radical copolymerization of BMA and 1-octene was undertaken and the influence of type and concentration of Lewis acid as well as molar ratio of monomers on the copolymer characteristics has been investigated.

EXPERIMENTAL

Materials

In this study, all chemicals and reagents were attained from Merck (Germany). Butyl methacrylate (≥ 99%) and 1-octene (98%) were distilled using CaH_2 under vacuum, and then stored under inert atmosphere. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%) was recrystallized from methanol. Aluminum chloride ($AlCl_3$, anhydrous, 99.99%), aluminum oxide (Al_2O_3, ≥ 98%), toluene (≥ 99%) and methanol (99.8%) were used as received.

Synthesis of copolymers

The copolymerization of butyl methacrylate and 1-octene was performed in a round-bottom flask under an inert atmosphere. Initially, the materials were accurately weighed according to the recipes in Table 1 and added into a 25 mL round-bottom flask. Toluene was utilized as a media of reaction. The reaction mixture was stirred in a 70°C oil bath for 6 h. The prepared samples were cooled, filtered and precipitated in an excess amount of methanol. The precipitated copolymers were dried under vacuum at about 60°C. According to the gravimetric analysis, the monomer conversion based on butyl methacrylate was at least 80%.

Characterization

NMR

All nuclear magnetic resonance (NMR) experiments were performed on a Bruker Avance 400 mHz NMR spectrometer (Germany). The sample concentration was about 5% (w/v). ^{1}H NMR spectra were attained using 32 K data points, spectral width 16 ppm, acquisition time 1.56 s, relaxation delay 10 s, pulse width 30° and 4 scans.

FTIR

Characterization of the synthesized copolymers was also performed using Fourier transform infrared spectroscopy (FTIR, Bruker-IFS48 spectrometer, Germany) in the wave number range of 4000 to 400 cm^{-1}.

GPC

Gel permeation chromatography (GPC) analyses were carried out on an Agilent 1100 (USA) equipped with a

Table 1. Data of copolymer at different molar ratios of 1-octene and Lewis acids to BMA(a).

Sample Name	[1-octene/BMA]	[$AlCl_3$/BMA]	1-octene incorp. (mol%)	M_n (×10^{-4})(b)	M_w (×10^{-4})(b)	Đ(b)
CSC1	1	0.5	8.2	3.0	5.8	1.89
CSC2	1	1.5	8.9	2.0	3.1	1.65
CSC3	2	1.5	12.4	1.9	3.0	1.56
CSC4	3	0.25	8.2	2.5	3.7	1.81
CSC5	3	0.5	10.3	2.2	3.8	1.75
CSC6	3	1	11.1	1.7	2.8	1.54
CSC7	3	1.5	13.7	1.5	2.4	1.52
CSO1	1	0.5	6.2	4.1	7.4	1.81
CSO2	1	1.5	7.5	3.9	7.0	1.79
CSO3	2	1.5	9.4	3.8	6.4	1.68
CSO4	3	0.25	7.2	3.9	7.1	1.80
CSO5	3	0.5	9.3	3.9	6.7	1.72
CSO6	3	1	9.6	3.7	6.5	1.61
CSO7	3	1.5	11.7	2.3	3.6	1.59

(a) Conditions: BMA, 2 gr; AIBN, 0.01 gr; Toluene, 30% w/v; 70°C, 6 hr.
(b) Measured by GPC

differential refractometer detector and PLgel 5 μm OH-MIXED C 300 x 7.5 mm (containing Agilent PS standard) at 30°C. The concentration of solution was 1 g/L.

DSC

In order to record the glass transition temperature of the synthesized samples, differential scanning calorimetry (DSC) measurement was carried out at the rate of 5 °C/min-1 and temperature range of -50 to 50°C using PL-DSC (England).

RESULTS AND DISCUSSION

Free radical polymerization is the one of most straightforward techniques to prepare acrylates/1-alkene copolymers. In this technique, addition of Lewis acid and its coordination to carbonyl group leads to an initial charge on the related sp^2-hybridized carbons. The terminal radical species of acrylate-Lewis acid complex are well-active in order to consecutively propagate with moderately electron-rich 1-alkene [18]. Therefore, the characterization of the synthesized copolymer and the influence of type and concentration of Lewis acid as well as molar ratio of monomers on the copolymer characteristics will be examined in the following.

Characterization of the synthesized poly(BMA-*co*-1-octene) copolymer

FTIR was used to verify the chemical structure of poly(BMA-*co*-1-octene) copolymer. As it can be seen from Figure 1, the absorption peaks in the range of 3000-2800 cm^{-1} correspond to the stretching vibrations of C-H bands for sp^3 carbon atoms (CH, CH_2 and CH_3 groups of 1-octene). The peaks appeared at 1465 cm^{-1} and 1375 cm^{-1} are attributed to the bending vibrations of C-H bands from CH_2 and CH_3 groups, respectively. The sharp peak at wave number of about 1720 cm^{-1} and the peaks at about 1230 cm^{-1}, 1140 cm^{-1} and 1060 cm^{-1} are related to the acrylate carboxyl group and C-O-C stretching vibration, respectively. The characteristic absorption peak at the wave number of 720 cm^{-1} corresponds to the bending vibrations associated with the CH_2 groups in the open chain (long-chain band) of 1-octene units.

Moreover, the absence of absorption peak in the range of 1670-1640 cm^{-1}, attributed to the stretching vibration of C=C bands, confirms the synthesis of poly(BMA-*co*-1-octene) copolymer [19].

The chemical structure of the prepared copolymers

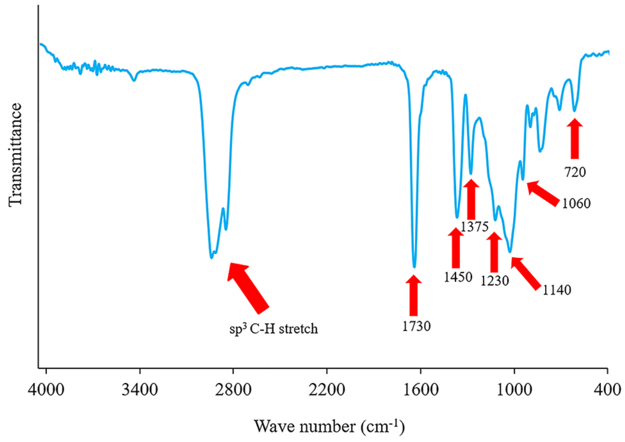

Figure 1. FTIR spectrum of poly(BMA-*co*-1-octene) copolymer (sample CSC7) synthesized by free radical polymerization in the presence of $AlCl_3$ at 70°C.

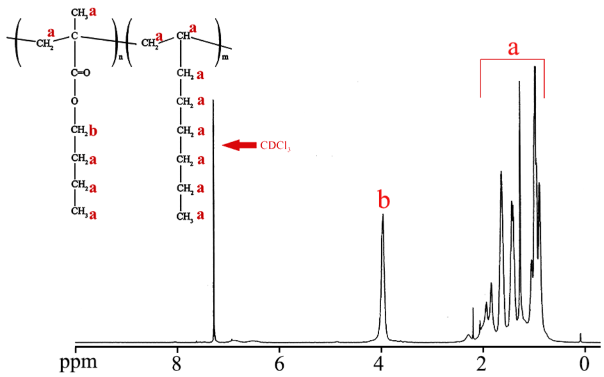

Figure 2. ^{1}H NMR spectrum of poly(BMA-1-octene) copolymer (Sample CSC7) synthesized by free radical polymerization in the presence of $AlCl_3$ at 70°C.

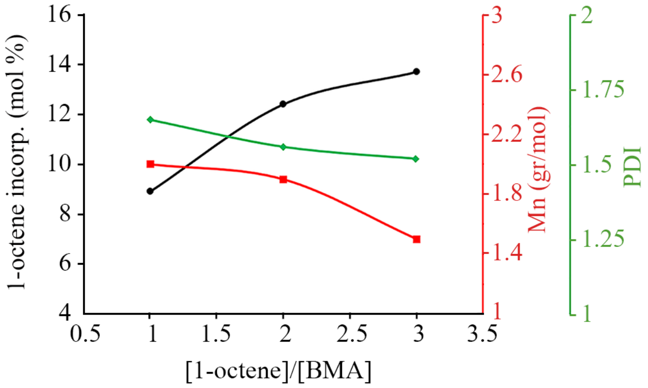

Figure 3. 1-Octene incorporation, relative molecular mass and Đ as a function of molar ratio of 1-octene to BMA (at constant [AlCl3/BMA] of 1.5 mol%).

was further investigated by ^{1}H NMR. Figure 2 demonstrated the ^{1}H NMR of the synthesized poly(BMA-*co*-1-octene). It could be observed that the chemical shifts appeared at 0.89-2.20 ppm are related to the variety of saturated aliphatic protons of -CH, -CH_2, and -CH_3 groups of poly(BMA-*co*-1-octene) copolymer. It should be mentioned that triple peaks at the chemical shift range of 0.89-1.0 ppm are attributed to the -CH_3 protons of 1-octene unit. However, the peak at 3.96 ppm is assigned to the -CH_2 protons of ester group of BMA. It is well-documented that the signals at chemical shift range of 1.0-2.0 ppm are assigned to the -CH_2 and -CH protons of 1-octene as well as -CH_2 protons of BMA [19]. The incorporation of 1-octene in the copolymers was designated from the relative areas of the proton resonance intensity of -CH, -CH_2, and -CH_3 groups of 1-octene unit and the -OCH_2 of BMA unit. This equation can be declared as:

$$Mole\ fraction\ of\ BMA = \frac{b/2}{a - 6b/12 + b/2} \tag{1}$$

$$Mole\ fraction\ of\ 1-octene = 1 - Mole\ fraction\ of\ BMA \tag{2}$$

Effect of monomer feed ratio and Lewis acids on the copolymerization of BMA and 1-octene

The incorporation of molar percentage of 1-octene in the copolymer chain plays a significant role in the copolymerization characteristics [20]. Table 1 represents the influence of molar ratio of 1-octene and both $AlCl_3$ and Al_2O_3 to BMA on the incorporation of 1-octene and molecular weight as well as polydispersity of the final products. The results clearly demonstrated that the molar ratio of 1-octene to BMA has a positive correlation with the incorporation of 1-octene in the copolymer backbone. Similar result was reported by Kaur et al. [21]. Moreover, as depicted in Figure 3, the linear decrease of M_n with incorporation of 1-octene and narrower polydispersity (Đ) of prepared poly(BMA-*co*-1-octene) were observed. The maximum incorporation of 1-octene (13.7%) was detected for sample CSC7 having [1- octene/BMA] of 3mol% and [$AlCl_3$/BMA] of 1.5 mol%.

In order to have deep insight in the copolymerization of BMA and 1-octene, the influence of molar ratio of $AlCl_3$ and Al_2O_3 to BMA was analyzed. As depicted in Figure 4, with intensification of molar ratio of $AlCl_3$ to BMA, the incorporation of 1-octene rises, M_n declines and the Đ becomes wider. Similar trend was observed when Al_2O_3 was used as Lewis acid. For example, at constant [1-octene/BMA] of 3 mol%, when molar ratio of $AlCl_3$ enhanced to 1.5 mol% from 0.25 mol%, the incorporation of 1-octene grew up to 11.7% from 7.2%. These results indicated that the increase in the molar ratio of the Lewis acid to BMA leads to improve the complexation of acid with C=O band of BMA, suggesting higher electrophilicity of - C=C of BMA

Table 2. Effect of molar ratio of 1-octene to BMA on the T_g of the synthesized copolymers.

Sample Name	[1-octene/BMA]	[$AlCl_3$/BMA]	1-octene incorp. (mol%)	M_n ($\times 10^{-4}$)	T_g (°C)
CSC1	1	0.5	8.2	3.0	19.2
CSC5	3	0.5	10.3	2.0	12.9

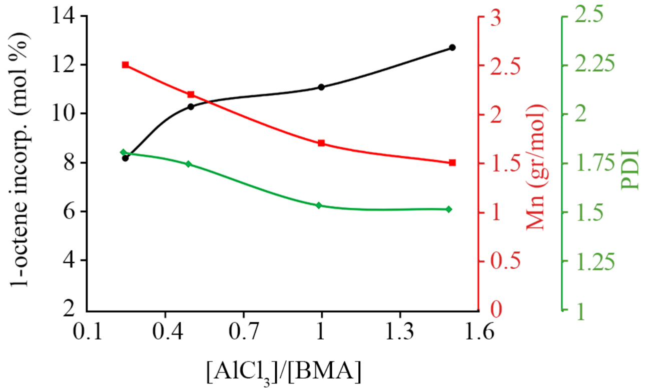

Figure 4. 1-Octene incorporation, relative molecular mass and Đ versus molar ratio of AlCl3 to BMA (at constant [1-octene/BMA] of 3 mol%).

which is valuable for copolymerization of BMA with 1-octene [22]. It is worth pointing out that by increasing Lewis acid in the free radical polymerization system, the radical concentration enhances, demonstrating a prompt action of acids on the AIBN decomposition, being beneficial for growing of polymerization rate [23]. However, compared to Al_2O_3 the incorporation of 1-octene was more in the presence of $AlCl_3$ (Figure 5). This is since, in the case of Lewis acids, the charge or size ratio at the center of the metal is one of the crucial evaluations of their strength which directly relates to their ability to promote the copolymerization [24].

It is crucial to mentioned that the glass transition temperature (T_g) predominately depends on molecular weight and copolymer composition [25, 26]. Table 2 presents the effect of molar ratio of 1- octene to BMA on the T_g of synthesized copolymers. As shown in this table, an increase in the molar ratio of the 1-octene to BMA led to a reduction in M_n and consequently decrement in T_g. These results are in good agreement with the GPC and ^{1}H NMR data.

Effect of polymerization temperature

To investigate the effect of reaction temperature on the incorporation of 1-octene, the temperature is declined from 70°C to 60°C and the corresponding results are depicted in Figure 6. As can be seen from this figure, the copolymerization of BMA and 1-octene shows the sensitivity to the reaction temperature. In detail, a decrease in the reaction temperature led to a decline in the incorporation of 1-octene in the copolymer backbone. In fact, a decrease in the reaction temperature reduces the effective collisions and the terminal radical species of acrylate-Lewis acid complex which is directly related to the incorporation of 1-octene to the copolymer backbone [27]. Moreover, reduction in the reaction temperature could directly influence the decomposition rate of AIBN [28].

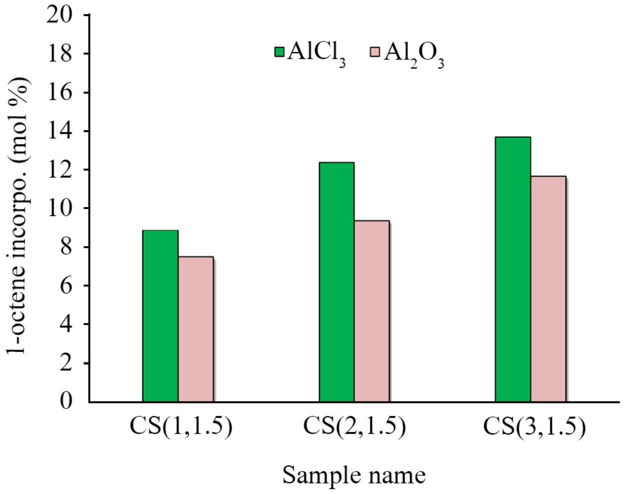

Figure 5. Effect of different Lewis acid types on the 1-octene incorporation in the copolymer backbone at different [1-octene/BMA] (1, 2 and 3 mol%) and constant [Lewis acid/ BMA] (1.5 mol%).

Effect of monomer type

In order to further study, the effect of type of acrylate monomer on the incorporation of 1-octene was investigated. According to Table 2, incorporation of 1-octene was higher when the butyl acrylate was used as monomer. The GPC results also approved the higher incorporation of 1-octene by demonstrating the lower M_n. It is worth noting that there is a noticeably less steric hindrance to the copolymerization in the case of the butyl acrylate than the butyl methacrylate, which satisfactorily describes the alteration in the M_n and the incorporation of 1-octene [29]. Also, in comparison with BMA, the influence of Al_2O_3 complexing to carbonyl on the –C=C group is more robust in the case of butyl acrylate,

Table 3. Effect of type of acrylate monomer on the incorporation of 1-octene in the copolymer backbone.

Sample Name	[1-octene/acrylate]	[Al_2O_3/acrylate]	1-octene incorp. (mol%)	M_n (×10^{-4})	M_w (×10^{-4})	Đ
BMA-co-1-octene	3	1.5	11.7	2.3	3.6	1.59
BA-co-1-octene	3	1.5	18.9	1.2	1.8	1.65

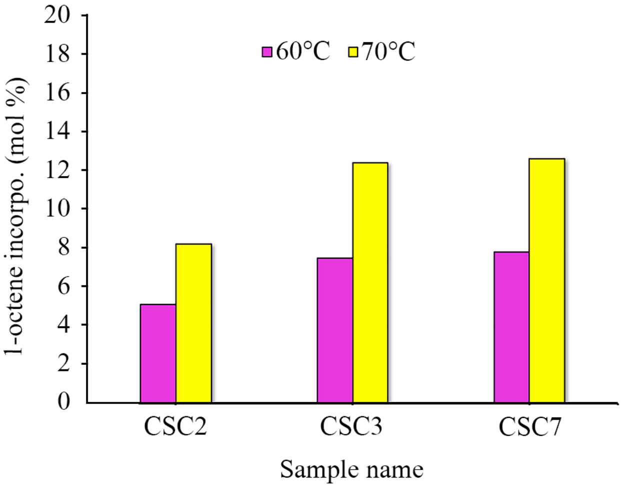

Figure 6. Effect of reaction temperature on the incorporation of 1-octene in the copolymer backbone.

due to the lack of electron-donating effect of the methyl group [11].

CONCLUSION

In this particular study, free radical copolymerization of BMA and 1-octene was carried out in the presence of $AlCl_3$ and Al_2O_3. The effect of monomer feed ratio and the type and concentration of Lewis acids was investigated. The preparation of poly(BMA-*co*-1-octene) copolymer was confirmed by FTIR as well as ^{1}H NMR spectroscopy. It was revealed that an increase in the molar percentage of 1-octene and Lewis acid led to an increase in 1-octene incorporation and a decrease in M_n. Compared to the Al_2O_3, using $AlCl_3$ improved the incorporation of 1-octene in the copolymer backbone. The DSC results confirmed the results of ^{1}H NMR and GPC tests, indicating a reduction in T_g by increasing the molar ratio of 1-octene to BMA. Lowering the reaction temperature decreased the incorporation of 1-octene. The results also showed that at similar conditions, the substitution of BMA by BA led to an increase in 1-octene incorporation due to lower steric hindrance of BA than BMA.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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