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Controlled Copolymerization of *n*-Butyl Acrylate with Nonpolar 1-Alkenes Using Activators Regenerated by Electron Transfer for Atom-Transfer Radical Polymerization

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ABSTRACT: Controlled copolymerization of *n*-butyl acrylate with 1-octene was achieved by ARGET (activators regenerated by electron transfer) ATRP (atom transfer radical polymerization) in anisole. When a normal ATRP of *n*-butyl acrylate and 1-octene was conducted, the polymerization resulted in relatively low conversion ($<$50%), limited control over the polymerization process, and high polydispersity (PDI = 1.6). This was due to formation of a dormant species by reaction of 1-octene radicals with Cu(II) deactivator that could not be reactivated. However, in ARGET ATRP with 10 ppm amounts of Cu-based catalyst, higher yields and a better controlled copolymerization were obtained because the low concentration of Cu(II) deactivator reduced the frequency of producing the nonreactive dormant species. When *n*-butyl acrylate and 1-octene were copolymerized with 10 ppm of $CuCl_2$/TPMA vs monomer and 10 mol % of $Sn(EH)_2$ vs initiator, a copolymer was prepared in higher yield and with low polydispersity (PDI $<$ 1.4).

Introduction

Copolymers of polar and nonpolar monomers have been the subject of research for a long time because the properties of the resulting copolymer can be controlled by combining two kinds of monomers with very different properties, making them attractive materials for a number of applications. There have been several review articles on the copolymerization of 1-alkenes with polar monomers.[1−5] Recent studies have shown that late-transition-metal complexes exhibit some promise as polar/nonpolar copolymerization catalysts. Brookhart reported that copolymerization of methyl acrylate and ethylene could be carried out using a Pd(II) cationic diimine compound as catalyst.[6] The copolymers exhibited a highly branched structure, and the molecular weight distribution was high. Drent also reported that a Pd(II) catalyst system is capable of copolymerizing ethylene and alkyl acrylates but produced poorly controlled copolymers.[7] Although these catalytic systems can copolymerize 1-alkenes with polar monomers, it was difficult to control all aspects of the copolymerization due to the significant difference of the reactivity between these monomers.

Radical polymerization is another method for copolymerization because of high tolerance of growing radicals for both polar and nonpolar monomers. Copolymers were produced using conventional free radical polymerization, but only limited control was reported.[8] More recently, Sen[9] and Klumperman[10] reported that copolymerization of methyl acrylate with 1-alkenes, such as 1-hexene or 1-octene, could be[11] conducted using Cu-based atom transfer radical polymerization (ATRP).[12−17] These results showed that ATRP provides better control when compared with conventional free radical polymerization. However, one of the disadvantages of ATRP is that it requires a transition metal complex at the concentration range from 0.1 to 1 mol % with respect to the monomer, and this catalyst needs to be removed from final polymer.[18] In addition, when using 1-alkenes as one of the comonomers, the Cu catalyst had limited solubility in the reaction medium because of the low polarity of the1-alkene, which reduces the level of control over the polymerization.

In this paper, we report well-controlled copolymerization of *n*-butyl acrylate with 1-octene using ATRP conducted with very low concentration of Cu catalyst, based on activators regenerated by electron transfer (ARGET).[19,20] Low concentrations of Cu catalyst, ranging from 5 to 10 ppm, allowed the preparation of copolymers of *n*-butyl acrylate and 1-octene with higher yield and lower polydispersity than standard ATRP, making this approach more attractive commercially.

Experimental Section

Materials. *n*-Butyl acrylate (*n*BA) (99%, Aldrich) and 1-octene (Oct) (98%, Aldrich) were purified by passing through a column filled with neutral alumina to remove the stabilizer and stored over molecular sieves at −15 °C. Tris[(2-pyridyl)methyl]amine (TPMA) was synthesized following a previously reported procedure.[21−23] Ethyl 2-bromoisobutyrate (EtBriB) (Acros, 98%), methyl 2-bromopropionate (MBP) (Aldrich, 98%), copper(II) chloride (Acros, 99%), copper(I) chloride (Acros, 99%), copper(0) powder (Aldrich, <75 μm, 99%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$) (Aldrich), and anisole (Aldrich, 99%) were used as received.

Copolymerization of *n*BA and 1-Octene by Normal ATRP (Targeted Number-Average Degree of Polymerization (DP_n) of 200). CuCl (14 mg, 14×10^{-2} mmol), $CuCl_2$ (1.9 mg, 1.4×10^{-2} mmol), and TPMA (41 mg, 14×10^{-2} mmol) were added to a Schlenk flask, and the flask was dried under vacuum and backfilled with nitrogen. Degassed *n*BA (2.0 mL, 14 mmol), 1-octene (2.2 mL, 14 mmol), and anisole (1.1 mL) were added via a degassed syringe, and the mixture was stirred for 10 min in order to preform the CuCl/TPMA and $CuCl_2$/TPMA complexes. Then EtBriB (20.5 μL, 14.0×10^{-2} mmol) was added to initiate the polymerization. An initial sample was taken, and the sealed flask was placed in a thermostated oil bath at 80 °C. Samples were taken at timed intervals and analyzed by gas chromatography (GC) and gel-permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

Copolymerization of *n*BA and 1-Octene by ARGET ATRP (Targeted Number-Average Degree of Polymerization (DP_n) of

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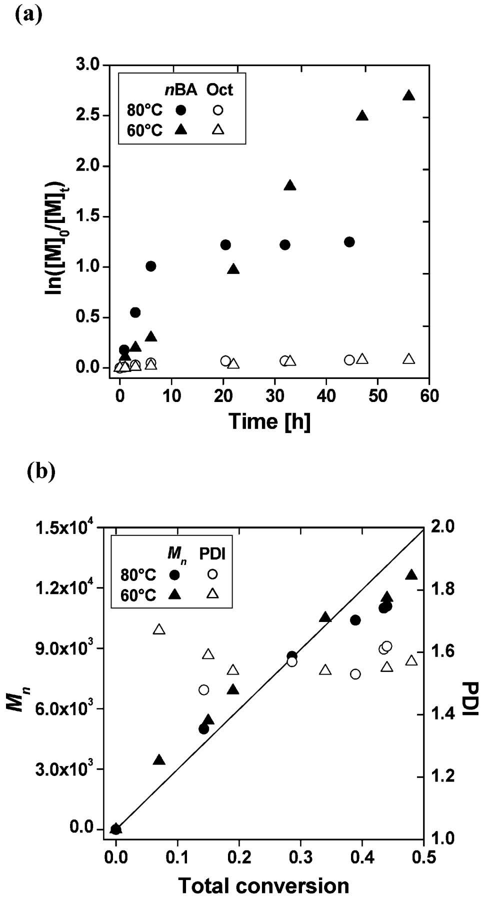

Figure 1. Kinetic plots (a) and evolution of molecular weights and polydispersities with conversion (b) for normal ATRP of *n*BA and 1-octene at 60 and 80 °C. Experimental conditions: [*n*BA]/[Oct]/[EtBriB]/[$CuCl_2$]/[CuCl]/[TPMA] = 100/100/1/1/0.1/1, in anisole.

200) with 10 ppm of Cu Catalyst. Degassed *n*BA (2.0 mL, 14.0 mmol), 1-octene (2.2 mL, 14.0 mmol), and anisole (0.6 mL) were transferred via degassed syringes to a dry, nitrogen-purged Schlenk flask, and a solution of Cu complex ($CuCl_2$ 0.19 mg, 0.14×10^{-2} mmol; TPMA 1.22 mg, 0.4×10^{-2} mmol) in degassed anisole (0.2 mL) was added. The resulting mixture was stirred for 10 min, and then a purged solution of $Sn(EH)_2$ (4.52 μL, 1.4×10^{-2} mmol) in anisole (0.3 mL) was added. Then EtBriB (20.5 μL, 14.0×10^{-2} mmol) initiator was added to initiate the polymerization. An initial sample was taken, and the sealed flask was placed in thermostated oil bath at 80 °C. Samples were taken at tied intervals and analyzed by gas chromatography (GC) and gel-permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

Copolymerization of *n*BA and 1-Octene with Cu(0) Catalyst (Targeted Number-Average Degree of Polymerization (DP_n) of 200). *n*BA (2.0 mL, 14.0 mmol), 1-octene (2.2 mL, 14.0 mmol), Cu(0) powder (8.87 mg, 14.0×10^{-2} mmol), TPMA (40.5 mg, 14.0×10^{-2} mmol), and anisole (2.1 mL) were added to a Schlenk flask. The reaction mixture was then frozen in liquid nitrogen and deoxygenated with three consecutive standard freeze−pump−thaw cycles, and then the flask was filled with nitrogen. An initial sample was taken, and the sealed flask was placed in a thermostated oil bath at 25 °C. Then MBP (18.2 μL, 14.0×10^{-2} mmol) initiator was added to initiate the polymerization. Samples were taken at tied intervals and analyzed by gas chromatography (GC) and gel-permeation chromatography (GPC) to follow the progress of the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air.

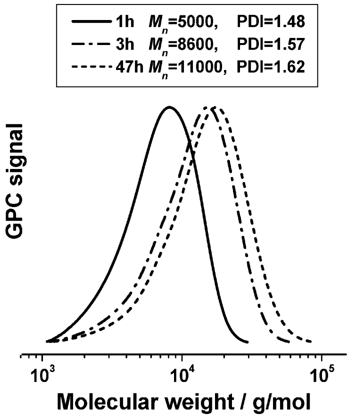

Figure 2. Evolution of GPC traces for normal ATRP of *n*BA and 1-octene at 80 °C.

Analysis. Molecular weight and polydispersity were determined by GPC, conducted using a Waters 515 pump and a Waters 2414 differential refractometer using PSS columns (Styrogel 10^5, 10^3, and 10^2 Å) with THF as an eluent at 35 °C and at a flow rate of 1 mL/min. Linear polystyrene standards were used for calibration. Conversion of *n*BA and 1-octene was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column and anisole as an internal standard. Injector and detector temperatures were kept constant at 250 °C. Analysis was carried out isothermally at 40 °C for 2 min followed by an increase of temperature to 140 °C at a heating rate of 20 °C/min and holding at 140 °C for 2 min. Conversion was calculated by detecting the decrease of the monomer peak area relative to the peak areas of the standards.

Results and Discussion

Copolymerization of *n*BA and 1-Octene Using Normal ATRP. The mechanism of ATRP is based on establishing a rapid dynamic equilibration between growing radicals and dormant species. This system allows for the synthesis of (co)polymers with control over the molecular weight and a narrow molecular weight distribution.[24−29]

Copolymerization of *n*BA and 1-octene by ATRP was conducted with ethyl 2-bromoisobutyrate (EtBriB) as an initiator and Cu/TPMA as the catalyst in anisole at 60 and 80 °C. Experimental conditions and results of copolymerization by ATRP are shown in Table 1. As shown in Figures 1 and 2, polydispersities were high even at 60 °C, and a low molecular weight tailing of the peak in GPC traces was observed. This was due to irreversible formation of a 1-octene dormant species by reaction of 1-octene radicals with $CuCl_2$/TPMA deactivator.[10] Once the 1-octene dormant species are produced, the alkyl−halogen bond of this dormant species cannot be cleaved by the CuCl/TPMA activator. Therefore, as a result of this accumulation of dead polymer, which increased with conversion, poly-

Table 1. Conditions and Results for Copolymerization of *n*BA and 1-Octene by ATRP

			conversion [%]						
entry[a]	temp [°C]	*t* [h]	*n*BA	Oct	total	1-octene incorporation [mol %]	$M_{n,theo}$ [g/mol]	$M_{n,GPC}$ [g/mol]	M_w/M_n
1	60	47	96.0	18.6	47.7	16.2	14 600	12 600	1.57
2	80	47	84.5	18.6	44.0	18.0	13 100	11 000	1.62

[a] Molar ratio of reactants: [*n*BA]/[Oct]/[EtBriB]/[CuCl]/[$CuCl_2$]/[TPMA] = 100/100/1/1/0.1/1, in anisole (20% v/v vs monomer).

Table 2. Conditions and Results for Copolymerization of *n*BA and 1-Octene by ARGET ATRP; Effect of the Amount of Copper

				conversion [%]						
entry[a]	Cu[c] [ppm]	temp [°C]	*t* [h]	*n*BA	Oct	total	1-octene incorporation [mol %]	$M_{n,theo}$ [g/mol]	$M_{n,GPC}$ [g/mol]	M_w/M_n
1	0.5	80	45	88.4	29.0	53.2	24.7	14 800	12 900	1.65
2	1	80	46	86.0	21.2	52.5	19.8	13 600	9 400	1.56
3	5	80	44	87.2	18.6	46.1	17.6	10 500	13 500	1.46
4	10	60	21	23.6	2.9	11.8	10.9	3 500	3 700	1.52
5	10	80	45	88.2	16.4	51.3	15.7	13 300	10 100	1.39
6	10	100	46	95.6	23.5	54.4	19.7	15 100	9 600	1.69
7	50	80	40	63.2	11.7	32.6	15.6	6 000	8 300	1.56
8[b]	500	80	33	39.5	8.8	21.7	18.2	6 100	5 900	1.52

[a] Molar ratio of reactant: [*n*BA]/[Oct]/[EtBriB]/[TPMA]/[$Sn(EH)_2$] = 100/100/1/0.03/0.1, in anisole (20% v/v vs monomer). [b] 0.05 equiv of TPMA was used instead of 0.03 equiv. [c] Molar ratio vs monomer.

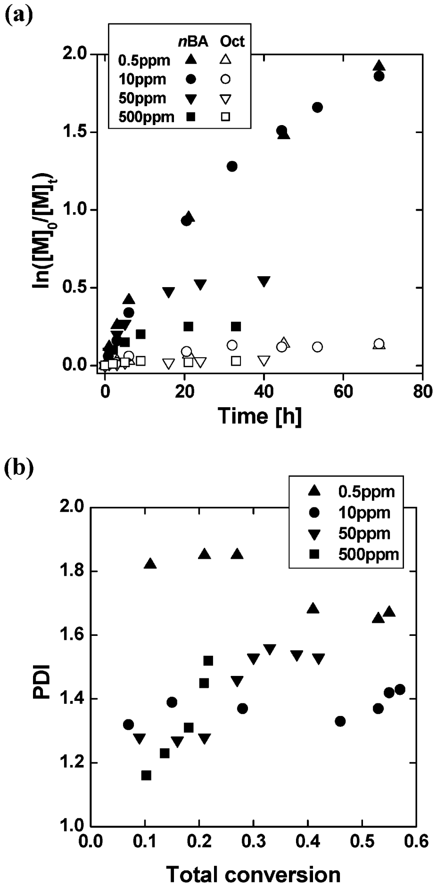

Figure 3. Kinetic plots (a) and evolution of molecular weights and polydispersities with conversion (b) for ARGET ATRP of *n*BA and 1-octene with 0.5, 10, 50, and 500 ppm of copper. Experimental conditions: [*n*BA]/[Oct]/[EtBriB]/[TPMA]/[$Sn(EH)_2$] = 100/100/1/0.03/0.1, T = 80 °C, in anisole.

dispersity also increased. However, in the case of ATRP copolymerization of polar and nonpolar monomers, a copolymer including nonpolar monomer units was obtained. Some 1-octene was incorporated into the polymer main chain by cross-propagation because the rate of cross-propagation was faster than the rate of termination by Cu(II) deactivator.[30] The 1-octene incorporation into copolymer was 16.2 mol % at 60 °C and 18.0 mol % at 80 °C.

In addition, the Cu catalyst did not dissolve completely in the reaction medium because of low polarity of 1-octene. The copolymer obtained was colored due to residual copper.

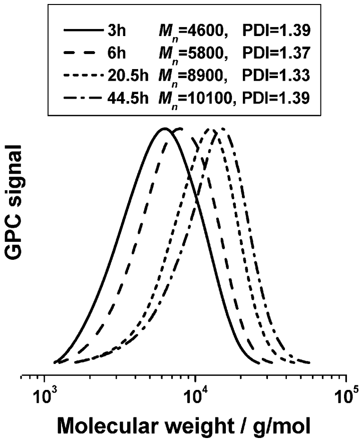

Figure 4. Evolution of GPC traces for ARGET ATRP of *n*BA and 1-octene with 10 ppm of copper.

Copolymerization of *n*BA and 1-Octene by ARGET ATRP. The recently developed ARGET ATRP process allows ATRP to be conducted with significantly lower concentrations of catalyst in the system. Parts per million of the Cu catalyst is used in conjunction with a reducing agent such as tin(II) ethylhexanoate, $Sn(EH)_2$,[31,32] or ascorbic acid,[33,34] which continuously reduces Cu(II) to Cu(I) in situ while preserving an appropriate ratio of Cu(I) to Cu(II). Thus, a low concentration of Cu(II) deactivator remains in the reaction medium.

Experimental conditions and results of copolymerization by ARGET ATRP are shown in Table 2. We deliberately targeted relatively low molecular weight polymers (below 20K) in order to suppress potential transfer to α-olefins.[35] ARGET ATRP of *n*BA and 1-octene was first conducted with 10 ppm of $CuCl_2$/TPMA catalyst in the presence of $Sn(EH)_2$ in anisole at 80 °C (Figure 3 and Table 2, entry 5). The polymerization proceeded to high conversion, and polydispersities remained low. A slight curvature of kinetic plots indicates that the number of growing radicals decreased. Nevertheless, copolymerization with tiny amounts of Cu catalyst using ARGET ATRP was better controlled than that for normal ATRP. This demonstrates that low concentration of Cu(II) deactivator suppressed production of the stable 1-alkene dormant species compared to normal ATRP. The rate of deactivation is a product of deactivation rate constant and concentration of Cu(II) species. Because the concentration of Cu(II) species is lower in ARGET ATRP, the overall number of dead chains is also lower. This allows propagation to proceed to higher conversion and form polymer with higher MW and narrow PDI. In the end of the polymerization, polydispersities increased quickly because termination increased due to higher concentrations 1-octene in the reaction medium. The 1-octene incorporation in the obtained copolymer using ARGET ATRP was comparable to normal ATRP. Furthermore, this system alleviates the problem of catalytic dissolution, and the obtained copolymer was essentially colorless.

Table 3. Conditions and Results for Copolymerization of *n*BA and 1-Octene by ARGET ATRP; Influence of Monomer Feed Ratio

			conversion [%]						
entry[a]	*n*BA/Oct feed ratios	*t* [h]	*n*BA	Oct	total	1-octene incorporation [mol %]	$M_{n,theo}$ [g/mol]	$M_{n,GPC}$ [g/mol]	M_w/M_n
1	140/60	52	95.7	20.2	69.1	17.4	18 700	15 400	1.41
2	100/100	54	90.0	22.2	55.1	19.8	14 200	9 800	1.42
3	60/140	32	46.7	2.8	12.9	5.7	6 300	3 900	1.38

[a] Molar ratio of reactant: [EtBriB]/[CuCl$_2$]/[TPMA]/[Sn(EH)$_2$] = 1/0.002/0.03/0.1, T = 80 °C, in anisole (20% v/v vs monomer).

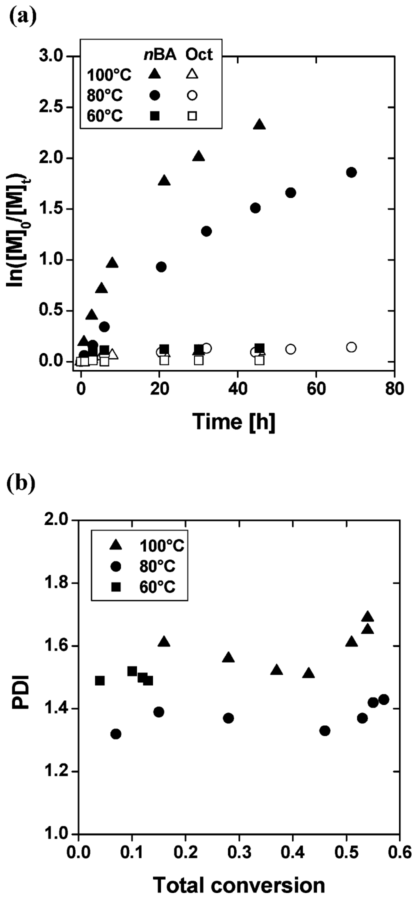

Figure 5. Kinetic plots (a) and evolution of polydispersities with conversion (b) for ARGET ATRP of *n*BA and 1-octene with 10 ppm of copper. Experimental conditions: [*n*BA]/[Oct]/[EtBriB]/[CuCl$_2$]/[TPMA]/[Sn(EH)$_2$] = 100/100/1/0.002/0.03/0.1, T = 80 °C, in anisole.

Effect of the Amount of Cu Catalyst on AREGET ATRP of *n*BA and 1-Octene. To examine the effect of the amount of Cu catalyst, the copolymerization of *n*BA and 1-octene was conducted with varying amounts of Cu catalyst at 80 °C. The amount of reducing agent, Sn(EH)$_2$, was kept constant at 10 mol % vs initiator. The experimental conditions and results are shown in Table 2 and Figure 3. When the Cu catalyst was used at a level of 0.5 and 1 ppm vs monomer, the polymerization proceeded to high monomer conversion, but polydispersities were much higher, which would indicate that there was not enough Cu catalyst to completely control the exchange between active and dormant species (Table 2, entries 1 and 2). However, as shown in Figure 3b, when 50 and 500 ppm vs monomer of the Cu catalyst were used, polydispersities increased dramatically and conversion was lower. Polymerization stopped at around 60% and 40% *n*BA conversion, respectively, which indicates that higher levels of the inactive dormant species, derived from 1-octene, were formed when larger amounts of Cu catalyst were present (Table 2, entries 7 and 8). This demonstrates that higher concentrations of Cu(II) deactivator enhanced the rate of termination, in comparison with the rate of propagation. Thus, more copolymer chain ends were converted to the inactive alkyl−halogen bond during the earlier stage of copolymerization, and polymerization stopped at lower conversion. Another way to look at the data is that more monomer units were added to the growing chain during each activation cycle at low catalyst concentrations, 0.5 and 1 ppm, which would be expected to lead to broader MWD if the dormant chains ends were equally active. This was observed, and better results were obtained with 10 ppm amount of Cu catalyst.

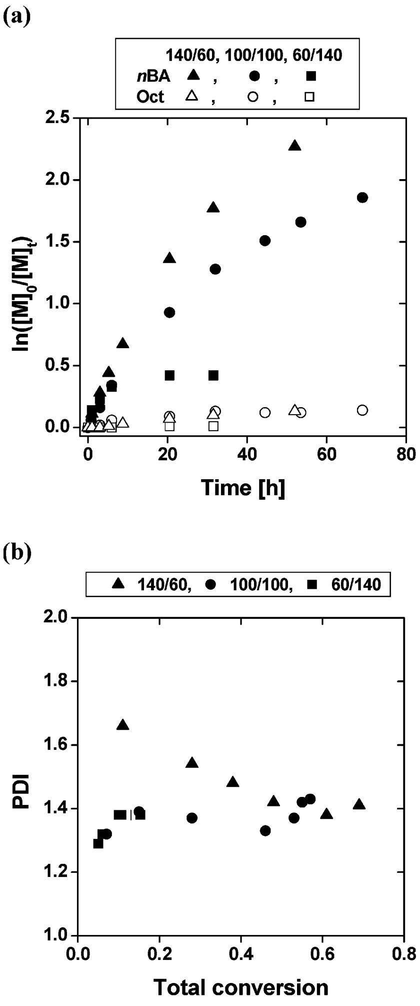

Figure 6. Kinetic plots (a) and evolution of polydispersities with conversion (b) for ARGET ATRP of *n*BA and 1-octene with 10 ppm of copper in 140/60, 100/100, and 60/140 ratios of *n*BA and 1-octene. Experimental conditions: [EtBriB]/[CuCl$_2$]/[TPMA]/[Sn(EH)$_2$] = 1/0.002/0.03/0.1, T = 80 °C, in anisole.

Effect of Temperature on AREGET ATRP of *n*BA and 1-Octene. ARGET ATRP of *n*BA and 1-octene was conducted with 10 ppm of Cu catalyst at different temperatures. A higher polymerization temperature enhanced the rate of polymerization, but polydispersities were also higher, again more units added during each activation−deactivation cycle. On the other hand,

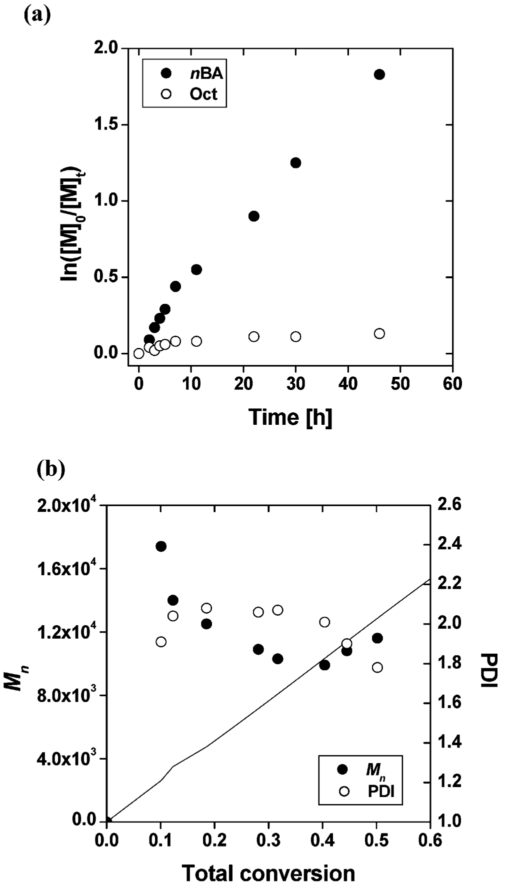

Figure 7. Kinetic plots (a) and evolution of molecular weights and polydispersities with conversion (b) for copolymerization of *n*BA and 1-octene with Cu(0). Experimental conditions: [*n*BA]/[Oct]/[MBP]/[Cu(0)]/[TPMA] = 100/100/1/1/1, *T* = 25 °C, in anisole.

at 60 °C the polymerization stopped after ~30% *n*BA conversion, which also indicates that formation of the inactive dormant species was enhanced by reducing k_{atrp}. At lower temperature, the rate of reaction and cross-propagation decreased significantly, which caused a higher probability of termination of the olefinic chain end. In normal ATRP, the polymerization proceeded to higher monomer conversion even at 60 °C. ARGET ATRP of polar and nonpolar monomer is more sensitive to temperature and requires the appropriate rate of polymerization.

Influence of Monomer Ratio on AREGET ATRP of *n*BA and 1-Octene. To evaluate the influence of monomer feed ratio on the copolymerization of *n*BA and 1-octene, ARGET ATRP was conducted with 10 ppm amounts of Cu catalyst at 80 °C. Experimental conditions and results are shown in Table 3 and Figure 6. When a 140/60 ratio of *n*BA to 1-octene was used, the rate of polymerization was faster and polymerization proceeded to higher conversion. Polydispersity was initially high because of the increased rate of polymerization and the lower influence of 1-octene, but polydispersity gradually decreased with conversion and a well-defined copolymer incorporating 17.4 mol % 1-octene was obtained. These results were not significantly different from those of copolymerization with 100/100 ratios of *n*BA and 1-octene by ARGET ATRP although PDI of polymer samples was lower throughout the early stages of the reaction. On the other hand, polymerization stopped at low monomer conversion with higher concentration of 1-octene in the copolymer (19.8%). These results indicate that formation of inactive dormant species was enhanced by higher 1-octene concentration because the probability of irreversible termination depends on 1-octene concentration. This is further borne out when a 60/140 ratio of reagents was employed since the polymerization stopped at 46.7% overall conversion. Thus, copolymerization of polar and nonpolar monomer by ARGET ATRP was influenced significantly by nonpolar monomer concentration.

Copolymerization of *n*BA and 1-Octene with Cu(0) Catalyst. Percec et al. have shown that well-controlled living radical polymerization (LRP) of methyl acrylate could be carried out by using a reactive Cu(0) catalyst through a mechanism described as an outer-sphere single-electron-transfer mechanism (SET-LRP).[36] However, earlier work of use of Cu(0)-activated ATRP[37,38] combined with the development of ARGET[20,39] indicates that the "classic" ATRP mechanism may operate.

Copolymerization of *n*BA and 1-octene was carried out with Cu(0) catalyst at 25 °C; methyl 2-bromopropionate was used as initiator and TPMA as a ligand. Anisole was selected as the solvent instead of DMSO because 1-octene does not dissolve in DMSO. The rate of polymerization was higher than that of ARGET ATRP with 10 ppm amounts of Cu catalyst at 80 °C, and the monomer conversion of *n*BA and 1-octene reached 89.9% and 21.7%, respectively, after 46 h. The rate of 1-octene incorporation was nearly same as that with ARGET ATRP (SET-LRP, 19.4 mol %; ARGET ATRP, 19.8 mol %). However, polydispersity was high (PDI = 1.78). Thus, this system could not give well-defined copolymer with control over the molecular weight and a narrow polydispersity.

Conclusions

A well-controlled linear copolymer of *n*BA and 1-octene with low polydispersity was obtained using an ARGET ATRP. ATRP with higher concentration of catalyst has some limitations for the synthesis of a well-controlled copolymer of polar and nonpolar monomers due to the irreversible generation nonpolar dormant species. Furthermore, in a normal ATRP, the Cu catalyst did not completely dissolve in the reaction medium, and the resulting copolymer was colored. In an ARGET ATRP, the copolymerization, with ppm amounts of Cu catalyst, was better controlled than that in normal ATRP. This indicates that lower concentration of Cu(II) deactivator reduces the occurrence of the irreversible generation of 1-alkene dormant species, as compared to normal ATRP. ARGET ATRP resulted in the preparation of better controlled copolymer with lower polydispersity at higher conversion and can avoid the problem of Cu catalyst removal.

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