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Copolymerization of (Meth)acrylates with Olefins Using Activators Regenerated by Electron Transfer for Atom Transfer Radical Polymerization (ARGET ATRP)

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Summary: Controlled copolymerization of polar (meth)acrylates with non-polar olefin monomers (1-octene, norbornene, vinylcyclohexane) was studied by ARGET (activators regenerated by electron transfer) ATRP (atom transfer radical polymerization). When a normal ATRP of *n*-butyl acrylate (*n*BA) and 1-octene was conducted, the polymerization resulted in relatively low conversion, 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 was obtained ($PDI < 1.4$), because the low concentration of Cu(II) deactivator reduced the formation of the non-reactive dormant species. The influence of the amount of Cu catalyst, ligand structure, initiators with different halogens, the reaction temperature, and monomer feed ratio were also investigated for ARGET ATRP. In copolymerization of (meth)acrylates with non-polar alkenes, the level of control and the total conversion in ARGET ATRP were higher than those for normal ATRP.

Keywords: activators regenerated by electron transfer (ARGET); atom transfer radical polymerization (ATRP); copolymerisation; non-polar monomer; olefins

Introduction

Copolymers of polar vinyl monomers and non-polar 1-alkene monomers have been the subject of research for a long time because the properties of the copolymer can be controlled by combining two kinds of monomers with very different properties making them attractive materials for a number of applications. Recent studies have shown that late-transition-metal complexes such as a Pd(II) cationic diimine compound exhibit some promise as polar/non-polar copolymerization catalysts.[1–3] However, the copolymers exhibited a highly branched structure and the molecular weight distribution (M_w/M_n) was broad. More recently, atom transfer radical polymerization (ATRP)[4–9] has been successful in preparing polar/non-polar linear copolymers with relatively low polydispersity. It was reported that copolymerization of methyl acrylate, methyl methacrylate with non-polar 1-alkene, such as propene, 1-octene, or ethene could be conducted by ATRP under mild condition.[10–15] This ATRP process provided the random polar/non-polar copolymers with relatively narrow M_w/M_n, as compared to the conventional free radical polymerization. However, in the presence of higher mole % of 1-alkene in the monomer feed the control and yield of copolymers were reduced. Moreover, a transition metal complex was used at relatively high concentrations (from 0.1 to 1 mol% with respect to the monomer) and this catalyst had to be removed from final polymer.

In this report, we present well-controlled copolymerization using ATRP conducted

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with very low concentration of Cu catalyst (ppm amounts), based on activators regenerated by electron transfer (ARGET).[16–21] Low concentrations of Cu catalyst allowed the preparation of polar/non-polar copolymers with higher yield and lower polydispersity than standard ATRP making this approach more attractive commercially.

Experimental Part

Materials

n-Butyl acrylate (*n*BA), methyl methacrylate (MMA), 1-octene (Oct), vinylcyclohexane (VCH) were purified by passing through a column filled with neutral alumina. Tris[(2-pyridyl)methyl]amine (TPMA),[22,23] Tris(2-(dimethylamino)ethyl)amine (Me_6TREN),[24] methyl 2-iodopropionate (MIP)[25] were synthesized following a previously reported procedure. Norbornene (NB), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), ethyl 2-bromoisobutyrate (EBiB), methyl 2-chloropropionate (MCP), methyl 2-bromopropionate (MBP), copper(II) chloride, copper(I) chloride, copper(II) bromide, tin(II) 2-ethylhexanoate ($Sn(EH)_2$), and anisole were used as received.

Typical Procedure for Normal ATRP and ARGET ATRP of *n*BA and 1-octene and Analysis

Normal ATRP and ARGET ATRP of polar with non-polar 1-alkene monomer were carried out following a previously reported procedure.[26]

Molecular weights and polydispersities were determined by GPC using PSS columns (Styrogel 10^5, 10^3, 10^2 Å) with THF as an eluent. Polystyrene standards were used for calibration of *n*BA copolymer, and PMMA were used for calibration of MMA copolymer. Conversion was obtained by Shimazu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column.

Results and Discussion

Copolymerization of Polar and Non-Polar Monomers using Normal ATRP

Copolymerization of *n*BA and 1-octene monomers using ATRP was first conducted with EBiB as an initiator and CuCl/TPMA as the catalyst (Table 1). The feed ratio of *n*BA and 1-octene was 100/100 (molar) with respect to the initiator, and relatively low molecular weight copolymers ($M_n < 20{,}000$) were deliberately targeted in order to suppress potential transfer to α-olefins. The kinetic plots present that the rate of polymerization at 60 °C was lower than that at 80 °C, but polydispersities were relatively high (Figure 1). This was due to the irreversible formation of 1-octene dormant species by the abstraction of the chlorine atom from $CuCl_2$/TPMA deactivator by chain end radicals derived from 1-octene. Once the 1-octene dormant species are produced, the alkyl-halogen bond in this dormant species is too strong and cannot be cleaved by the CuCl/TPMA activator. Therefore, as a result of the accumulation of dead polymer, which increased with conversion, polydispersity also increased. A low molecular weight tailing of the peak in GPC traces also indicates that the amount of dead polymer increased from the earlier

Table 1.
Conditions and results for copolymerization of *n*BA and 1-octene by ATRP.

Entry	Temp	t	Conversion [%]	Oct	$M_{n,theo}$	$M_{n,GPC}$	M_w/M_n
	[°C]	[h]	*n*BA/Oct/Total	[mol%]	[g/mol]	[g/mol]	
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

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

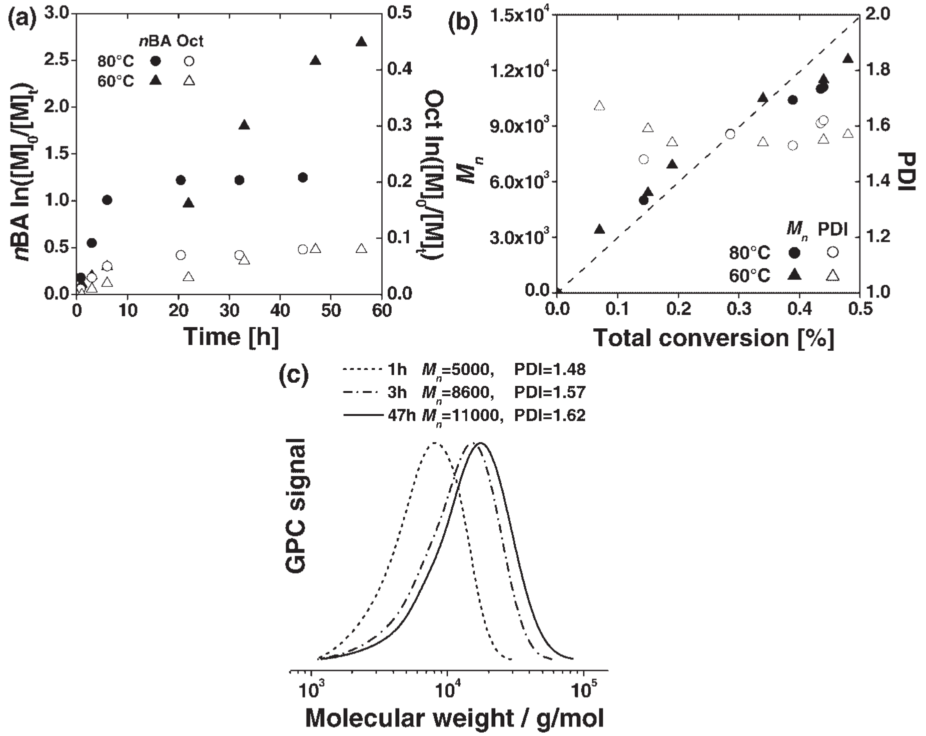

Figure 1.
Kinetic plots (a), evolution of molecular weights and polydispersities with conversion (b), and evolution of GPC traces (c) for normal ATRP of *n*BA and 1-octene. Experimental conditions: [*n*BA]/[Oct]/[EBiB]/[CuCl]/[$CuCl_2$]/[TPMA] = 100/100/1/1/0.1/1, in anisole (20 vol% vs. monomer). The dashed line in 1b presents the theoretical molecular weight.

stage of copolymerization (Figure 1c). In this system, 1-octene was incorporated into the polymer main chain by cross-propagation reaction. The 1-octene derived chain end radical can react with *n*BA before irreversible formation of dormant species, if the rate of crosspropagation is faster than the rate of its deactivation by Cu(II) species.[27] Under typical ATRP conditions, copolymers with high polydispersity were obtained and 1-octene incorporation was below 18 mol%, because concentration of Cu-based catalyst was high. The copolymers obtained were colored due to high concentration of the residual copper.

Copolymerization of Polar and Non-Polar Monomers Using 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) 2-ethylhexanoate, $Sn(EH)_2$,[28] or ascorbic acid,[29] 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 is maintained in the reaction medium.

Effect of the Amount of Cu Catalyst

ARGET ATRP of *n*BA and 1-octene was conducted with $CuCl_2$/TPMA catalyst in the presence of $Sn(EH)_2$ (Table 2). To examine the effect of the amount of Cu catalyst, various amounts of Cu catalyst vs. monomer were used in this system. Kinetic plots showed a slight curvature, which indicates the number of growing radicals decreased gradually during the polymerization (Figure 2). When the Cu catalyst was

Table 2.
Conditions and results for copolymerization of *n*BA and 1-octene by ARGET ATRP. Effect of the amount of copper and polymerization temperature.

Entry	Cu[b)]	Temp	t	Conversion [%]	Oct	$M_{n,theo}$	$M_{n,GPC}$	M_w/M_n
	[ppm]	[°C]	[h]	*n*BA/Oct/Total	[mol%]	[g/mol]	[g/mol]	
1	0.5	80	45	88.4/29.0/53.2	24.7	14,800	12,900	1.65
2	10	60	21	23.6/2.9/11.8	10.9	3,500	3,700	1.52
3	10	80	45	88.2/16.4/51.3	15.7	13,300	10,100	1.39
4	10	100	46	95.6/23.5/54.4	19.7	15,100	9,600	1.69
5	50	80	40	63.2/11.7/32.6	15.6	6,000	8,300	1.56
6[a)]	500	80	33	39.5/8.8/21.7	18.2	6,100	5,900	1.52

Molar ratio of reactants; [*n*BA]/[Oct]/[EBiB]/[TPMA]/[Sn(EH)$_2$] = 100/100/1/0.03/0.1, in anisole (20% v/v vs. monomer).

[a)] 0.05 equiv of TPMA was used instead of 0.03 equiv.

[b)] Molar ratio vs. monomer.

used at a level of 0.5 ppm vs. monomer, the rate of polymerization was fast and the polymerization proceeded to high monomer conversion, but polydispersities were much higher, which indicates that there was not enough Cu catalyst to sufficiently control the exchange between active and dormant species (Table 2, entry 1). When 50 and 500 ppm of the Cu catalyst vs. monomer was used, polydispersities increased dramatically and conversion was lower. Polymerization stopped at around 60% and

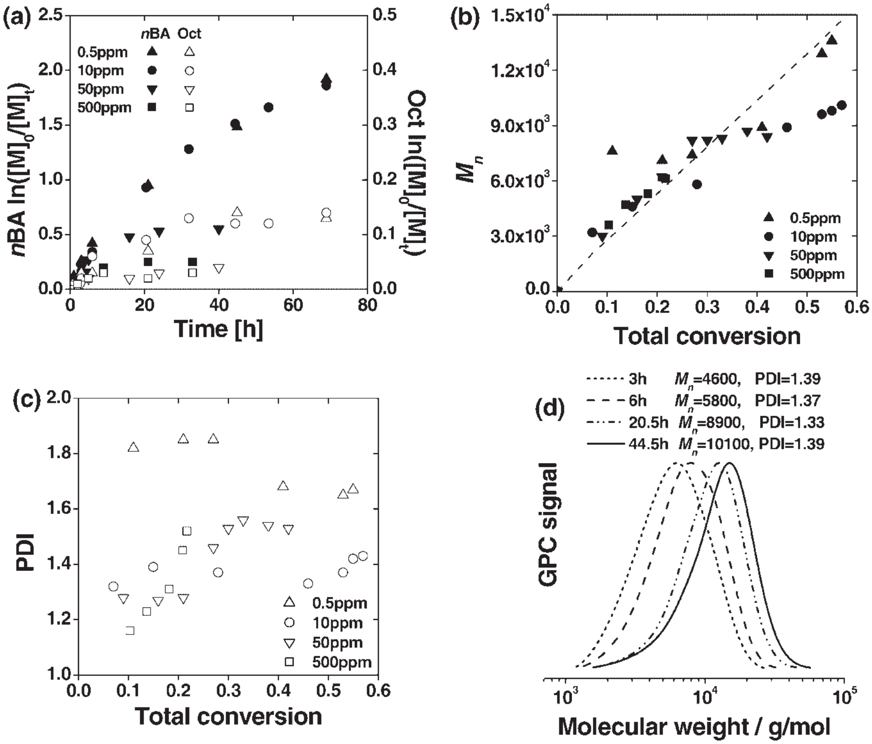

Figure 2.
Kinetic plots (a), and evolution of molecular weights (b), and polydispersities with conversion (c), and evolution of GPC traces for 10 ppm Cu (d) for ARGET ATRP of *n*BA and 1-octene with 0.5, 10, 50 and 500 ppm of copper. Experimental conditions: [*n*BA]/[Oct]/[EBiB]/[TPMA]/[Sn(EH)$_2$] = 100/100/1/0.03/0.1, T = 80 °C, in anisole (20% v/v vs. monomer). The dashed line in 2b presents the theoretical molecular weight.

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, entry 5 and 6). This demonstrates that in ARGET ATRP higher concentrations of Cu(II) deactivator enhanced the rate of irreversible deactivation, in comparison with the rate of (cross)propagation. Thus, more copolymer chain ends were converted to the inactive alkyl-halogen species during the earlier stage of copolymerization and polymerization stopped at lower conversion.

However, when 10 ppm vs. monomer of the Cu catalyst was used, the polymerization proceeded to higher monomer conversion and polydispersity remained low (Table 2, entry 3). This indicates that the reduced concentration of Cu(II) deactivator suppressed formation of the stable 1-alkene dormant species because the rate of deactivation is a product of deactivation rate constant and concentration of Cu(II) species. Since the concentration of Cu(II) deactivator is lower in ARGET ATRP, the overall number of dead chains is also lower. This allows propagation to proceed to higher conversion and form copolymer with higher molecular weight and lower polydispersity. The 1-octene incorporation in the obtained copolymer using ARGET ATRP was comparable to normal ATRP. Furthermore, this system alleviates the problem of catalysts handling (starting with air stable Cu(II)) and dissolution, and the obtained copolymer was essentially colorless.

Effect of Temperature

The influence of the temperature was tested for ARGET ATRP of *n*BA and 1-octene with 10 ppm Cu catalyst at different temperatures (Table 2, entry 2-4). A higher polymerization temperature enhanced the rate of polymerization, but polydispersities were also higher, since more units added during each activation-deactivation cycle (Figure 3). On the other hand, at 60 °C the polymerization stopped after ~30% *n*BA conversion, which indicates that formation of the inactive dormant species was enhanced by reducing the cross-propagation rate constant. At lower temperature, the rate of (cross)propagation decreased, which caused a higher probability of termination of the olefinic chain end. ARGET ATRP of polar and non-polar monomer is sensitive to polymerization temperature and requires the appropriate polymerization rate.

Effect of Halogen

In ATRP, alkyl halides (RX) are typically used as the initiators and halogen (X) plays

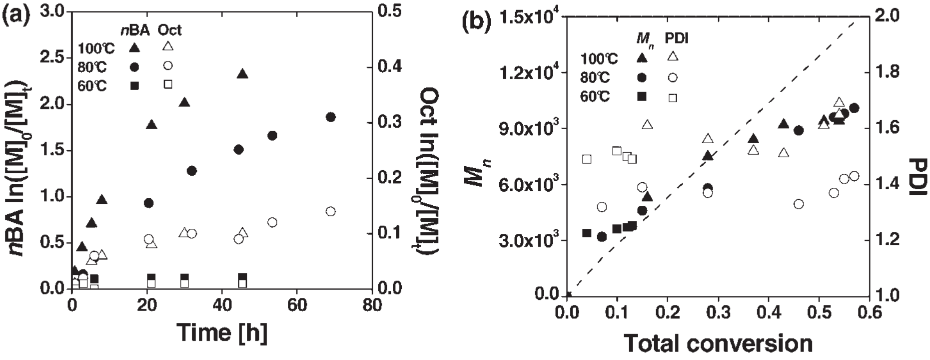

Figure 3.

Kinetic plots (a) and evolution of molecular weights and polydispersities with conversion (b) for ARGET ATRP of *n*BA and 1-octene. Experimental conditions: [*n*BA]/[Oct]/[EBiB]/[$CuCl_2$]/[TPMA]/[$Sn(EH)_2$] = 100/100/1/0.002/0.03/0.1, T = 60, 80 and 100 °C, in anisole (20% v/v vs. monomer). The dashed line in 3b presents the theoretical molecular weight.

Table 3.
Conditions and results for copolymerization of *n*BA and 1-octene by ARGET ATRP. Influence of initiator halides, ligand structure and monomer feed ratio.

Entry	Initiator/Ligand	t [h]	Conversion [%] *n*BA/Oct/Total	Oct [mol%]	$M_{n,\text{theo}}$ [g/mol]	$M_{n,\text{GPC}}$ [g/mol]	M_w/M_n
1	MCP/TPMA	69	87.7/20.7/49.5	19.1	13,700	10,500	1.73
2	MBP/TPMA	45	84.1/15.4/44.8	15.5	12,700	10,600	1.40
3	MIP/TPMA	21	20.5/6.8/12.7	25.0	3,600	4,000	1.64
4	EBiB/TPMA	69	92.0/24.3/57.2	20.9	14,700	10,100	1.43
5	EBiB/Me_6TREN	69	93.2/21.4/49.9	18.7	14,500	11,300	1.67
6	EBiB/PMDETA	11	83.8/17.6/44.2	17.4	12,600	11,900	2.16
7[b)]	EBiB/TPMA	52	95.7/20.2/69.1	17.4	18,700	15,400	1.41
8[b)]	EBiB/TPMA	32	46.7/2.8/12.9	5.7	6,300	3,900	1.38

Molar ratios: [Monomer]/[Initiator]/[$CuCl_2$]/[Ligand]/[$Sn(EH)_2$] = 200/1/0.002/0.03/0.1; T = 80 °C, in anisole (20% v/v vs. monomer);
[a)] $CuBr_2$ was used instead of $CuCl_2$;
[b)] nBA/Oct = 100/100, except entry 7: nBA/Oct = 140/60, and entry 8: 60/140.

an important role to migrate rapidly between growing radical and transition metal complex. To examine the effect of halogen structure, ARGET ATRP of *n*BA and 1-octene was conducted with methyl 2-chloropropionate (MCP), methyl 2-bromopropionate (MBP), and methyl 2-iodopropionate (MIP) initiators using 10 ppm $CuBr_2$/TPMA as the catalyst (Table 3, entry 1–3). As shown in Figure 4, the rate of MBP initiated reaction was faster than MCP initiated reaction, but copolymerization was well controlled and polydispersity was below 1.4. This indicates that CuBr/$CuBr_2$/TPMA catalyst system derived from alkyl bromide initiator is more efficient than CuCl/$CuCl_2$/TPMA catalyst, promoting both faster activation and deactivation reaction. In case of alkyl chloride initiator, initial molecular weight and polydispersities were very high because CuCl/$CuCl_2$/TPMA catalyst could not control the exchange between active and dormant species. When MIP initiator was used, the resulting alkyl iodides are less stable and light sensitive, and this could explain lower conversion and higher polydispersity. Thus, the structure of halogen significantly affected the copolymerization.

Effect of Ligand

The influence of ligand structure was tested for ARGET ATRP of *n*BA and 1-octene. For comparison, three ligands, TPMA,

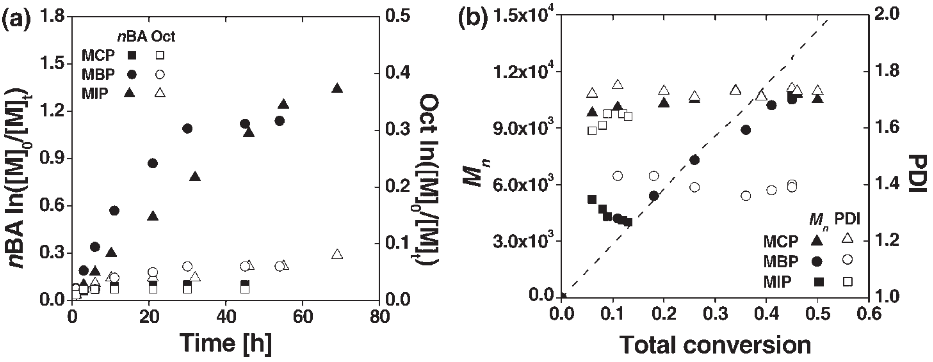

Figure 4.
Kinetic plots (a) and evolution of molecular weights and polydispersities with conversion (b) for ARGET ATRP of *n*BA and 1-octene with MCP, MBP and MIP initiators. Experimental conditions: [*n*BA]/[Oct]/[initiator]/[$CuBr_2$][TPMA]/[$Sn(EH)_2$] = 100/100/1/0.002/0.03/0.1, T = 80 °C, in anisole (20% v/v vs. monomer). The dashed line in 4b presents the theoretical molecular weight.

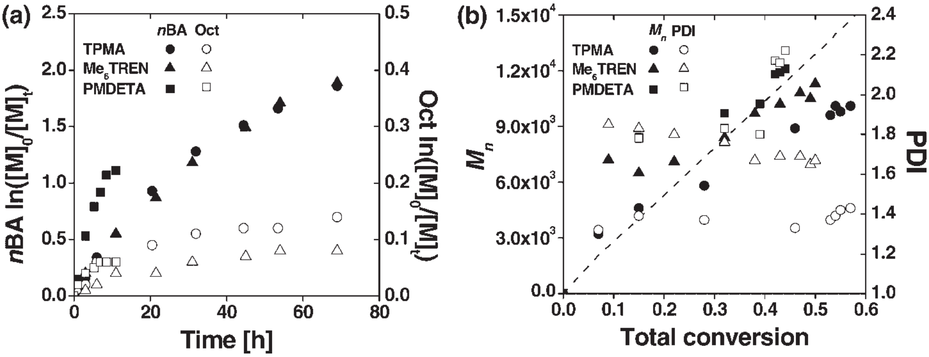

Figure 5.

Kinetic plots (a) and evolution of molecular weights and polydispersities with conversion (b) for ARGET ATRP of *n*BA and 1-octene with TPMA, Me$_6$TREN and PMDETA ligands. Experimental conditions: [*n*BA]/[Oct]/[EBiB]/[CuCl$_2$]/[Ligand]/[Sn(EH)$_2$] = 100/100/1/0.002/0.03/0.1, T = 80 °C, in anisole (20% v/v vs. monomer). The dashed line in 5b presents the theoretical molecular weight.

Tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN) and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) were used under the identical condition (Table 3, entry 4–6). As shown in Figure 5, the catalytic activity of PMDETA ligand was much larger, but the polymerization was not controlled (PDI = 2.2). This is due to lower activity and lower stability of Cu(I) and Cu(II)/PMDETA complexes at higher dilution and at higher temperatures.[30,31] On the other hand, Cu complexes with TPMA and Me$_6$TREN are more stable and more active. The ln([M]$_0$/[M]$_t$) versus time plots for TPMA and Me$_6$TREN were similar, but polymerization was better controlled for TPMA. In ARGET ATRP, CuCl and CuCl$_2$/TPMA complexes provided the best controlled polymerization process with a reasonable polymerization rate.

Influence of Comonomer Ratio

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 CuCl$_2$/TPMA catalyst (Table 3, entry 4, 8 and 9). 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 (Figure 6). Polydispersity was initially high because of the increased rate

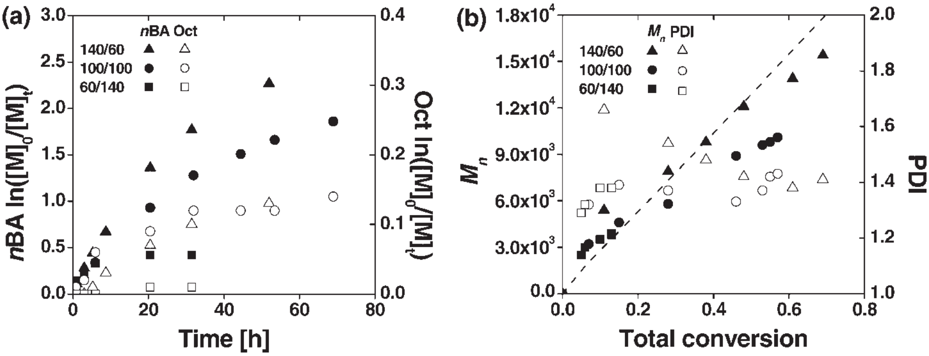

Figure 6.

Kinetic plots (a) and evolution of molecular weights and polydispersities with conversion (b) for ARGET ATRP in 140/60, 100/100, and 60/140 ratios of *n*BA and 1-octene. Experimental conditions: [EBiB]/[CuCl$_2$]/[TPMA]/[Sn(EH)$_2$] = 1/0.002/0.03/0.1, T = 80 °C, in anisole (20% v/v vs. monomer). The dashed line presents the theoretical molecular weight.

of polymerization but gradually decreased with conversion and a well defined copolymer containing 17.4 mol% 1-octene was obtained. On the other hand, polymerization stopped at 12.9% overall monomer conversion with higher concentration of 1-octene (60/140 ratio). These results indicate that formation of inactive dormant species was enhanced at higher 1-octene concentration because the probability of irreversible deactivation depends on 1-octene concentration. Thus, copolymerization of acrylate and non-polar olefin was significantly influenced by the non-polar monomer concentration.

Copolymerization of other Polar and Non-Polar Monomers Using Normal ATRP and ARGET ATRP

Normal ATRP and ARGET ATRP of other polar and olefin monomers were carried out under identical condition (Table 4). In normal ATRP of methyl methacrylate (MMA) and 1-octene, the polymerization stopped at low conversion after 6 h and control over molecular weight distribution was poor. This indicates that all polymer chain ends were converted to inactive 1-octene dormant species, while normal ATRP of *n*BA and 1-octene proceeded to relatively high monomer conversion with lower polydispersity. This is because the cross-propagation rate constant of nucleophilic 1-octene radical towards more electron rich *n*BA is higher than towards less electron rich MMA.. Slower reaction with MMA enhanced the irreversible deactivation by Cu(II) leading to 1-octene dormant species.

Similar experiments with norbornene and vinylcyclohexane as non-polar monomers in normal ATRP also stopped at low conversion and polydispersities were high, as compared to ARGET ATRP system.

In ARGET ATRP, the low concentration of Cu(II) deactivator reduced the rate of irreversible deactivation, and hence promoted the cross-propagation reaction even for less reactive MMA. Therefore, higher yields and better controlled copolymerization were obtained. The incorporation rate of non-polar monomer in ARGET ATRP using *n*BA as comonomer were around 20 mol%, and using MMA were around 10 mol%. As a result of higher yields, the incorporation of non-polar monomer was also higher than in normal ATRP. Thus, a variety of polar and

Table 4.
Conditions and results for copolymerization of some polar and non-polar monomers by normal ATRP and ARGET ATRP.

Entry[a)]	Monomer[b)]	t	Conversion [%]	M_2	$M_{n,\text{theo}}$	$M_{n,\text{GPC}}$	M_w/M_n
	M_1/M_2	[h]	M_1/M_2/Total	[mol%]	[g/mol]	[g/mol]	
1	*n*BA/Oct	47	84.5/18.6/44.0	14.6	13,100	10,500	1.61
2	*n*BA/NB	21	31.1/6.6/17.7	17.6	4,800	4,800	1.75
3	*n*BA/VCH	10	66.9/6.7/31.5	9.0	9,500	8,800	1.80
4[c)]	MMA/Oct	6	49.2/2.4/17.1	4.6	5,400	11,500	2.12
5[c)]	MMA/NB	6	25.9/0.9/9.4	3.3	2,900	9,400	2.87
6	*n*BA/Oct	69	92.0/24.3/57.2	20.9	14,700	10,100	1.43
7	*n*BA/NB	26	87.527.0/58.0	23.6	14,000	9,500	1.46
8[d)]	*n*BA/NB	71	81.1/20.2/50.6	19.9	27,100	28,500	1.42
9[e)]	*n*BA/NB	32	54.3/7.7/31.0	8.7	29,700	25,900	1.61
10	*n*BA/VCH	46	75.9/15.2/38.0	16.7	11,600	8,800	1.62
11[c)]	MMA/Oct	50	91.5/9.8/34.9	9.7	10,100	14,600	1.74
12[c)]	MMA/NB	50	95.4/11.5/37.4	10.8	10,500	14,000	2.09

[a)] Normal ATRP: entries 1–5; ARGET ATRP: entries 6-12. Molar ratio of reactants, Normal ATRP: [polar]/[non-polar]/[EBiB]/[CuCl]/[$CuCl_2$]/[TPMA] = 100/100/1/1/0.1/1; ARGET ATRP: [polar]/[non-polar]/[EBiB]/[$CuCl_2$]/[TPMA]/[$Sn(EH)_2$] = 100/100/1/0.002/0.03/0.1, T = 80 °C, in anisole (20% v/v vs. monomer);

[b)] M_1 = polar monomer, M_2 = non-polar monomer, NB = norbornene, VCH = vinylcyclohexane;

[c)] In anisole (100% v/v vs. monomer);

[d)] Entry 8, [*n*BA]/[NB] = 100/100, and P*n*BA macroinitiator with M_n = 14,800 g/mol and M_w/M_n = 1.13 was used;

[e)] Entry 9, [*n*BA]/[NB] = 150/100, and P*n*BA macroinitiator with M_n = 18,600 g/mol, M_w/M_n = 1.17 was used.

non-polar 1-alkene monomers could be copolymerized with better control over molecular weight and lower polydispersity by using ARGET ATRP rather than normal ATRP.

Block copolymerization was attempted using P*n*BA macroinitiators and [*n*BA]/[NB] = 100/100 comonomer ratio in entry 8 (Table 4) and [*n*BA]/[NB] = 150/100 in entry 9 (Table 4). In the former case molecular weight increased from $M_n =$ 14,800 g/mol to $M_n = 18{,}500$ g/mol and in the latter case from $M_n = 18{,}600$ g/mol to $M_n = 25{,}900$ g/mol. After incorporation of the second block with NB segments, polydispersity increased due to the irreversible deactivation (termination).

Conclusions

Normal ATRP and ARGET ATRP of polar with non-polar 1-alkene monomers were investigated. Normal ATRP carried out with higher catalyst concentration has some limitations in the synthesis of a well controlled copolymers. In ARGET ATRP with ppm amounts of Cu catalyst, higher yields of better controlled copolymers with lower polydispersity were obtained because low concentration of Cu(II) deactivator reduces the irreversible deactivation of 1-alkene chain end radicals. Temperature, monomer feed ratio, halogen in the initiator and ligand also significantly affect the ATRP process. ARGET ATRP was also successfully applied to the block copolymer synthesis. Small amount of the Cu catalyst may additionally simplify the residual catalyst removal in ARGET ATRP process.

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