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Polymerization of *n*-Butyl Acrylate by Atom Transfer Radical Polymerization. Remarkable Effect of Ethylene Carbonate and Other Solvents

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ABSTRACT: Atom transfer radical polymerization (ATRP) of *n*-butyl acrylate with the homogeneous catalyst, $Cu^{I}Br$/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy), in benzene, afforded well-defined poly(*n*-butyl acrylate) with predetermined molecular weights and low polydispersities, $M_w/M_n = 1.1$. The number-average molecular weight, M_n (measured by GPC and MALDI-TOFMS), was close to the theoretical molecular weight, predetermined by $DP_n = \Delta[M]/[I]_0$. A similar polymerization in benzene using 2,2′-bipyridine (bpy) as ligand instead of dNbpy displayed poor control, yielding a polymer whose molecular weight was higher than the theoretical value and demonstrating high polydispersity ($M_w/M_n = 2.4$). Several solvents were subsequently employed for the polymerizations with the $Cu^{I}Br$/bpy catalyst system. Good control of molecular weight and polydispersity were achieved using ethylene carbonate, and in this system the observed rate of polymerization was even faster than in bulk. The rate of polymerization with the $Cu^{I}Br$/bpy catalyst in ethylene carbonate was first order with respect to the catalyst concentration; a reduction in the concentration of the catalyst led to an increase in the polydispersity of the resulting polymer. Polydispersity decreased on addition of $Cu^{II}Br_2$ or by reducing the amount of ethylene carbonate used. The polymerization in ethylene carbonate with $CuPF_6$/bpy catalyst gave results similar to those observed for the $Cu^{I}Br$/bpy catalyst system. The rapid rate of polymerization in ethylene carbonate was attributed to a monomeric structure of the $Cu^{I}Br$/bpy catalyst, as found for $Cu^{I}PF_6$.

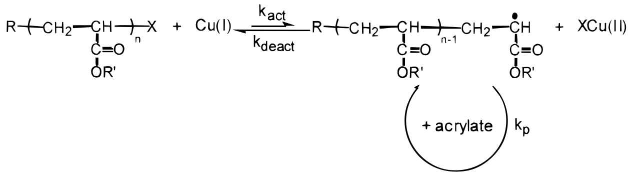
Introduction

Poly(*n*-butyl acrylate) is an industrially important polymer due to its low glass transition temperature (T_g) and durability. Because of these properties, poly(*n*-butyl acrylate) can be used as a soft segment in thermoplastic elastomers. The large demand for polyacrylates has prompted research toward improving processes for the polymerization of acrylates. Although acrylates can be polymerized anionically, the preparation of well-defined polymers is hindered by a number of side reactions.[1] Several methods have been developed to overcome this problem,[2,3] but most polyacrylates are still produced by free radical polymerization. However, in comparison to anionic and cationic polymerizations, free radical polymerizations have historically proved difficult to control.

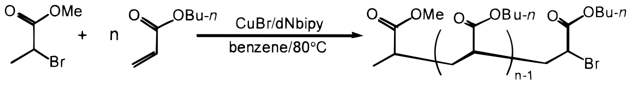
Recently, several approaches to controlled/“living” free radical polymerizations have been reported. Most of these methods have utilized a dynamic equilibrium between the growing radicals and dormant species. The equilibrium is shifted strongly toward the dormant species, so that the concentration of the active radicals is very low, thereby limiting radical−radical coupling reactions as the principal mode of termination. A fast dynamic equilibrium also allows each polymer chain to grow equally, resulting in low polydispersities. The methods described in the literature are thermal cleavage of dithiocarbamates,[4] alkoxyamines,[5−8] or organometallic species;[9] catalytic cleavage of alkyl halides by transition metal complexes;[10−21,25] and degenerative transfer with alkyl iodides[22] or a methacrylate group (addition-fragmentation).[23,24]

We and others have previously reported atom transfer radical polymerization (ATRP) catalyzed by copper halides complexed with 2,2′-bipyridine (bpy) and its derivatives.[11−15,18−20] ATRP is effective for the polymerization of various monomers, including styrenes,[11,13−15,18,19] acrylonitrile,[20] methacrylates,[12,25] and acrylates.[12,26] The key aspect of ATRP is the equilibrium established between radicals and alkyl halides, which is accompanied by the copper(I)/copper(II) redox process, as shown in Scheme 1.

Scheme 1



Scheme 2



Polymerization by ATRP provides well-defined polymers with low polydispersities ($1.05 < M_w/M_n < 1.5$); degrees of polymerization are determined by the ratio of concentrations of reacted monomer to initiator ($DP_n = \Delta[M]/[I]_0$). Previously, we have studied the ATRP of methyl acrylate with respect to the controllability,[12] kinetics,[26] and the effect of the anion.[27]

In this paper we describe the well-controlled polymerization of *n*-butyl acrylate using both homogeneous and heterogeneous ATRP catalyst systems (Scheme 2). We also report a remarkable solvent effect in the ATRP of *n*-butyl acrylate with bpy as the ligand when ethylene carbonate was used as the solvent.

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Experimental Section

Materials. *n*-Butyl acrylate (BA), methyl 2-bromopropionate, and benzene were distilled over CaH_2. THF was distilled over Na/benzophenone. Cu^IBr was purified by stirring in acetic acid, washing with methanol, and then drying. $Cu(CH_3CN)_4PF_6$ was prepared according to literature procedures and was recrystallized from CH_3CN.[28] 4,4′-Di(5-nonyl)-2,2′-bipyridine (dNbpy) was prepared by the coupling of 4-(5-nonyl)pyridine with a 5% Pd/C catalyst at 200 °C for 7 days. Purification was achieved by distillation of the product at 10^{-4} mmHg.[18] All other reagents were used as received.

Analysis. SEC measurements were carried out using a Waters 510 LC pump equipped with four Phenogel columns (100 Å, 1000 Å, linear, and guard) in series with a 410 differential refractometer and a Waters 991 UV detector. Calibration was based on narrow molecular weight polystyrene standards using Polymer Standards Service software. A 300 MHz Bruker spectrometer was used for ^1H NMR analysis. GC measurements were carried out using a Shimadzu GC-14A instrument equipped with a wide-bore capillary column (J&W Scientific, DB-WAX). MALDI-TOFMS data were collected using a PerSeptive Biosystems Voyager Elite MALDI-TOF mass spectrometer, equipped with a nitrogen laser (wavelength 337 nm) and using delayed extraction methods.

Atom Transfer Radical Polymerization of *n*-Butyl Acrylate with Cu^IBr/dNbpy Catalyst. The polymerization of *n*-butyl acrylate was carried out under argon, in a dried flask equipped with a magnetic stirring bar. The flask was charged with Cu^IBr (0.250 g; 1.74×10^{-3} mol) and dNbpy (1.42 g; 3.48×10^{-3} mol), sealed with a rubber septum, and then degassed to remove oxygen. Degassed benzene (10.0 mL), *n*-butyl acrylate (10.0 mL; 6.98×10^{-2} mol), and *n*-dodecane (0.4 mL; GC standard) were added using a syringe. Finally, methyl 2-bromopropionate (0.194 mL; 1.74×10^{-3} mol) was added, and the flask was immersed in an oil bath heated at 80 °C. Conversion was determined by GC measurements of aliquots removed from the reaction mixture at regular time intervals. After heating was stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was then passed over alumina to remove Cu complexes prior to removal of the solvent.

General Procedure for the ATRP of *n*-Butyl Acrylate with Cu^IBr/bpy Catalyst. Polymerization of *n*-butyl acrylate was carried out under argon, in a dried flask equipped with a magnetic stirring bar. Cu^IBr (0.250 g; 1.74×10^{-3} mol), bpy (0.816 g; 5.23×10^{-3} mol), and ethylene carbonate (10 g) were weighed into the flask, which was then sealed with a rubber septum. The flask contents were then cycled between vacuum and argon three times to remove oxygen. Degassed *n*-butyl acrylate (10.0 mL; 6.98×10^{-2} mol) was added using a syringe, followed by methyl 2-bromopropionate (0.194 mL; 1.74×10^{-3} mol). The flask was then immersed in an oil bath heated at 80 °C. Conversion was monitored by GC measurements of aliquots removed from the reaction mixture at regular time intervals. Each sample of reaction mixture was passed through a short alumina column and the solvent removed. Ligand-to-copper ratios of 1:2 and 1:3 were used for both homogeneous and heterogeneous systems, in agreement with earlier reported studies.[11,18] Reaction rates and the polymers obtained at both of these ratios were very similar.

MALDI-TOFMS Sample Preparation. All reagents were obtained from Aldrich and used as received. Polymer sample solutions (10^{-3} M) were prepared in THF. A 0.1 M solution of *trans*-3-indoleacrylic acid (IAA) matrix was prepared in THF and doped with sodium trifluoroacetate (0.1 M in THF) in a 10:1 ratio of matrix to salt. IAA and the polymer solution were mixed in a 1:1 volumetric ratio prior to spotting on a gold-plated sample slide. Data were collected in linear mode, using delayed extraction, with a delay time of 150 ns. All spectra were averaged over 128 laser shots.

Results and Discussion

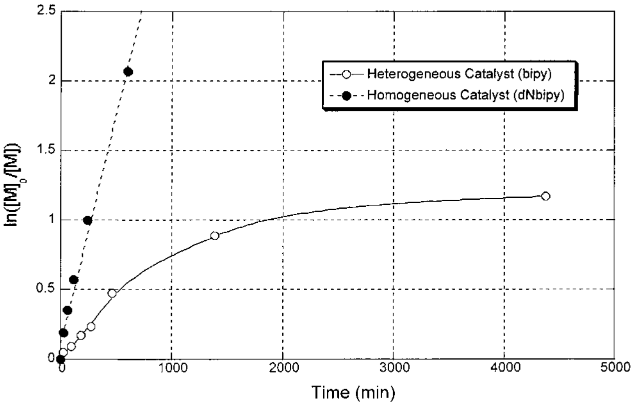

Figure 1. First-order kinetic plots for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate with a homogeneous catalyst (Cu^IBr/2dNbpy) and a heterogeneous catalyst (Cu^IBr/2bpy) in benzene at 80 °C. $[M]_0 = 3.2$ M, $[I]_0 = 0.079$ M, $[Cu^IBr] = 0.079$ M, [ligand] = 0.16 M.

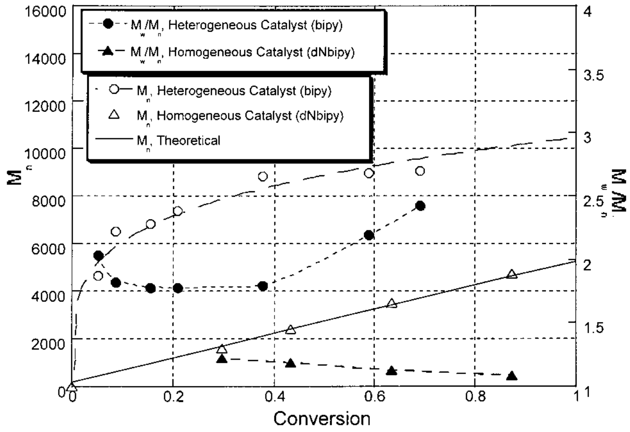

Figure 2. Dependence of molecular weight, M_n, and polydispersity, M_w/M_n, on monomer conversion for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate with a homogeneous catalyst (Cu^IBr/2dNbpy) and a heterogeneous catalyst (Cu^IBr/2bpy) in benzene at 80 °C. $[M]_0 = 3.2$ M, $[I]_0 = 0.079$ M, $[Cu^IBr] = 0.079$ M, [ligand] = 0.16 M.

Polymerization of *n*-Butyl Acrylate by ATRP with Cu^IBr/dNbpy and Cu^IBr/bpy Catalyst Systems. As with styrene,[14,18] the polymerization of *n*-butyl acrylate by ATRP was controlled under homogeneous conditions using dNbpy as ligand. The polymerization was carried out under argon, using methyl 2-bromopropionate as initiator, in a 50% w/w benzene solution at 80 °C. The molar ratios of [M]:[I]:[CuBr]:[bpy] were 40:1:1:2. The first-order kinetic plots of the polymerization, shown in Figure 1, were linear to above 85% monomer conversion, indicating that the number of active species remained constant during the polymerization.

A heterogeneous catalyst system, Cu^IBr/bpy, has also been efficient for the ATRP of styrene.[11] This system did not, however, give controlled polymerization of *n*-butyl acrylate in benzene. Figure 1 compares the first-order kinetic plots for the homogeneous and heterogeneous systems. It is apparent that the rate of polymerization was slow in the heterogeneous reaction and decreased after 40% conversion.

The dependence of the number average molecular weight (M_n) and polydispersity (M_w/M_n) on monomer conversion for the homogeneous system is shown in Figure 2. A linear increase of M_n versus monomer conversion was noted. The observed M_n's and the theoretical values based on $\Delta[M]/[I]_0$ match well, even though the molecular weights obtained by SEC were

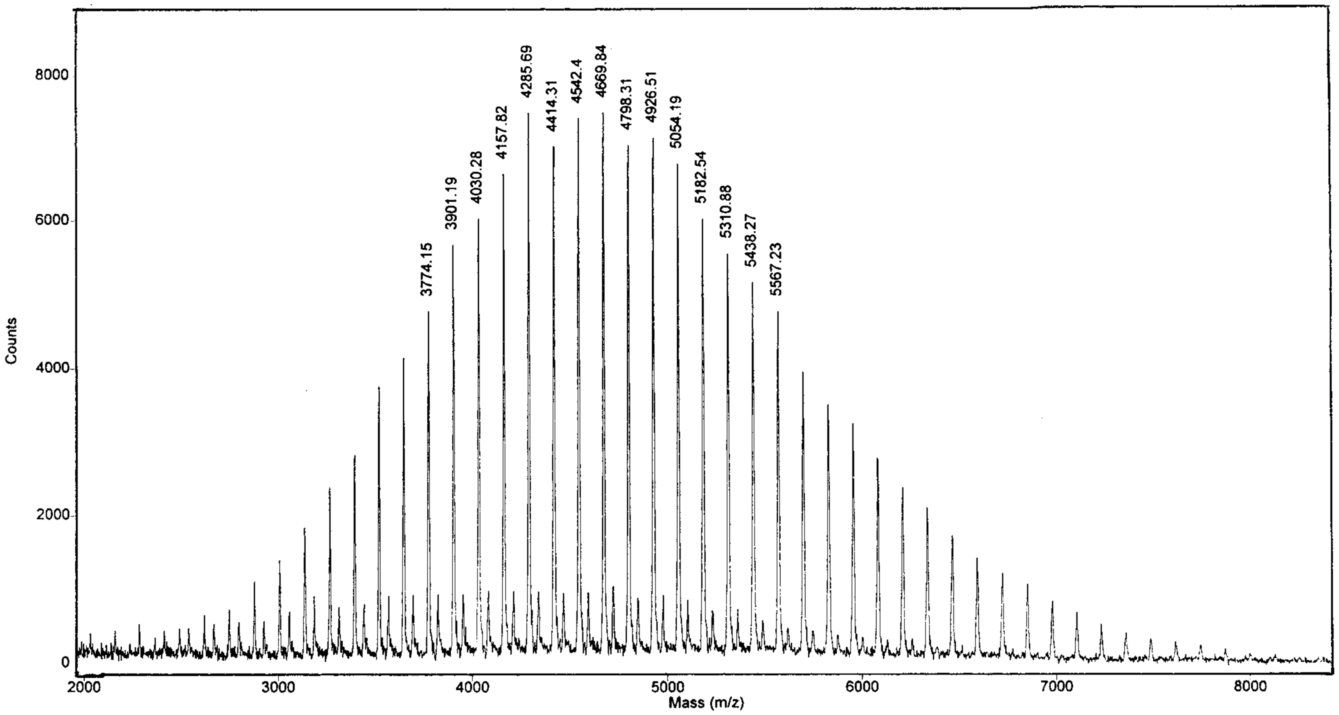

Figure 3. MALDI-TOF mass spectrum of poly(*n*-butyl acrylate) prepared by ATRP. The primary series corresponds to $[CH_3CHCO_2CH_3(CH{-}CHCO_2C_4H_9)_nBr + Na]^+$. $M_{n(MALDI)} = 4539$ and $M_w/M_{n(MALDI)} = 1.07$; these agree well with values obtained by SEC, $M_{n(SEC)} = 4700$ and $M_w/M_{n(SEC)} = 1.06$.

compared to those of polystyrene standards. This result indicates that an insignificant degree of transfer occurred during the polymerization. The molecular weight distribution decreased as the reaction proceeded, becoming very narrow, $M_w/M_n < 1.1$. The final polymer gave $M_n = 4700$ and $M_w/M_n = 1.06$.

Conversely, the polymer produced under heterogeneous conditions was uncontrolled. Figure 2 shows the dependence of M_n and M_w/M_n on monomer conversion for the heterogeneous system. The M_n values obtained were much higher than the predicted values, and the polydispersities were also large, $M_w/M_n > 2$. This lack of control is attributed to the poor solubility of the $Cu^{II}Br$/bpy in benzene. The polydispersity of the polymer is indicative of the rate of deactivation of the active species in the polymerization; it is defined by $M_w/M_n = 1 + (k_p[R{-}X]_0/k_d[Cu^{II}Br_2])([2/p] - 1)$, where k_p and k_d are the rate constants of propagation and deactivation respectively, $[R{-}X]_0$ is the initial concentration of initiator, $[Cu^{II}Br_2]$ is the concentration of deactivator, and p is the conversion of monomer.[29] Since $Cu^{II}Br$ is poorly soluble in the reaction medium, higher polydispersities are observed. For styrene the use of a heterogeneous ligand (bpy) has resulted in the successful preparation of well-defined polymers with relatively low polydispersities ($M_w/M_n < 1.5$); this can be ascribed to the much lower k_p value for styrene. Thus, k_p for butyl acrylate $\approx 46\,080$ M^{-1} s^{-1} at 80 °C,[31] in comparison to styrene, $k_p \approx 665$ M^{-1} s^{-1} at 80 °C.[32]

The polymer produced under homogeneous conditions with the Cu^I/dNbpy system was analyzed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOFMS). The spectrum is shown in Figure 3. The molecular weight distribution is narrow and quite symmetrical. The mass of each major peak matches the expected value for the structure, i.e., [87.11 ($CH_3{-}CHCO_2CH_3$) + {$n \times 128.17$ (*n*-butyl acrylate)} + 79.9 (Br) + 23 (Na^+)]. The series of small peaks was assigned as a fragment species, where HBr had been eliminated from the oligomer chains. Since no unsaturated end groups have been detected in ^1H NMR of these samples, the fragmentation was attributed to the MALDI-TOF technique. M_n and M_w/M_n calculated from MALDI-TOFMS were close to the values obtained by SEC and predicted from $\Delta M/[I]_0$.

Polymerization of *n*-Butyl Acrylate by ATRP with Cu^IBr/bpy Catalyst in a Variety of Solvents. Since dNbpy is not commercially available, it was interesting to optimize reaction conditions (solvent, temperature, concentrations) for a more available catalyst, Cu^IBr/bpy. Several solvents were investigated for the ATRP of *n*-butyl acrylate using the Cu^IBr/bpy catalyst at 100 °C, with a monomer concentration of 50% (w/w) for all reactions. The first-order kinetic plots of the polymerizations are shown in Figure 4.

Most solvents gave faster rates of polymerization than those observed in benzene. This is partially attributable to the difference in reaction temperature, 100 °C vs 80 °C. There was, however, a dramatic increase in the rate of polymerization when ethylene carbonate was used as solvent. The BA polymerization rate in ethylene carbonate solution was faster than the rate of the bulk polymerization, where the latter had twice the concentration of initiator and catalyst. In agreement with the reported rate laws,[18] the bulk polymerization is expected to proceed 4 times faster than a reaction in 50% solution; hence the rate increase in EC was unexpected. The polymerization using Cu^IBr/bpy in ethylene carbonate was *even faster* than the reaction with the homogeneous Cu^IBr/dNbpy catalyst in bulk.

Figure 5 shows the plots of M_n as a function of monomer conversion for different polymerization systems. In most cases M_n approached the theoretical value at the end of the reaction, except during the polymerization in benzene at 80 °C. Initially molecular weights were higher than predicted, indicating inef-

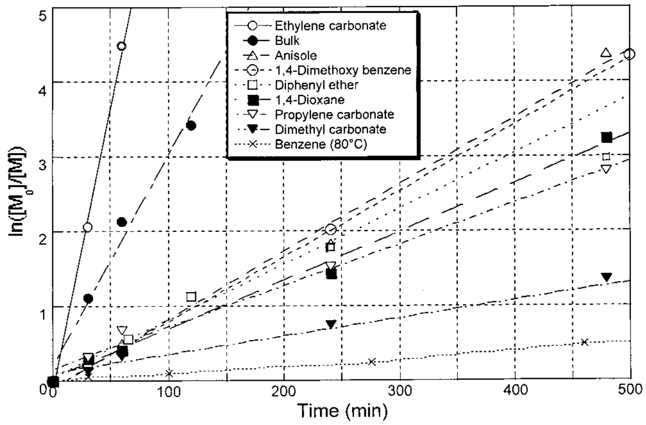

Figure 4. First-order kinetic plots for ATRP of *n*-butyl acrylate initiated by 1-phenylethyl bromide with $Cu^IBr/2bpy$ in various solvents (50% w/w) at 100 °C. $[M]_0:[I]_0:[CuBr]_0:[bpy]_0 = 40:1:1:2$. (Note: The polymerization in benzene was carried out at 80 °C.)

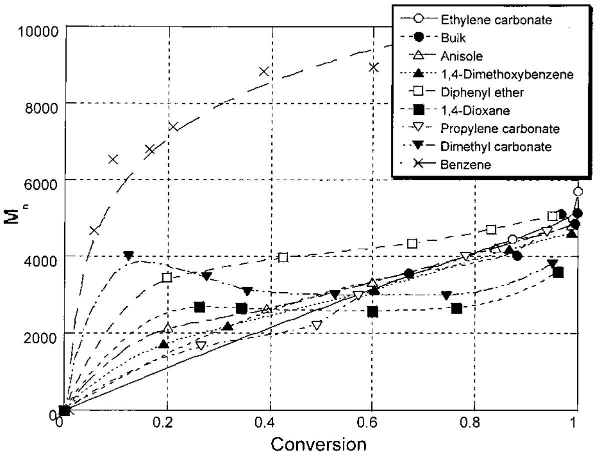

Figure 5. Dependence of molecular weight, M_n, on monomer conversion for the ATRP of *n*-butyl acrylate initiated by 1-phenylethyl bromide with Cu^IBr/bpy in various solvents (50% w/w) at 100 °C. (Note: The polymerization in benzene was carried out at 80 °C.)

ficient initiation, presumably caused by slow deactivation.

A large difference was also observed in the polydispersities of polymers in different solution systems (Figure 6). Anisole, 1,4-dimethoxybenzene, propylene carbonate and ethylene carbonate lead to polymers with relatively low polydispersities, $M_w/M_n < 1.5$. In the case of ethylene carbonate, polydispersity increased at the very end of the polymerization. This increase is thought to be caused by coupling reactions (the polymerization was very fast and was completed to above 99% monomer conversion in 60 min, but the reaction mixture was heated for 240 min). From these results, the ATRP of *n*-butyl acrylate with $Cu^IBr/dNbpy$ in ethylene carbonate was considered to be an attractive candidate for further studies.

Effect of Several Parameters on Polymerization of *n*-Butyl Acrylate in Ethylene Carbonate. Polymerizations in ethylene carbonate catalyzed by Cu^IBr/bpy appeared to be homogeneous. No precipitation of catalyst or polymer was observed, although a slight phase separation was noted at the end of polymerization, due to the limited solubility of poly(*n*-butyl acrylate) in ethylene carbonate. For the homogeneous system, first-order dependence of the polymerization rate (k_{app}) upon the concentration of catalyst is expected, in agreement with earlier results for styrene polymerizations.[18]

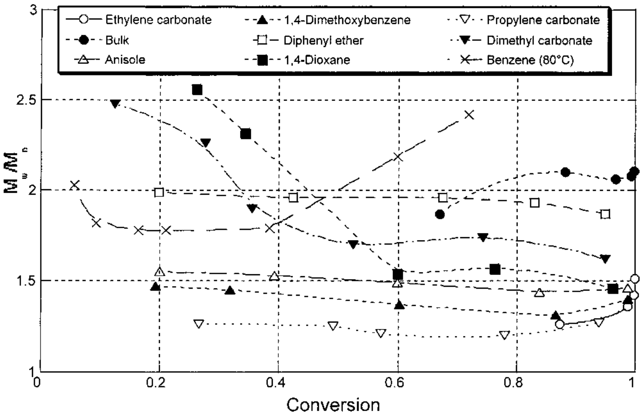

Figure 6. Dependence of polydispersity, M_w/M_n, on monomer conversion for the ATRP of *n*-butyl acrylate initiated by 1-phenylethyl bromide with $Cu^IBr/2bpy$ in various solvents (50% w/w) at 100 °C (polymerization in benzene carried out at 80 °C).

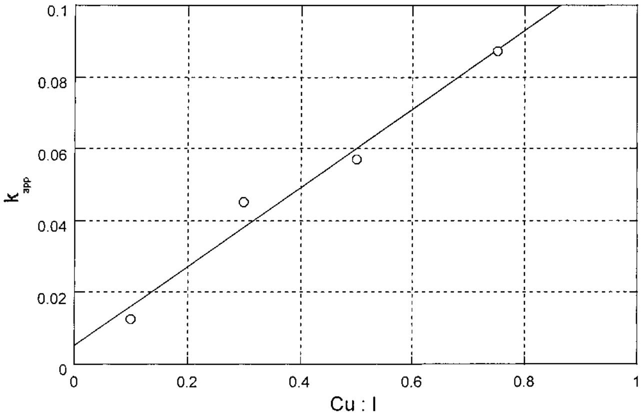

Figure 7. Plots of k_{app} as a function of the initial ratio of catalyst to initiator $[Cu^IBr]:[bpy] = 1:3$ for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate ($[M]_0:[I]_0 = 40:1$) in ethylene carbonate (10 g) at 80 °C.

ATRP of *n*-butyl acrylate in ethylene carbonate, initiated by methyl 2-bromopropionate ($[M]_0:[I]_0 = 40:1$) and catalyzed by Cu^IBr/bpy (1:3), was carried out at 80 °C using a variety of $[I]:[Cu^I]$ ratios. In all cases a linear increase in the first-order kinetic plots was initially observed, although deceleration occurred near the end of the polymerization (conversion > 90%). This can be ascribed to the limited solubility of poly(*n*-butyl acrylate) in ethylene carbonate or to progressively higher concentrations of deactivator (CuX_2) formed by the termination of propagating chains when excessive concentrations of CuX were used. Cu^{II} species are formed by termination of growing radicals, leading to a persistent radical effect.[33,34] They are formed proportionally to the concentration of Cu^I and the RX species. Plots of the apparent polymerization rate constant (k_{app}) based on monomer consumption as a function of catalyst quantity with constant initiator concentration are shown in Figure 7. The amount of catalyst quantity is marked as the molar ratio with respect to the initiator.

Some deviations from the linear dependence, found at higher catalyst concentrations ($[Cu] > [I]_0$), could be attributed to the limited solubility of the Cu^IBr/bpy species. The dependence of M_n on monomer conversion is shown in Figure 8. In all cases, M_n increased

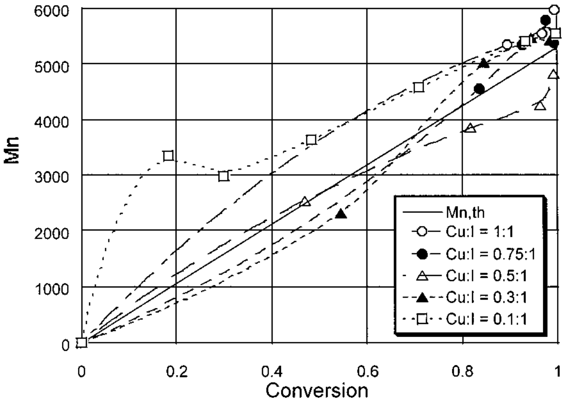

Figure 8. Dependence of molecular weight, M_n, on monomer conversion for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate ($[M]_0:[I]_0 = 40:1$) with varying amounts of catalyst ($[Cu^IBr]:[bpy] = 1:3$) in ethylene carbonate (10 g) at 80 °C.

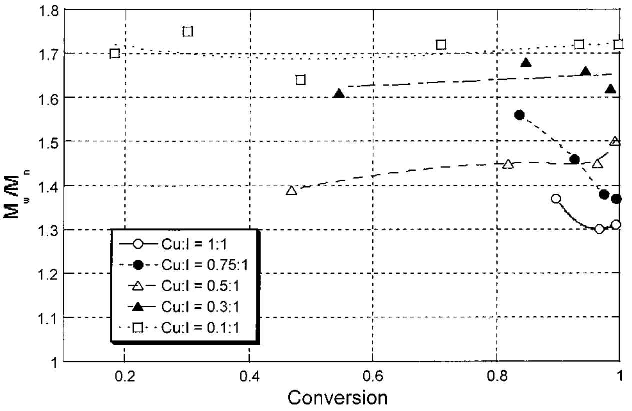

Figure 9. Dependence of polydispersity, M_w/M_n, on monomer conversion for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate ($[M]_0:[I]_0 = 40:1$) with varying amounts of catalyst ($[Cu^IBr]:[bpy] = 1:3$) in ethylene carbonate (10 g) at 80 °C.

monotonically with conversion and, at the end of the polymerization, approached the theoretical value. When the lowest concentration of catalyst was utilized, molecular weights were initially higher than predicted. This may be caused by less efficient initiation, due to slow deactivation related to lower concentrations of spontaneously formed deactivator.

Figure 9 shows the dependence of M_w/M_n upon monomer conversion. Polydispersity increased when the catalyst concentration was decreased. Again, the increase in polydispersity as catalyst concentration decreases can be explained by the lower concentration of copper(II) formed during the reaction. This in turn results in slower deactivation of the propagating radicals, leading to an increase in the number of monomer units added to the active radical during a single activation/deactivation cycle.

To reduce the polydispersities, two methods were employed: one was addition of $Cu^{II}Br_2$ to the reaction mixture; the other was a decrease of the amount of ethylene carbonate added, since the composition of the reaction mixture could affect the structure of the catalyst (vide infra). Thus, for a ratio of [initiator]:$[Cu^IBr] = 1:0.3$, 10 mol % of $Cu^{II}Br_2$ was added relative to Cu^IBr. The rate of polymerization was about 10 times slower (Figure 10), the observed M_n's were close to the theoretical values throughout the reaction, and the polydispersities decreased to $M_w/M_n \leq 1.3$ (Figure 11).

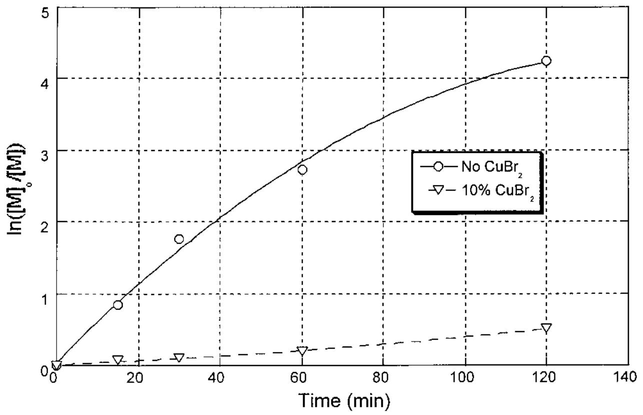

Figure 10. First-order kinetic data for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate in ethylene carbonate at 80 °C; $[M]_0:[I]_0:[CuBr]_0:[bpy]_0:[Cu^{II}Br_2]_0 = 40:1:0.3:1:0.03$.

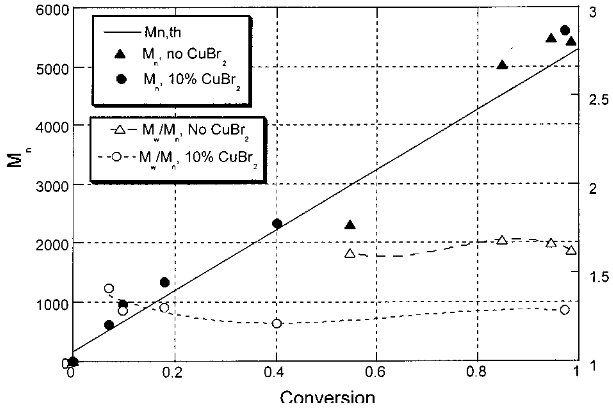

Figure 11. Dependence of molecular weight, M_n, and polydispersity, M_w/M_n, on monomer conversion for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate in ethylene carbonate at 80 °C; $[M]_0:[I]_0:[CuBr]_0:[bpy]_0:[Cu^{II}Br_2]_0 = 40:1:0.3:1:0.03$.

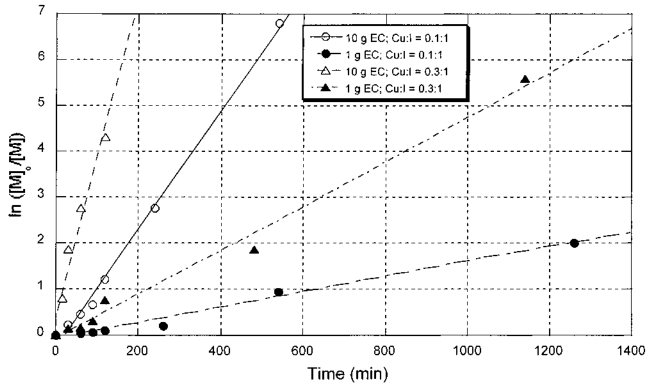

Figure 12. First-order kinetic plots for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate with variable amounts of ethylene carbonate for 10 mL of monomer at 80 °C; $[M]_0:[I]_0:[CuBr]_0:[bpy]_0 = 40:1:0.3:0.9$ and $40:1:0.1:0.3$.

With the same ratio of $[I]:[Cu^IBr]$ (1:0.3), the amount of ethylene carbonate was decreased from 10 to 1 g for 10 mL of the monomer. As the polymerization conditions tended toward almost bulk reaction conditions, the concentrations of catalyst and initiator were practically doubled, which should have resulted in a faster polymerization rate. However, just the opposite was observed: the rate decreased (Figure 12). The linearity of the first-order kinetics was maintained and M_n was close to the theoretical value. The polydispersities

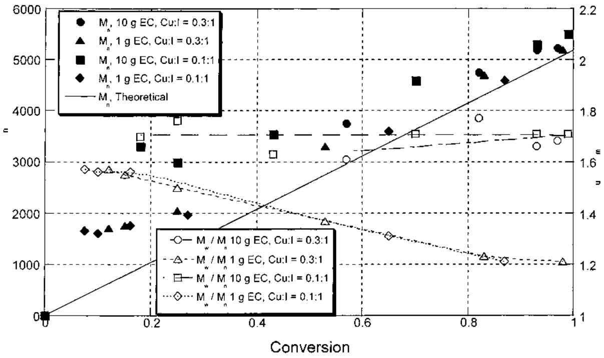

Figure 13. Dependence of M_n and M_w/M_n on monomer conversion for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate with variable amounts of ethylene carbonate for 10 mL of monomer at 80 °C; $[M]_0:[I]_0:[CuBr]_0:[bpy]_0 = 40:1:0.3:0.9$.

decreased to 1.2 at the end of the polymerization (Figure 13).

Both a reduction in the amount of ethylene carbonate or an addition of copper(II) produced similar effects on kinetics, molecular weights, and polydispersities. Overall, the polarity of the EC (1 g) reaction mixture was much lower than the EC (10 g) solution; this resulted in a lower concentration of Cu^I in solution, which consequently reduced the rate of polymerization. Apparently, the solubility and reactivity of Cu^{II} were not strongly affected, because the polydispersities were lowest when only 1 g of ethylene carbonate was used (Figure 13).

Two explanations can be considered for the effect of ethylene carbonate on the polymerization of *n*-butyl acrylate with the Cu^IBr/bpy catalyst: the first is related to the homogeneity of the copper complex and its concentration in solution; the second is due to the structure of the copper species. It has been reported that the CuX/bpy complex can exist as a monomeric species or, alternatively, as a dimer with bridging halogens between the two copper atoms;[30] another possibility involves the ions $[Cu(bpy)_2]^+$ and $[CuX_2]^-$. We have also recently reported a dramatic acceleration of the ATRP of methyl acrylate when $CuPF_6$/dNbpy was used as the catalyst.[27] This was ascribed to a change in the structure of the copper complex, i.e., the formation of monomeric copper species with the PF_6^- counterion. If the polymerization rates described herein are due to the formation of a monomeric copper species in ethylene carbonate, the $CuPF_6$ catalyst should have a similar activity compared to Cu^IBr/bpy in ethylene carbonate. Indeed, when a polymerization was conducted using the $CuPF_6$/bpy catalyst, the polymerization rate of *n*-butyl acrylate, as well as the dependence of M_n and M_w/M_n on conversion were very similar to those of the Cu^IBr/bpy system in EC. This could support the premise that the rate increase in the polymerization using EC is due to the formation of a monomeric copper species with noncoordinated (dissociated) anions.

During the polymerization of *n*-butyl acrylate in EC (10 g) solution, the reaction was initially homogeneous. However, by the end of the polymerization, phase separation of the poly(*n*-butyl acrylate) from the ethylene carbonate was observed. This was due to low solubility of the polymer in ethylene carbonate. Throughout this study, low molecular weight polymers, with degrees of polymerization defined by $DP = \Delta[M]:[I]_0 = 40$, have been prepared. It was important to verify that a higher molecular weight polymer could be synthesized despite the phase separation incurred during the polymerization (Figures 14 and 15). It was noted that the incomplete polymer solubility did not affect the control of molecular weights and led only to a small increase of polydispersities, indicating that both the catalyst, Cu^I, and the deactivator, Cu^{II}, were accessible to dormant and active structures, thus ensuring the rapid exchange of these species.

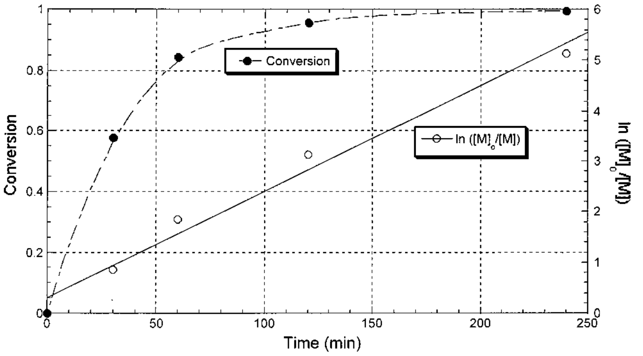

Figure 14. First-order kinetic plot and dependence of conversion on time, for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate with Cu^IBr catalyst in ethylene carbonate at 80 °C; $[M]_0:[I]_0:[CuBr]_0:[bpy]_0 = 160:1:4:12$.

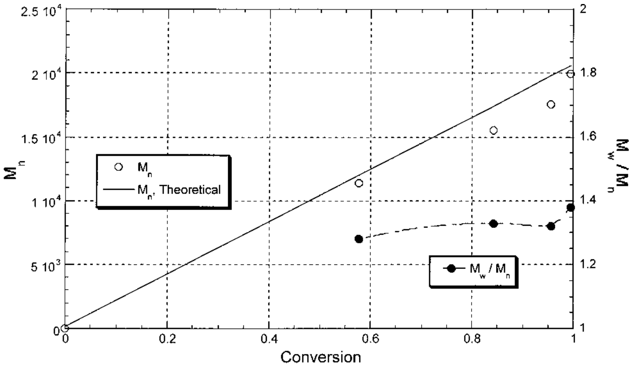

Figure 15. Dependence of M_n and M_w/M_n on monomer conversion for the ATRP of *n*-butyl acrylate initiated by methyl 2-bromopropionate with Cu^IBr catalyst in ethylene carbonate (10 g) at 80 °C; $[M]_0:[I]_0:[CuBr]_0:[bpy]_0 = 160:1:4:12$.

Conclusions

Atom transfer radical polymerization (ATRP) of *n*-butyl acrylate using the homogeneous catalyst Cu^IBr/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) in benzene has produced well-defined poly(*n*-butyl acrylate) with predetermined molecular weights and low polydispersities, $M_w/M_n \approx 1.1$. The number average molecular weights, M_n, measured by SEC and MALDI-TOFMS, were in agreement with the theoretical molecular weights predicted by $DP_n = \Delta[M]/[I]_0$. A similar polymerization in benzene using 2,2′-bipyridine (bpy) as the ligand, instead of dNbpy, displayed poor control, yielding a polymer with molecular weights higher than the theoretical values and with high polydispersities, $M_w/M_n = 2.4$. A variety of solvents were employed for the polymerizations with the Cu^IBr/bpy catalyst system. Ethylene carbonate was found to provide good control of molecular weights and polydispersities with a surprisingly fast rate of polymerization, even faster than that observed in the bulk reaction. The rate of the polymerization with the Cu^IBr/bpy catalyst in ethylene carbonate was first order in catalyst concentration.

However, reducing the concentration of the catalyst led to an increase in the polydispersity of the resulting polymer. The polydispersity was improved by the addition of $Cu^{II}Br_2$ or by decreasing the amount of ethylene carbonate. This polymerization system was also applied to form higher molecular weight poly(*n*-butyl acrylate), $M_n = 20\,000$, and exhibited good control. The polymerization in ethylene carbonate with $Cu^{I}PF_6$/bpy catalyst produced results similar to those observed for the $Cu^{I}Br$/bpy catalyst system.

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