Atom Transfer Radical Polymerization of *n*-Butyl Methacrylate in an Aqueous Dispersed System

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ABSTRACT: Atom transfer radical polymerization of *n*-butyl methacrylate (BMA) was conducted in an aqueous dispersed system with different kinds of copper complexes. The partitioning behavior of the copper complexes, including CuCl/4,4′-di(5-nonyl)-2,2′-bipydine (dNbpy), $CuCl_2$/dNbpy, CuCl/2,2′-bipydine (bpy), $CuCl_2$/bpy, CuCl/bis(*N,N*′-dimethylaminoethyl)ether (bde), and $CuCl_2$/bde between the monomer (BMA), and water was studied in detail with ultraviolet–visible spectroscopy. The results show that with a less hydrophobic ligand, such as bpy or bde, most of the Cu(I) or the Cu(II) complexes migrated from the BMA phase to the aqueous phase, the atom transfer equilibrium was destroyed, and the polymerization was nearly not controlled; it converted to classical emulsion polymerization. As to the very hydrophobic ligand dNbpy, although the partitioning study of the copper complexes indicated that not all the copper species were restricted to the organic phase, the linear correlation between the molecular weight and the monomer conversion and the narrow polydispersities confirmed that the polymerization was still quite well controlled. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3175–3179, 2003

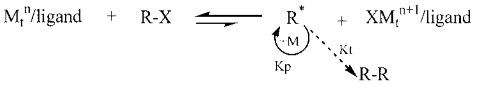
Key words: atom transfer radical polymerization (ATRP); emulsion polymerization; catalysts

INTRODUCTION

The synthesis of polymers that have well-defined structures (e.g., predictable molecular weight and low polydispersity) and functionality with radical intermediates has been an area of intense interest in recent years.[1] In particular, atom transfer radical polymerization (ATRP), reported by Wang and colleagues, has been used to produce a variety of novel polymer architectures.[2–4] However, most controlled/"living" radical polymerizations have been confined to bulk or solution polymerizations.[5] During the past years, several attempts to apply the existing controlled radical polymerization techniques to the aqueous dispersed systems have been reported. The methods included stable free-radical polymerization,[6] ATRP,[7–9] reversible addition–fragmentation chain transfer,[10] and degenerative transfer polymerization based on the iodine atom exchange.[11]

Of all controlled/living radical polymerizations, ATRP in aqueous dispersed systems is the most interesting one. Although most transition-metal complexes decompose rapidly in water, Pd, Ru, and Cu complexes that catalyze ATRP are fortunately quite stable. With ruthenium[12] and palladium[13] catalytic systems, relatively well-controlled polymerizations were achieved in aqueous systems with or without surfactant. The copper-mediated water-borne ATRP has so far been the most versatile system.[14] It has been successfully employed for the (co)polymerization of styrene, acrylate, and methacrylates. Most studies have been focused on the polymerization of *n*-butyl methacrylate (BMA).[15–20] The polymerization starts either with an alkyl halide and a Cu(I) complex[21] or with a conventional radical initiator and a Cu(II) complex;[20] the latter process is called *reverse ATRP*.

The key to a controlled radical polymerization is the maintenance of a fast equilibrium between the growing radicals and the dormant species. In ATRP or reverse ATRP, such an equilibrium is achieved with a metal complex that switches between *n* and *n* + 1 oxidation states:



$$M_t^n/\text{ligand} + \text{R-X} \rightleftharpoons \text{R}^* + XM_t^{n+1}/\text{ligand} \quad (1)$$

where M_t^n/ligand is a metal complex at the lower oxidation state, XM_t^{n+1}/ligand is a metal complex at the higher oxidation state, R* is radical, R-X is alkyl halide.

The same principle holds for aqueous dispersed systems. Because the polymer chains grow in the organic phase, the first requirement for control over the polymerization is a sufficient concentration of both the activator (a metal complex at the lower oxidation state) and the deactivator (a metal complex at the higher oxidation state) in the organic phase. Otherwise, either no polymerization or an uncontrolled po-

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TABLE I
Typical ATRP Recipe

Component		Amount	
Monomer	BMA	1.5 mL	200
Water		9 g	Monomer/water = 15/100 w/w
Initiator	$BrCH_3CHCOOC_2H_5$	12 μL	1 equiv
Catalyst	CuCl	0.007 g	1.5 equiv
Ligand	dNbpy	0.05 g	3 equiv
	bpy	0.033 g	4.5 equiv
	bde	0.034 g	4.5 equiv
Surfactant	Brij35	0.2 g	2 wt % versus water

lymerization would occur. Therefore, the choice of the proper ligand becomes crucial. As reported in the literature,[21] successful polymerizations were only achieved when ligands that displayed sufficient hydrophobicity were employed, such as 4,4′-di(5-nonyl)-2,2′-bipydine (dNbpy), 4,4′-dialkyl-2,2′-bipydine (alkyl: mixture of *n*-pentyl and 5-nonyl), or *N,N*-bis(2-pyridylmethyl)octadecylamine. However, ligands, such as 2,2′-bipydine (bpy), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine or tris[2-(dimethylamino)ethyl-]amine, that function very well in bulk or solution polymerizations led to uncontrolled polymerizations in aqueous dispersed systems. We ascribed this outcome to the different partitioning behavior of the metal complexes.

In this study, the ATRP of BMA was conducted in an aqueous dispersed system with different kinds of copper complexes, and to better understand the catalyst performance in the heterogeneous system, we measured the partitioning of CuCl/bpy, $CuCl_2$/bpy, CuCl/bis(N,N′-dimethylaminoethyl)ether (bde), $CuCl_2$/bde, CuCl/dNbpy, and $CuCl_2$/dNbpy between BMA and water.

EXPERIMENTAL

Materials

BMA was dried over CaH_2 and distilled *in vacuo*. dNbpy was obtained from Aldrich Chemical Co. (USA) and was used as received. bpy was recrystallized from ketone. bde was obtained from Tokyo Kasei Kogyo Co. (Japan) and was used as received. Poly(oxyethylene oleyl ethers) (Brij35) were obtained from Sigma Co. (USA). Ethyl 2-bromopropinate was synthesized according to a modified literature procedure. CuCl and $CuCl_2$ were purified according to literature.[22]

General polymerization procedure

Table I lists the typical recipe used for the ATRP. The polymerization was carried out in a previously dried flask equipped with a magnetic stirring bar under argon. BMA, CuCl, and dNbpy (or bpy, bde) were put into the flask, the flask was degassed three times by repeated freeze/vacuum/thaw cycles, and then, the surfactant solution (previously purged with argon) was added via syringe. After an emulsion formed under stirring, the flask was placed in a 85–90°C oil bath under argon. The initiator was finally added, which corresponded to the zero point of the polymerization.

Characterization

The monomer conversion was determined gravimetrically. Molecular weight and polydispersities were determined by gel permeation chromatography (Wyatt Technology Corp., USA). All samples were run in tetrahydrofuran at 25°C with a flow rate of 0.8 mL/min.

Partitioning experiments

Solutions of CuCl/bpy, $CuCl_2$/bpy, CuCl/bde, $CuCl_2$/bde, CuCl/dNbpy, and $CuCl_2$/dNbpy in BMA were prepared with a 1.5/200 mol/mol ratio. The solutions were mixed with deionized water at a 15/100 w/w ratio. The biphasic mixture was stirred at room temperature for at least 1 h (the absorption of the organic phase did not change with longer stirring times, indicating the partition equilibrium had been reached). The two phases were then separated and measured with an ultraviolet–visible (UV–vis)/near infrared (NIR) spectrometer (Lambda 17, PerkinElmer, USA). In the case of CuCl/L (Ligand), the experiment was performed under nitrogen.

RESULT AND DISCUSSION

Partitioning of the metal complex

CuCl/dNbpy and $CuCl_2$/dNbpy

Copper complexes display characteristic absorption in the UV–vis region; therefore, UV–vis spectroscopy was used to measure the partitioning of the complexes between BMA and water, as described in the Experimental section. The higher the amount of CuCl/dNbpy or $CuCl_2$/dNbpy used, the larger the percentage of Cu(I) or Cu(II) species that remained in the organic phase. Figures 1 and 2 show the absorption spectra of

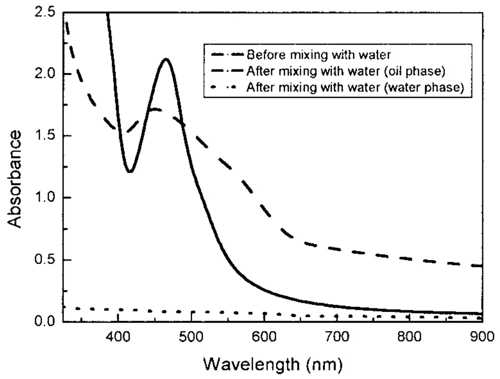

Figure 1 Absorbance spectra of CuCl/dNbpy in BMA at room temperature before and after mixture with water.

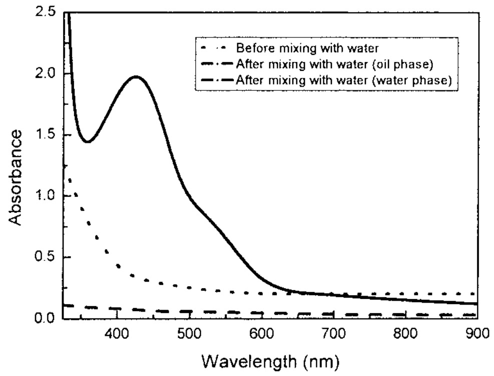

Figure 3 Absorbance spectra of CuCl/bpy in BMA at room temperature before and after mixture with water.

Cu(I) and Cu(II), respectively, in the organic phase or aqueous phase before and after mixture with water. As shown in Figure 1, before mixture with water, there was a relative intensity of the peaks around 460 nm, which most likely came from the $[Cu(dNbpy)_2]^+$ complex; after mixture with water, the absorption spectra of the Cu(I) in the organic phase did not change much; it only decreased in intensity. However, after mixture with water, the Cu(I) nearly did not have any absorption in the aqueous phase. Figure 2 reveals a remarkable change in the relative intensity of the peaks around 530 and 740 nm. The former absorbance most likely came from $CuCl_3^-$ or $CuCl_4^{2-}$ anions, as suggested in the literature, whereas the latter was from the trigonalbipyramidal complex $[Cu(dNbpy)_2Cl]^+$. A reasonable explanation for the decrease in the 530 nm peak was that $CuCl_3^-$ or $CuCl_4^{2-}$ dissociated into $CuCl_2$ and Cl^- on contact with water. The complex $[Cu(dNbpy)_2Cl]^+$ partially dissociated and released Cu^{2+}, which was preferentially soluble in the aqueous phase, and the majority of free dNbpy and the remaining $[Cu(dNbpy)_2Cl]^+$ stayed in the organic phase. When the ratio of dNbpy to $CuCl_2$ increased, the absorption at 530 nm progressively decreased until it totally disappeared, whereas the absorption at 740 nm was relatively unaffected. Compared with the Cu(II) species, the Cu(I) complex was much more soluble in the organic phase; the partitioning was little influenced by the concentration. From the partitioning behavior of CuCl/dNbpy and $CuCl_2$/dNbpy between BMA and water, we know dNbpy was quite hydrophobic; little metal complexes migrated from the BMA phase to the aqueous phase. In ATRP, the first requirement for control polymerization is a sufficient concentration of both the activator and the deactivator in the organic phase, which may maintain a fast equilibrium between the growing radicals and the dormant species. Although dNbpy was not the ideal ligand to keep most of the copper species in the organic phase, it still afforded reasonable control over the polymerization in the aqueous dispersed system. CuCl/dNbpy and $CuCl_2$/dNbpy were good catalysts for the ATRP in this aqueous dispersed system.

CuCl/bpy and $CuCl_2$/bpy

Figures 3 and 4 show the absorption spectra of the CuCl/bpy and $CuCl_2$/bpy before and after mixture with water, respectively. From the absorption spectra, we know that the solubility of CuCl/bpy and $CuCl_2$/bpy in BMA were small, especially the CuCl/bpy, which nearly had no absorption in the BMA phase before mixture with water, although there were relative intensities of the peaks around 450 or 730 nm in

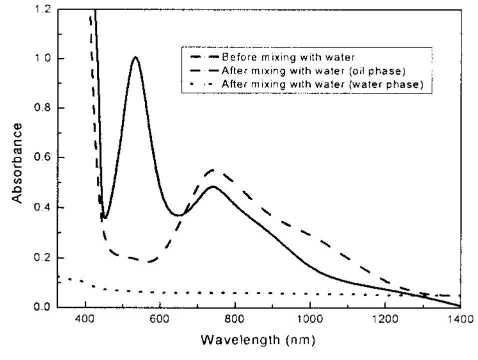

Figure 2 Absorption spectra of $CuCl_2$/dNbpy in BMA at room temperature before and after mixture with water.

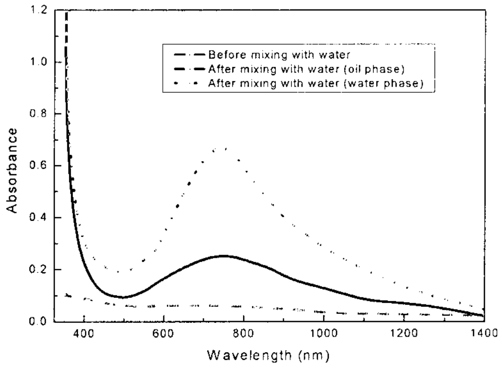

Figure 4 Absorbance spectra of $CuCl_2$/bpy in BMA at room temperature before and after mixture with water.

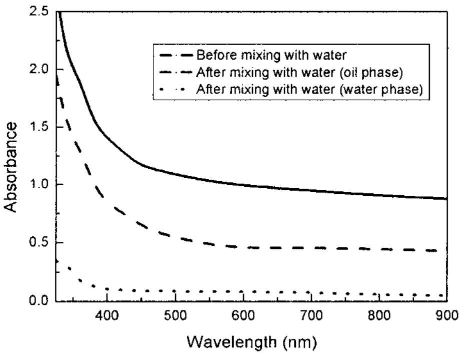

Figure 5 Absorbance spectra of CuCl/bde in BMA at room temperature before and after mixture with water

the aqueous phase after mixture with water. bpy was less hydrophobic, and the CuCl/bpy and $CuCl_2$/bpy had good water solubility when mixed with water. The metal complexes migrated easily to the aqueous phase, the equilibrium between the growing radicals and the dormant species was destroyed, and uncontrolled polymerization occurred. So CuCl/bpy and $CuCl_2$/bpy complexes were not the good catalysts for the ATRP of BMA in this aqueous dispersed system.

CuCl/bde and $CuCl_2$/bde

Figures 5 and 6 show the absorption spectra of CuCl/bde and $CuCl_2$/bde, respectively. CuCl/bde and $CuCl_2$/bde did not have any absorption in the organic phase or aqueous phase, which revealed that the solubility of CuCl/bde and $CuCl_2$/bde in both the organic phase and aqueous phase was small. The poor solubility of the catalyst indicates that it was difficult to achieve equilibrium between the growing radicals and the dormant species in the ATRP.

The partitioning studies were performed in the absence of the surfactant. It is possible that the partition behavior may change in systems where surfactant is involved. Nevertheless, we anticipate that the previous results still provide valuable estimates of the partitioning behavior of the metal complexes in those cases.

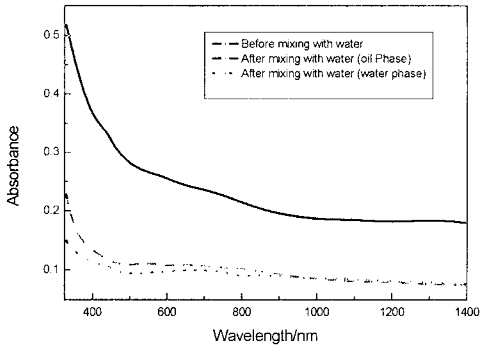

Figure 6 Absorbance spectra of $CuCl_2$/bde in BMA at room temperature before and after mixture with water.

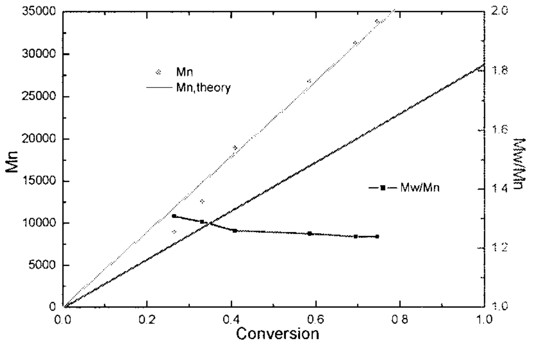

Figure 7 Dependence of the molecular weight and dispersity on the conversion for the emulsion polymerization of BMA by ATRP. [CuCl] = [$BrCH_3CHCOOC_2H_5$] = 0.0047 mol/L; [dNbpy] = 0.0094 mol/L; [BMA] = 0.943 mol/L; [Brij35] = 0.5 g/L. M_w = weight-average molecular weight.

Polymerization

To better understand the kinetics of ATRP in aqueous dispersed system, we conducted a typical ATRP under the conditions described in Table I.

CuCl/dNbpy

Figure 7 shows the molecular weight and the polydispersities of poly(*n*-butyl acrylate) (pBMA) with conversion. As shown in Figure 7, two important features of controlled radical polymerization were observed in the typical ATRP in the aqueous dispersed system. The first was the linear increase of molecular weight with monomer conversion, indicating that the number of chains was constant; in other words, chain-transfer reactions were negligible, and the molecular weight corresponded with that predicted by theory. The second feature was the low polydispersities of the polymer chains (1.31–1.24), meaning that nearly all the chains started to grow simultaneously, which confirmed the influence of CuCl/dNbpy partitioning behavior on polymerization.

Compared with the bulk ATRP carried out under similar conditions, the drawback of the aqueous dispersed system is the relatively low initiation efficiency (0.5 vs. 0.7 for the homogeneous system), which means although the polymerization was controlled, the existence of the aqueous phase unavoidably influenced the controllability of the polymerization.

CuCl/bpy

As shown in Figure 8, when the conversion was lower than 30%, the polymerization is controlled, the molecular weight of the pBMA increased lineally with conversion, but it did not correspond with predicted values [conversion = 30%, number-average molecular weight (M_n) = 64,000, theoretical number-average molecular weight ($M_{n,\text{theory}}$) = 8500]. The polydispersities decreased with increasing conversion but with broad molecular weight distributions (2.08 when conversion = 30%). When the conversion was higher than 30%, the molecular weight and the polydispersities did not change any more with increasing conversion, which behaved as if it was a conventional radical polymerization, and the total conversion was only 50%. CuCl/bpy had good water solubility, the metal complexes migrated to the aqueous phase, and the polymerization was uncontrolled and converted to a conventional radical polymerization.

CuCl/bde

Figure 9 shows the molecular weight and the polydispersities of pBMA with increasing conversion. As shown in Figure 9, the molecular weight did not increase linearly with conversion, it deviated greatly from the theoretical value, and the polydispersities were broader. The features of controlled radical polymerization were not clearly observed; however, they corresponded with conventional radical polymerization very well. However, some researchers reported that CuCl/bde was a good catalyst for ATRP in an aqueous system.[23] Further work should be done to understand this catalyst.

CONCLUSIONS

In this work, the ATRP of BMA was successfully carried out in an aqueous dispersed system. To control the polymerization, a hydrophobic ligand, dNbpy, was used together with CuCl to form a deactivator for the atom transfer reaction. Although the partitioning study of the copper complexes indicated that not all the copper species were restricted to the organic phase, the linear correlation between the molecular weight and the monomer conversion as well as the narrow polydispersities confirmed that the polymerization was still quite well controlled. With CuCl/bpy and CuCl/bde, less hydrophobic catalysts, the polymerization was nearly not controlled, most of them migrated from the BMA phase to aqueous phase, the atom transfer equilibrium was destroyed, and the polymerization converted to classical emulsion polymerization.

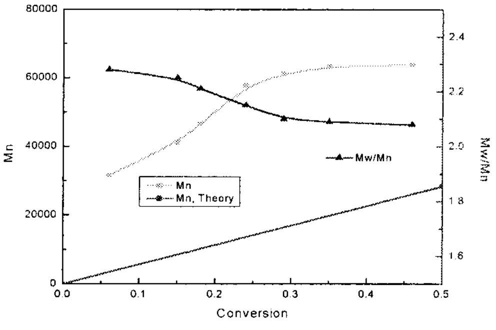

Figure 8 Dependence of the molecular weight and dispersity on the conversion for the emulsion polymerization of BMA by ATRP. [CuCl] = [$BrCH_3CHCOOC_2H_5$] = 0.0047 mol/L; [bpy] = 0.0147 mol/L; [BMA] = 0.943 mol/L; [Brij35] = 0.5 g/L. M_w = weight-average molecular weight.

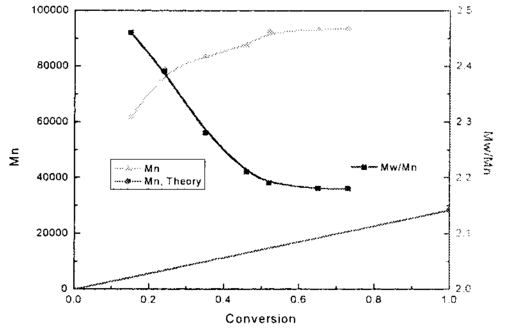

Figure 9 Dependence of the molecular weight and dispersity on the conversion for the emulsion polymerization of BMA by ATRP. [CuCl] = [$BrCH_3CHCOOC_2H_5$] = 0.0047 mol/L; [bde] = 0.0147 mol/L; [BMA] = 0.943 mol/L; [Brij35] = 0.5 g/L. M_w = weight-average molecular weight.

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