

INVESTIGATION OF THE ATRP OF *n*-BUTYL METHACRYLATE USING THE Cu(I)/*N,N,N',N'',N'''*-PENTAMETHYLDIETHYLENTRIAMINE CATALYST SYSTEM*

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Abstract The polymerization of *n*-butyl methacrylate was investigated using the Atom Transfer Radical Polymerization technique with CuBr and CuCl/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine catalytic systems. Various combinations of catalyst systems and initiators were utilized in order to optimize the polymerization conditions and to obtain well-defined polymers (*i.e.* controlled molecular weights and low polydispersities). It has been found that the optimal initiator for this system is a chlorine-based initiator, when the catalyst used is a Cu(I) salt in conjunction with the *N,N,N',N'',N'''*-pentamethyldiethylenetriamine ligand. Bromine-based initiators tend to result in large amounts of initial termination, leading to polymers with less than ideal chain end functionality, even if CuCl is used as the Cu(I) species to invoke the halogen exchange. Additionally, the effects of the polymerization temperature, copper(I) species and the initiator structure were determined.

Keywords ATRP, Atom transfer radical polymerization, Controlled/living radical polymerization, Butyl methacrylate, Pentamethyldiethylenetriamine

INTRODUCTION

The atom transfer radical polymerization (ATRP) has become an important method for preparing well-defined macromolecules. This technique offers control over the molecular weights, the chain end functionalities, and the chain architectures^[1–12]. It has been used extensively for the preparation of homopolymers, block, and random copolymers^[13–39], for the preparation of organic/inorganic hybrid materials^[40–54], as well as for combining various other living polymerization methods with ATRP to prepare novel polymer combinations^[55–64]. The polymerization of methacrylate-based monomers using highly active ATRP catalysts is challenging because the monomers produce inherently very reactive dormant species, forming a relatively stable tertiary radical species and resulting in a rather high equilibrium constant and a large concentration of active species. The reactivity of the monomers cannot be altered, so the key to the ATRP of methacrylates is to alter the equilibrium to such an extent that the polymerizations are controlled. This has been accomplished with less active catalysts like the copper(I) 2,2'-bipyridine or pyridineimine systems^[65–67] and the nickel^[16], rhodium^[68], or iron-based systems^[69–74]. With the use of new commercially available ligands like *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) for copper-mediated ATRP^[27, 75], which, because of its higher reactivity, promotes faster polymerizations of both acrylate and methacrylate type monomers, the challenge has been to find optimal conditions for the ATRP reactions that afford control over the structures of the final polymers.

Prior work with the ATRP of methyl methacrylate (MMA) catalyzed by the copper(I)/4,4'-di-(5-nonyl)-2,2'-

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bipyridine (dNbpy) system showed that to obtain polymers that were well-defined, *i.e.* had predictable molecular weights and narrow molecular weight distributions, the use of the halogen exchange technique was necessary^[67, 76–78]. The polymerization of MMA was initiated by a bromine containing alkyl halide and catalyzed by a CuCl/dNbpy system. Once the initiator was consumed, upon deactivation, there was a rapid exchange of the chlorine and the bromine to produce a Cu(I)Br/dNbpy complex and chlorine terminated polymer chains. This resulted in fast initiation, but at the same time, slowed down reactivation, allowing all the chains to grow at the same rate. Using an entirely bromine-based system produced polymers with experimental molecular weights that were higher than the theoretical values and had broad molecular weight distributions. The poly(methyl methacrylate) produced from the halogen exchange system had experimental molecular weights close to the theoretically predicted values and narrower molecular weight distributions^[67]. The success of using the halogen exchange for the dNbpy-based catalyst system led to extensive investigation of its use for the ATRP of *n*-butyl methacrylate using the PMDETA ligand as the complexing agent for the copper(I) salts.

EXPERIMENTAL

Materials

n-Butyl methacrylate (*n*BMA, Acros, 99%) was extracted 3 times with a 5% aqueous NaHCO₃ solution, followed by 3 extractions with water, then distilled under reduced pressure (69°C, 29 mmHg). CuBr (Acros, 98%) and CuCl (Acros, 99%) were purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, then dried under vacuum. Ethyl 2-bromoisobutyrate (EBriB, 98%), 3-bromopropionitrile (BPN, 98%), *p*-toluenesulfonyl chloride (TsCl, 99%), 2,2,2-trichloroethanol (TCE, 99%), all from Acros, acetone (Pharmco) and PMDETA (Aldrich, 99%) were all used as received.

General Polymerization Conditions

Addition of initiator to catalyst solution

CuBr (18 mg, 1.3×10^{-4} mol) was added to a 10 mL round bottom flask (rbf), which was sealed with a rubber septum and degassed and back-filled with N₂ three times. Deoxygenated acetone (2 mL) was added to the flask, followed by PMDETA (26 μ L, 1.3×10^{-4} mol). The solution was stirred to dissolve the metal complex, then *n*BMA (2 mL, 1.3×10^{-2} mol) and anisole (100 μ L, as an internal standard) were added. The solution was pale green. After the EBriB (18 μ L, 1.3×10^{-4} mol) was added, the solution became deeper green. An initial sample was removed and the flask was placed in an oil bath thermostated at the desired temperature. Samples were removed at timed intervals to measure the kinetics. This procedure was typical for all polymerizations using liquid initiators. The figure captions contain specific experimental details.

Separate initiator and catalyst solutions

(The reaction was scaled up from the above conditions to make transfer of the initiator solution easier.) CuBr (29 mg, 1.9×10^{-4} mol) was added to a 10 mL rbf, which was sealed with a rubber septum and degassed and back-filled with N₂ three times. Deoxygenated *n*BMA (3 mL, 1.9×10^{-2} mol) was added to the flask, followed by PMDETA (40 μ L, 1.9×10^{-4} mol). The solution was stirred to dissolve the metal complex. It became pale green. TsCl was added to a separate 5 mL rbf (36 mg, 1.9×10^{-4} mol), which was degassed and back-filled with N₂ three times before acetone (3 mL) was added. The initiator was dissolved, then the solution was canula-transferred into the catalyst solution. Again, the catalyst solution became deep green once the initiator was added. An initial sample was removed and the flask was placed in an oil bath thermostated at the desired temperature. Samples were removed at timed intervals to measure the kinetics. This procedure was typical for all polymerizations using TsCl as the initiator. The figure captions contain specific experimental details.

Characterization

Monomer conversions were determined using a Shimadzu GC-14A equipped with a J&W Scientific 30 m DB-WAX megabore column and an FID detector against anisole as the internal standard. Both the injector and detector temperatures were constant at 250°C and the heating rate was 40 K/min. Polymer molecular weights

were estimated via GPC analysis using a Waters WISP 712 autosampler, Polymer Standards Service columns (guard, 10^2 Å, 10^3 Å, 10^5 Å), and a Waters 410 RI detector against linear poly(methyl methacrylate) standards in THF (1 mL/min) at 35°C with toluene as an internal standard.

RESULTS AND DISCUSSION

The ATRP of *n*BMA using the commercially available ligand PMDETA was investigated. The effects of the temperature of the polymerization, the copper catalyst, and the structure of the initiator were all determined. The degree of polymerization was kept constant at DP = 100. Based on prior results using the PMDETA ligand in ATRP of tBA, the solvent used for the polymerizations was acetone, which promoted a better solubility of the catalyst in the relatively nonpolar *n*BMA^[27]. The molecular weights were determined against linear poly(methyl methacrylate) (PMMA) standards and although the trends in the molecular weight behavior are discussed, the actual numbers produced from the GPC analysis are not. This is because the behavior of poly(*n*-butyl methacrylate) in solution may differ from that of PMMA, resulting in inaccurate experimental molecular weights.

Temperature Effects

The results of the ATRP reactions performed at various temperatures are detailed in Fig. 1. The temperature was initially 60°C, but the reactions were poorly controlled, with high experimental molecular weights and relatively broad molecular weight distributions. The temperature was then lowered to 50°C and then further to room temperature. The semilogarithmic plot in Fig. 1(a) shows that the rate of the polymerization run at 50°C (circles) had a constant concentration of active species throughout the polymerization and the one at room temperature stopped at about 60% monomer conversion (squares). The molecular weight behavior was similar for both polymerizations (Fig. 1b), with experimental molecular weights increasing linearly with conversion and narrow molecular weight distributions ($M_w/M_n < 1.2$). However, the molecular weight no longer increased in the room temperature reaction once the polymerization stopped.

To fully understand this polymerization, the traces obtained from the GPC analysis must be considered. Figure 2 contains the GPC traces for the same ATRP of *n*BMA in acetone detailed in Fig. 1. Even though the kinetics plot did not indicate that excessive termination was occurring in the reaction, there was tailing to lower molecular weights to indicate that there were dead chains in the reaction. This can also result from slow initiation; however, this is not evident in the kinetic plot either. Tailing often results if the rate of the reaction is too fast, *i.e.* the concentration of active species is too high. To lower the concentration of active species in ATRP, the equilibrium constant must be adjusted. Since lowering the temperature of the reaction further did not appear to be a reasonable route, which should alter the equilibrium constant, other aspects of the polymerization were investigated to try to eliminate this behavior.

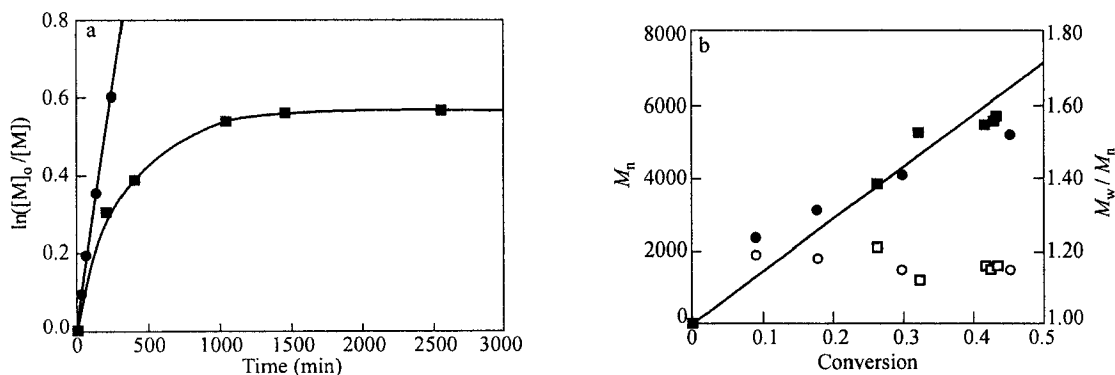


Fig. 1 Plots of (a) $\ln([M]_0/[M])$ versus time and (b) M_n (closed) and M_w/M_n (open) versus conversion for the ATRP of *n*BMA initiated by ethyl 2-bromoisobutyrate, catalyzed by CuCl/PMDETA in 50% acetone at various temperatures
 $[n\text{BMA}] = 3.2$ mol/L, $[\text{RX}] = 32$ mmol/L, $[\text{CuCl}] = [\text{PMDETA}] = 16$ mmol/L; (●, ○) = 50°C, (■, □) = room temperature

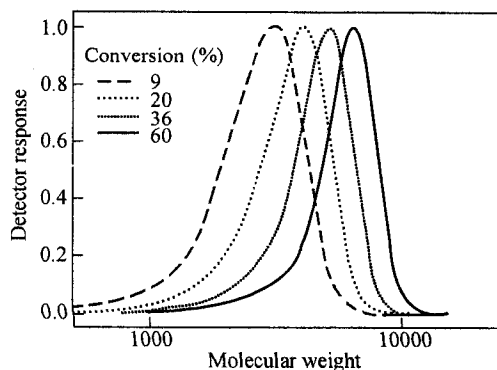
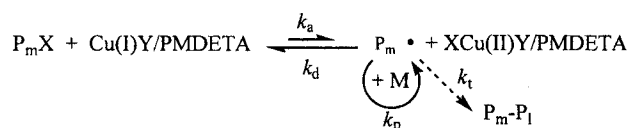


Fig. 2 GPC traces for the ATRP of *n*BMA initiated by ethyl 2-bromoisobutyrate, catalyzed by CuCl/PMDETA in 50% acetone at 50 °C
 $[n\text{BMA}] = 3.2 \text{ mol/L}$, $[\text{RX}] = 32 \text{ mmol/L}$, $[\text{CuCl}] = [\text{PMDETA}] = 16 \text{ mmol/L}$

Catalyst Effects

Adding Cu(II) to an ATRP reaction can affect the equilibrium by shifting it toward the dormant species and slowing down the rate, according to Scheme 1 (where P_mX is the dormant polymer chain, $\text{P}_m^\bullet$ is the active polymer chain, k_a is the rate constant of activation, and k_d is the rate constant of deactivation). The same effect can also be observed by lowering the catalyst concentration. Both these adjustments to the polymerization result in a decreased concentration of active species.



Scheme 1

Figure 3 shows the results for these attempts at achieving better control over the ATRP of *n*BMA using these approaches. The rate of the polymerization when either Cu(II)Cl₂/PMDETA was added (squares) or the catalyst concentration was decreased (triangles) was not constant, in contrast to the reaction run with a higher concentration of catalyst and no added Cu(II)Cl₂ (circles, Fig. 3a). The molecular weight behavior was similar in all the polymerizations initially, with a linear increase in the experimental molecular weights with conversion and narrow molecular weight distributions. However, once the rates began to decrease in the altered polymerizations, the molecular weights no longer increased, indicating a significant proportion of dead chains. Adjusting the equilibrium using these techniques was not successful.

Initiator Effects

Initiators of various reactivities were used for the ATRP of *n*BMA. EBriB may not be the best initiator for this polymerization due to the back strain effect, which can result in poor initiator efficiency and potentially increase the amount of termination in the reaction^[79–88]. In order to test this hypothesis, 2-bromopropionitrile^[89–91] (BPN) was used as the initiator with both Cu(I)Br and Cu(I)Cl as the copper(I) species for the ATRP at 60 °C. The results are presented in Fig. 4.

It is obvious from Fig. 4(a) that the concentration of the active species in these two polymerizations is decreasing with time. There is no difference between the reactions catalyzed by either Cu(I)Br or Cu(I)Cl, in terms of neither the rate of the polymerization nor the molecular weight evolution. The experimental molecular weights increase linearly with increasing monomer conversion, and the molecular weight distributions are narrow (Fig. 4b), however, the molecular weights are significantly higher than in the EBriB reaction, suggesting the initiation efficiency is lower here. There is still tailing to lower molecular weights in the GPC traces (Fig. 5), indicating that a portion of the chains are either dead or are growing slowly, as was the case for the EBriB initiated reaction run under similar conditions.

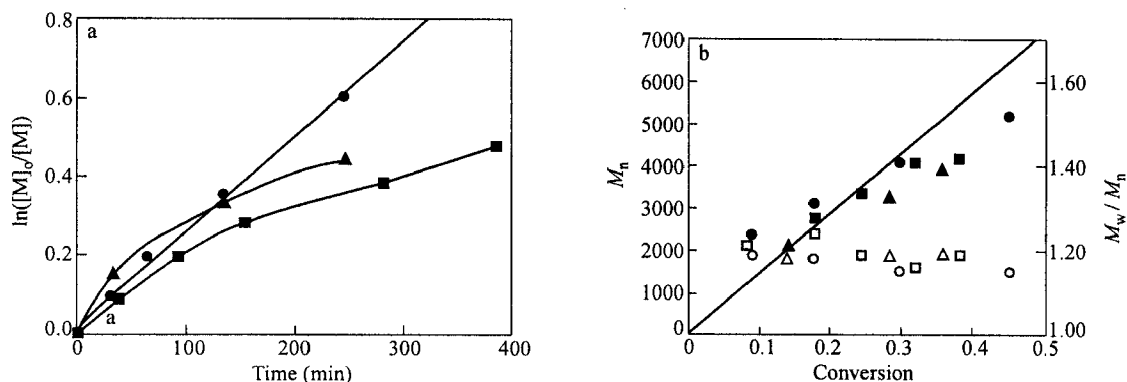


Fig. 3 Plots of (a) $\ln([M]_0/[M])$ versus time and (b) M_n (closed) and M_w/M_n (open) versus conversion for the ATRP of *n*BMA initiated by ethyl 2-bromoisobutyrate, catalyzed by CuCl/PMDETA in 50% acetone at various catalyst concentrations at 50°C [*n*BMA] = 3.2 mol/L, [RX] = 32 mmol/L, (●, ○): [CuCl] = [PMDETA] = 16 mmol/L; (▲, △): [CuCl] = [PMDETA] = 8 mmol/L, (■, □): [CuCl] = 16 mmol/L, [CuCl₂] = 0.8 mmol/L, [PMDETA] = 16.8 mmol/L

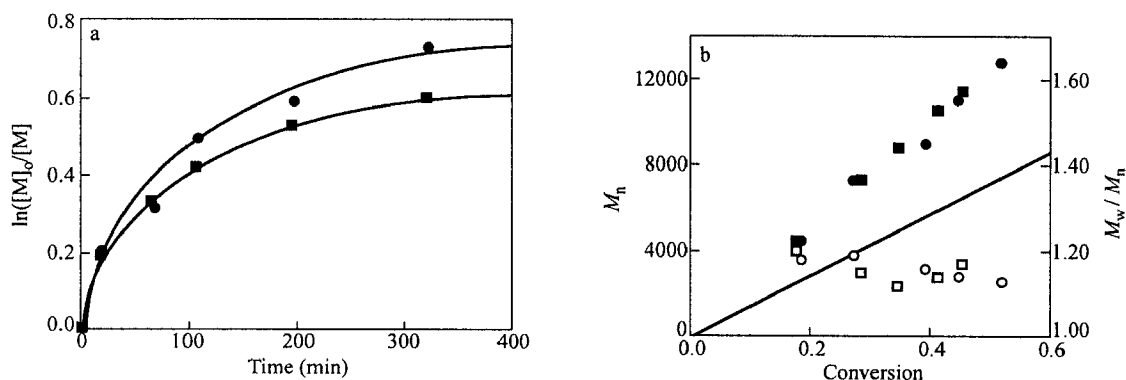


Fig. 4 Plots of (a) $\ln([M]_0/[M])$ versus time and (b) M_n (closed) and M_w/M_n (open) versus conversion for the ATRP of *n*BMA initiated by 2-bromopropionitrile, catalyzed by Cu(I)/PMDETA in 50% acetone with various Cu(I) species at 60°C [*n*BMA] = 3.2 mol/L, [RX] = 32 mmol/L, [Cu(I)] = [PMDETA] = 16 mmol/L; (●, ○): CuCl, (■, □): CuBr

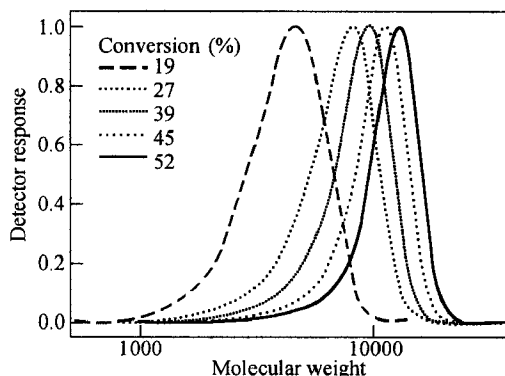


Fig. 5 GPC traces for the ATRP of *n*BMA initiated by 2-bromopropionitrile, catalyzed by CuCl/PMDETA in 50% acetone at 60°C [*n*BMA] = 3.2 mol/L, [RX] = 32 mmol/L, [CuCl] = [PMDETA] = 16 mmol/L

The results of the above reactions prompted an experiment where the temperature was lowered to 50°C to note the effect on the polymerization. Figure 6 shows that lowering the temperature decreased the rate slightly, however, some termination is still evident based on the curvature of the slope in Fig. 6(a). The experimental molecular weights are lower than previously, suggesting a higher initiation efficiency and there is little difference in the molecular weight distributions from the polymerization run at 60°C (Fig. 6b). The conditions for this polymerization still do not seem optimal, so the search for better initiators continued.

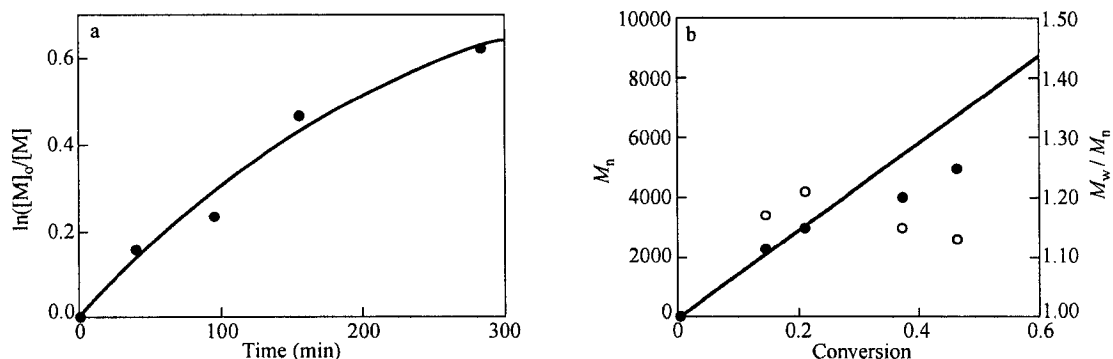


Fig. 6 Plots of (a) $\ln([M]_0/[M])$ versus time and (b) M_n (●) and M_w/M_n (○) versus conversion for the ATRP of *n*BMA initiated by 2-bromopropionitrile, catalyzed by CuCl/PMDETA in 50% acetone at 50°C [*n*BMA] = 3.2 mol/L, [RX] = 32 mmol/L, [CuCl] = [PMDETA] = 16 mmol/L

When the EBriB and BPN were added to the above reactions, the light green solutions immediately became much deeper and more intense in color, indicating some of the copper(I) had been converted to copper(II). Since these initiators were bromine-based, chloro-terminated initiators were substituted into the polymerization to note the effect. Both TsCl^[92] and TCE^[93] were used in conjunction with Cu(I)Br/PMDETA for ATRP of *n*BMA.

Figure 7 shows the results of the polymerizations initiated by TsCl and TCE under identical conditions. The rates of these two polymerizations were slower than when the EBriB and CuCl/PMDETA were used. The TsCl reaction (circles) was slightly faster than the TCE reaction (squares). The molecular weight evolution was similar for both polymerizations (Fig. 7b), with a linear increase in the experimental molecular weights with increasing conversion and narrow molecular weight distributions.

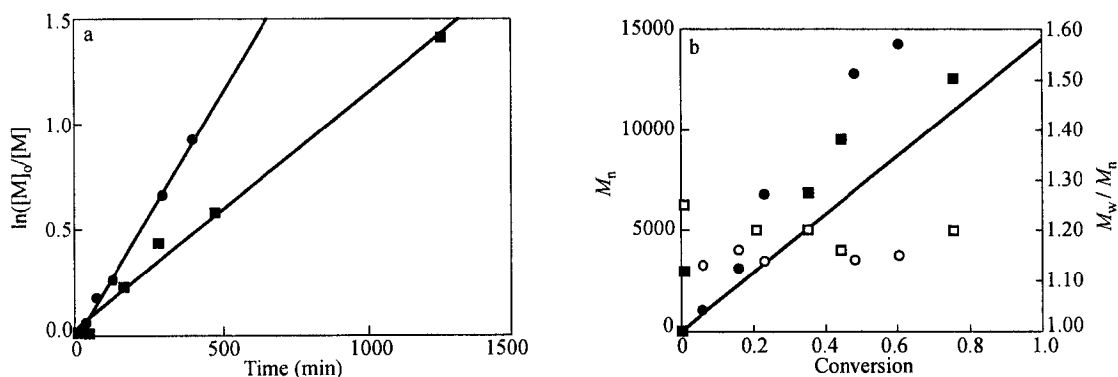


Fig. 7 Plots of (a) $\ln([M]_0/[M])$ versus time and (b) M_n (closed) and M_w/M_n (open) versus conversion for the ATRP of *n*BMA initiated by chlorine-terminated initiators, catalyzed by CuBr/PMDETA in 50% acetone at 60°C [*n*BMA] = 3.2 mol/L, [RX] = 32 mmol/L, [CuBr] = [PMDETA] = 16 mmol/L; (●, ○): *p*-toluenesulfonyl chloride, (■, □): 2,2,2-trichloroethanol

The GPC traces for the TCE initiated polymerization are shown in Fig. 8. The tailing has been reduced significantly, resulting in symmetrical distributions, even at higher conversions. The GPC traces for the TsCl-initiated reaction were similar to those in Fig. 2 and 5. While the tailing has been eliminated using TCE, there is a noticeable high molecular weight shoulder on the GPC traces at higher conversions. TCE appears to be acting as a multifunctional initiator in this system, producing some macromolecules that will contain two active sites per chain. The ability of 1,1,1-trichloroalkanes to act as multifunctional initiators has been observed in the ATRP of styrene and MMA^[93, 94]. Unfortunately, the ratio of the rates of initiation from the sites is constant and cannot be altered by modifying the experimental conditions. Increasing the catalyst concentration only serves to increase the rates of both reactions, not enhance one over the other (Table 1 and Fig. 9).

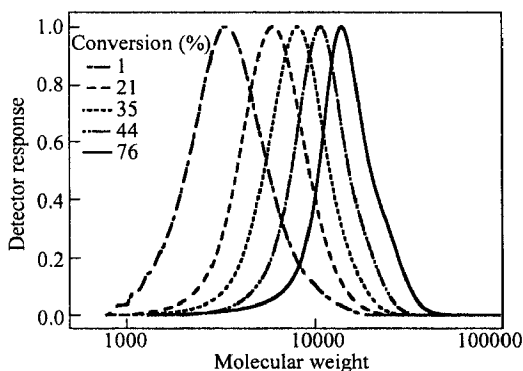


Fig. 8 GPC traces for the ATRP of *n*BMA initiated by 2,2,2-trichloroethanol, catalyzed by CuBr/PMDETA in 50% acetone at 60°C
[*n*BMA] = 3.2 mol/L, [RX] = 32 mmol/L, [CuCl] = [PMDETA] = 16 mmol/L

Table 1. Experimental results for the ATRP of *n*BMA initiated by 2,2,2-trichloroethanol, as detailed in Fig. 9

Sample	Time (min)	Conversion (%) ^a	M_n^b	M_w/M_n
1	25	3	2000	1.23
2	60	13	3260	1.20
3	143	24	4690	1.17
4	240	39	8320	1.13
5	370	53	12530	1.19
6	1320	89	21530	1.17

^a As determined from GC analysis

^b Determined against linear PMMA standards in THF

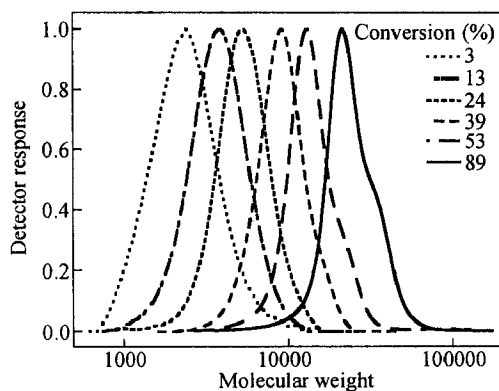


Fig. 9 GPC traces for the ATRP of *n*BMA initiated by 2,2,2-trichloroethanol, catalyzed by CuBr/PMDETA in 50% acetone at 60°C
[*n*BMA] = 3.2 mol/L, [RX] = 32 mmol/L, [CuCl] = [PMDETA] = 32 mmol/L

CONCLUSIONS

Using the Cu(I)/PMDETA system for ATRP of *n*-butyl methacrylate is challenging. The catalyst system is inherently very active, promoting a fast rate of polymerization, which, when combined with the reactive methacrylate-based monomers, results in a polymerization that is difficult to control. This system resembles another very active Me₆TREN/CuBr catalytic system applied to MMA polymerization^[95]. The key to controlling the polymerization is to adjust the concentration of active species through adjusting the ATRP equilibrium. Ethyl 2-bromoisobutyrate in conjunction with Cu(I)Cl/PMDETA resulted in controlled polymerization of *n*BMA, however, the tailing in the GPC traces indicated that either there were dead polymer chains or that slow initiation occurred. Using 2-bromopropionitrile as the initiator did not significantly improve the polymerization. Although the molecular weight distributions were narrow ($M_w/M_n < 1.15$), the rate of the polymerization decreased with time, indicating termination. Switching to the chloride-based initiators, *p*-toluenesulfonyl chloride or 2,2,2-trichloroethanol, with Cu(I)Br/PMDETA as the catalyst, produced a better controlled polymerization with polymer chains that appear to be fully functional. The drawback to using 2,2,2-trichloroethanol, however, is that a second site can initiate a chain and the resulting polymers are difunctional.

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