5958 *Macromolecules* **1998,** *31,* 5958−5959

Controlled/“Living” Radical Polymerization. Atom Transfer Radical Polymerization of Acrylates at Ambient Temperature

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Received May 7, 1998
Revised Manuscript Received July 6, 1998

Significant progress has been made in controlled/“living” radical polymerization in recent years.[1] Several new methodologies have been developed to provide control over both molecular weight and molecular weight distribution. One of the approaches is the transition metal catalyzed atom transfer radical polymerization (ATRP).[2−8] Of all the transition metals investigated, copper appears to be the most promising in terms of price and versatility. A variety of monomers, including styrene[9] and its derivatives,[10] (methyl)acrylic esters,[11,12] and acrylonitrile,[13] can be polymerized in a well-controlled fashion with degree of polymerization (DP) predetermined by the ratio of the change in monomer concentration and initial initiator concentration (DP = Δ[monomer]/[initiator]$_o$) with polydispersities (M_w/M_n) as low as 1.05.

Recently we have reported the use of multidentate amines as the ligands for copper mediated ATRP.[14] Multidentate amines are less expensive, the copper complexes with these ligands generate less color to the system, and rates of polymerization are faster compared to complexes with 2,2′-bipyridine and its derivatives. In this paper, we report an improved ATRP system for the polymerization of acrylates using a new multidentate amine ligand, tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN, Figure 1). The new system allows for the well-controlled polymerization of acrylates at ambient temperature with very fast polymerization rates. Me$_6$TREN can be easily prepared in a one-step synthesis using the literature procedure from commercially available tris(2-aminoethyl)amine (TREN).[15]

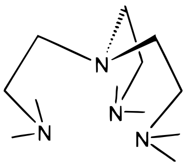

Figure 1. Structure of Me$_6$TREN.

Table 1. Bulk ATRP of Acrylates Using CuBr/Me$_6$TREN as the Catalyst

entry	[catalyst]$_o$/[2-EBP]$_o$	time (h)	conv (%)	$M_{n,Cal}$	$M_{n,SEC}$	f^a	M_w/M_n
1^b	1.0	0.50	66	13200	17900	0.74	1.24
2^b	0.5	0.75	63	12600	15700	0.80	1.15
3^b	0.2	1.00	57	11400	12600	0.90	1.10
4^b	0.1	1.00	41	8200	9100	0.90	1.09
5^c	0.2	0.75	76	15200	18000	0.84	1.10
6^d	0.1	0.10	8	1600	773500	0.002	2.98

[a] $f = M_{n,Cal}/M_{n,SEC}$. [b] Conditions: 22 °C; [MA]$_o$/[2-EBP]$_o$ = 232. [c] Conditions: 22 °C; [BA]$_o$/[2-EBP]$_o$ = 156. [d] TREN was used as the ligand with MA as the monomer.

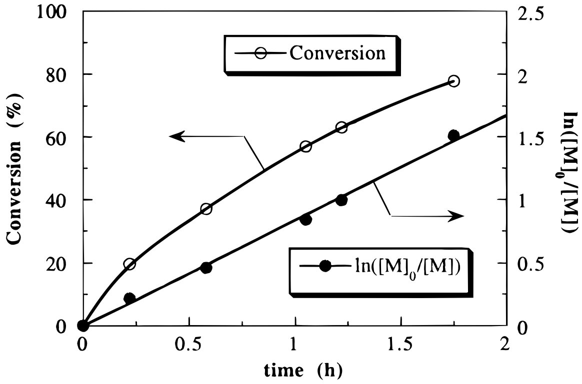

Figure 2. Kinetic plot for the bulk ATRP of MA using Me$_6$-TREN as the ligand. Conditions: 22 °C; [MA]$_o$ = 10.8 M, [2-EBP]$_o$ = 0.047 M, and [CuBr]$_o$ = [Me$_6$TREN]$_o$ = 0.0094 M.

When methyl acrylate (MA) was polymerized using ethyl 2-bromopropionate (2-EBP) as the initiator and CuBr/Me$_6$TREN as the catalyst (1.0 equiv to initiator) in a sealed tube at room temperature, the polymerization reached 85% conversion within 15 min to yield poly(methyl acrylate) (PMA) of $M_{n,SEC}$ = 21 600 ($M_{n,Cal}$ = 17 000) and M_w/M_n = 1.18. The polymerization was exothermic, causing the solution inside the tube to boil. Better heat transfer was achieved when the polymerization was carried out in a water bath. The representative results for the ATRP of acrylates using CuBr/Me$_6$TREN as the catalyst are summarized in Table 1. The data in Table 1 indicates that controlled polymerizations were achieved with different catalyst-to-initiator ratios and that all the polymerizations showed high initiator efficiencies (initiator efficiency $f = M_{n,Cal}/M_{n,SEC}$) and low polydispersities. Significantly, a catalyst-to-initiator ratio of 0.1 was enough to prepare PMA with a polydispersity as low as 1.09. With a decrease of the catalyst-to-initiator ratio, the rate of polymerization decreased and the initiator efficiency slightly increased. The relatively lower initiator efficiency at higher catalyst-to-initiator ratio was likely due to the higher radical concentration at the beginning of the polymerization which resulted in the termination of some of the propagating chains by radical coupling reactions. Other acrylates, such as butyl acrylate (Table 1, entry 5), were also polymerized under similar conditions to yield well-defined polymers with low polydispersities. The employment of unmethylated TREN as the ligand resulted in the uncontrolled polymerization of MA with a much higher than predicted molecular weight and high polydispersity (Table 1, entry 6).

When polymerization of MA was carried out using 2-EBP as the initiator and 0.2 equiv of CuBr/Me$_6$TREN to initiator at 22 °C, the reaction solution quickly became viscous, and the conversion of MA reached 80% within 2 h. The reaction mixture was light green and homogeneous at the beginning, but turned heterogeneous at higher conversions. The heterogeneity was likely due to the low solubility of copper(II), generated by irreversible chain termination reactions, in the polymerization solution. A linear plot of ln([M]$_o$/[M]) vs time was observed throughout the polymerization, indicating a constant number of growing chains (Figure 2). The molecular weight of the resulting PMA increased linearly with conversion, and the measured molecular weights were close to the calculated values

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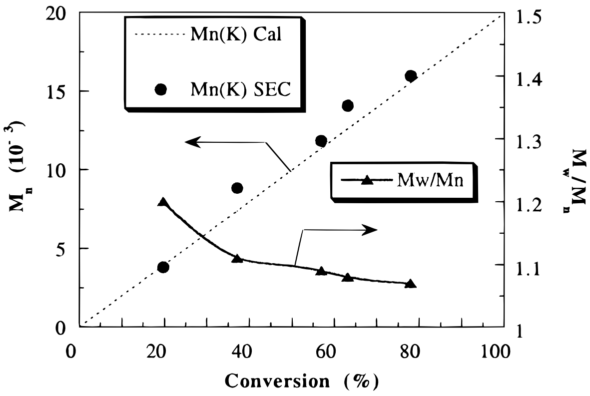

Figure 3. Dependence of molecular weight, $M_{n,SEC}$, and molecular weight distribution, M_w/M_n, on monomer conversion for the ATRP of MA using Me_6TREN as the ligand. See Figure 2 for conditions.

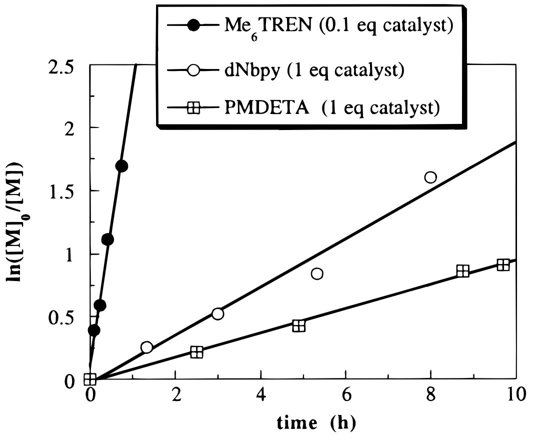

Figure 4. Effect of different ligands on the rate of bulk ATRP of MA at 50 °C: $[MA]_o = 10.8$ M; $[2\text{-EBP}]_o = 0.047$ M. For Me_6TREN as the ligand: $[CuBr]_o = [Me_6TREN]_o = 0.0047$ M. For dNbpy and PMDETA as the ligands: $[CuBr]_o = 0.047$ M; $[dNbpy]_o = 0.094$ M; $[PMDETA]_o = 0.047$ M.

(Figure 3). The molecular weight distribution remained quite low ($M_w/M_n < 1.2$). These results indicate that the rate of equilibration between the active radicals and dormant species is fast, and that termination and other side reactions are insignificant.

When polymerizations of MA were carried out using 0.2 equiv (to 2-EBP initiator) of CuBr/Me_6TREN, 1 equiv of CuBr/dNbpy, and 1 equiv of CuBr/PMDETA as the catalyst at 50 °C, dramatic differences in polymerization rate were observed (Figure 4). For polymerization using 0.2 equiv of CuBr/Me_6TREN, the reaction reached a conversion of 82% in 45 min. For polymerization using 1 equiv of CuBr/dNbpy, the same conversion was reached in 480 min. The rate differences can be ascribed to the differences in redox potentials, conformation changes, and solubilities of the coordination complexes between copper and different ligands. Control over the polymerization was maintained, despite the drastic increase in the polymerization rate, when CuBr/Me_6TREN was used. Polymers with predicted molecular weights and low polydispersities ($M_w/M_n \approx 1.1$) were obtained.

In conclusion, controlled/"living" atom transfer radical polymerization (ATRP) of acrylates has been successfully carried out at ambient temperature using CuBr/Me_6TREN as the catalyst. The polymers obtained have molecular weights close to the theoretical values and narrow molecular weight distributions. The rate of polymerization is significantly faster than that with dNbpy or PMDETA as the ligand. Well-defined polyacrylates can even be obtained with a 0.1 ratio of catalyst to initiator. Further studies concerning the use of Me_6TREN as the ligand for the ATRP of other monomers are in progress.

Acknowledgment. Financial support from the industrial members of the ATRP Consortium at Carnegie Mellon University is gratefully acknowledged.

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MA980725B