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Communications to the Editor

Atom Transfer Radical Polymerization of Methyl Methacrylate with Polyethylene-functionalized Ligands

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Atom transfer radical polymerization (ATRP) has been intensively studied since it can be applied to a wide variety of monomers and can lead to interesting polymer architectures.[1] Recent studies have produced many improvements in ligands, metal catalysts and initiators.[2,3] However, the drawback of removing the metal catalyst from the polymer has hindered the use of ATRP. A catalyst that is immobilized on a solid surface could be easily removed from the reaction mixture and would overcome this limitation. Recently, Haddleton and co-workers[4] developed an immobilized catalyst on silica gel that affords PMMA with polydispersity from 1.34 to 1.59 and some control of molecular weight. Matyjaszewski and co-workers[5] also studied similar surface-immobilized ligands. We used Haddleton's systems with comparable results in terms of molecular weight and molecular weight distribution. The lack of control may be due to the heterogeneous nature of the process. Limited ligand mobility on the surface does not provide a reasonable exchange rate between the active radical and the catalyst complex. This may lead to a higher molecular weight than expected and broader molecular weight distribution.

These results prompted us to consider using low molecular weight polyethylene (PE) end-capped with appropriate ATRP ligands. PE is soluble under reaction conditions but precipitates from solution at room temperature due to the crystallization of PE, a property that has been exploited by Bergbreiter and co-workers in the design of catalyst systems.[6,7] The aim of this study is to examine the use of a PE−ligand system in ATRP to eliminate the additional steps of removing metal contamination of the polymer. The synthesis of the PE−ligand is shown in Scheme 1.

Hydroxy-functionalized PE (PE−OH) was prepared using the method of Shea and co-workers.[8] We obtained PE−OH in 73% yield with $M_n = 2000$. PE−OH was reacted with methanesulfonyl chloride in toluene at 90 °C for 3 h to afford a quantitative yield of PE−O−SO_2−CH_3.[9] The sulfonyl chloride was quantitatively converted to PE−N_3 by reaction with sodium azide.[10] The azide functional group was converted to the primary amine (PE−NH_2) by reaction with triphenyl phosphine; yield = 83%.[11] The PE−ligand was obtained by reacting PE−NH_2 with pyridine 2-carboxyaldehyde; yield = 95%.[12] ^1H NMR spectra support the structure of the above products.[13]

Methyl methacrylate (MMA) was polymerized by ATRP at 100 °C in toluene using 2:1:1 PE−ligand:CuBr:ethyl 2-bromoisobutyrate and [MMA]:[initiator] = 200:1.[14] The results are summarized in Table 1. The plot of M_n vs conversion (Figure 1) shows that M_n corresponds closely at low conversion with theoretical M_n as a function of conversion for a living system. Deviation at high conversions may be attributed to some chain termination, which is more prevalent in this system as compared to traditional ATRP possibly due to the long reaction times. The first-order kinetic plot (Figure 2) also deviates from linearity at higher conversions, supporting the contention that some termination is occurring. Although the reaction rate was not as fast as the traditional ATRP reaction using small ligands, it reached 92% conversion in 26 h. We speculate that the slow propagation rate is due to the large size of macromolecular ligand. The activation−deactivation cycle in ATRP requires two bidentate ligands and the growing polymer chain. For our system, three oligomer/polymer chains (two PE−ligands and one growing chain) must participate in this cycle.

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Scheme 1. Synthesis of PE−ligand from PE−OH Precursor.

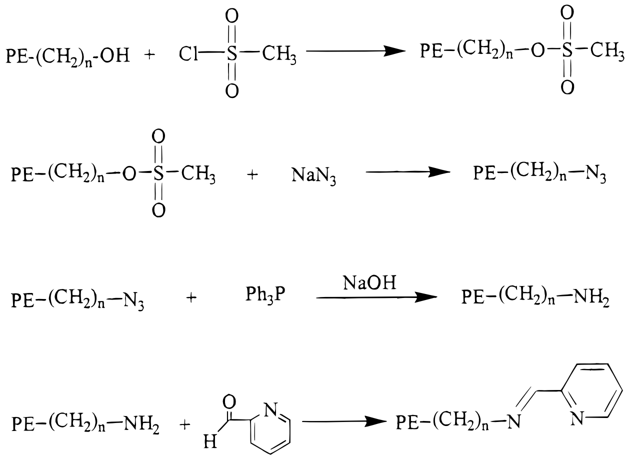

Table 1. Polymerization of MMA in Toluene Using PE−Ligand[a]

time (h)	convn (%)	M_n, theor	M_n, exptl	M_w/M_n
2	24	4800	6400	1.22
4	45	9100	9000	1.41
6	55	11300	11300	1.44
26	92	18400	15600	1.45

[a] Experimental conditions: [ligand]:[initiator]:[CuBr]:[MMA] = 2:1:1:200; conversion measured by ^{1}H NMR; M_n, M_w determined by GPC relative to PMMA standards.

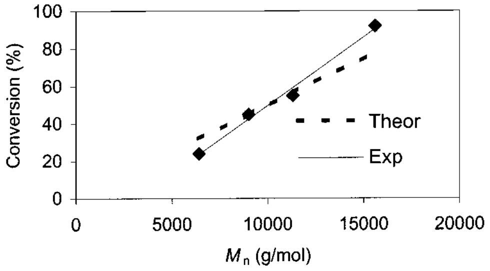

Figure 1. M_n vs percent conversion for MMA polymerization using PE−ligand for ATRP.

This study demonstrates the feasibility of using a PE−ligand in ATRP. After the PE-functionalized ligand was precipitated, the Cu remained complexed with the ligand affording a clean and colorless PMMA solution.[15] PMMA from this reaction required no purification other than a simple decantation. Compared with immobilized silica gel ligand, this new polymeric PE−ligand offered somewhat better control of molecular weight and polydispersity with improved percent conversion. However, ways to decrease the reaction time in order to decrease termination reactions need to be investigated.

Other aspects of these polymerizations being considered are the effect of PE molecular weight on the polymerizations and the possibility of PE with multidentate ligands.

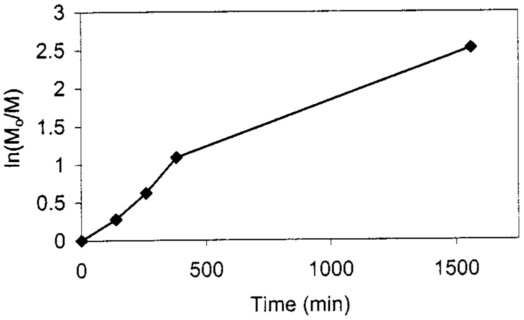

Figure 2. First-order kinetic plot: ln(M_o/M) vs time.

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(13) ^{1}H NMR (300 MHz, d_6-benzene, 60 °C) results. PE−OH: (δ) 3.36 (t, 2H, $-CH_2-OH$), 1.32 (b, $-(CH_2)_n-CH_2-OH$), 0.87 (m, CH_3-CH_2-, $-CH(CH_3)-$). PE−O−SO$_2$−CH$_3$: (δ) 3.93 (t, 2H, $-CH_2-O-SO_2-CH_3$), 2.11 (s, 3H, $-CH_2-O-SO_2-CH_3$). PE−N$_3$: (δ) 2.87 (t, 2H, $-CH_2-N_3$). PE−NH$_2$: (δ) 2.53 (t, 2H, $-CH_2-NH_2$). PE−ligand: (δ) 3.52 (t, 2H, $-CH_2-N{=}CH-$), 8.54 (s, 1H, $-CH_2-N{=}CH-$), 6.70 (t, 1H), 7.18 (t, 1H), 8.15 (d, 1H), 8.48 (d, 1H).

(14) Reaction conditions for ATRP reaction of MMA: A 25-mL Schlenk flask was charged with toluene (10 mL). CuBr (10 mg, 7 × 10^{-5} mol), PE ligand (0.304 g, 15 × 10^{-5} mol), and MMA (1.5 g, 0.015 mol) were added under argon flow. The solution was degassed by three freeze−pump−thaw cycles and then heated in an oil bath at 100 °C until the PE−ligand had dissolved. Initiator (ethyl 2-bromoisobutyrate, 0.0146 g, 7 × 10^{-5} mol) was added and the solution was refluxed at 100 °C for 26 (h) Aliquots were removed at time intervals to determine percent conversion (by ^{1}H NMR) and molecular weight (by GPC). When the reaction was complete, the flask was cooled to room temperature and then immersed in an ice bath. The solution was decanted from PE−ligand/catalyst and the polymer was precipitated in methanol (500 mL). Polymer was collected by filtration and dried under vacuum at 70 °C overnight.

(15) Our conclusion that Cu was removed is qualitatively based on visual inspection. We are currently performing quantitative experiments to more accurately measure the residual Cu after PE precipitation.

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