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Use of JandaJel Resins for Copper Removal in Atom Transfer Radical Polymerization

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ABSTRACT: Atom transfer radical polymerization (ATRP) ligands were supported onto JandaJel resins to allow for easy removal of the catalyst complex from the reaction mixture. Compared to divinylbenzene cross-linked resins, JandaJels have increased organic solvent compatibility and site accessibility due to the flexible cross-linker. These resins were chosen as the support in an attempt to obtain fast reaction times, good molecular weight control, and narrow polydispersity. The JandaJel ligands were used in ATRP of methyl methacrylate (MMA), styrene, and 2-(dimethylamino)ethyl methacrylate (DMAEMA). The MMA and DMAEMA polymerizations proceeded quickly to high conversion (>90%) and were well-controlled. The styrene polymerization was sluggish and proceeded only to 63% conversion. Recyclability of the catalyst was demonstrated by reusing the catalyst for a second ATRP reaction. A PMMA-*b*-PDMAEMA copolymer was also synthesized using JandaJel ligands. After polymerization was complete, the catalyst/ligand complex was easily removed by filtration. Elemental analysis indicated 0.05−0.07% residual copper in the unpurified polymers.

Introduction

Advances in atom transfer radical polymerization (ATRP) have made it a viable method for the synthesis of a wide variety of polymers in a controlled fashion.[1] A disadvantage of this method is the contamination of the polymer with a ligand/metal complex. Because of the expense of catalysts and postpolymerization workup, it is favorable to have a clean polymer solution after reaction and the potential to recycle the catalysts. Surface-immobilized catalysts have shown promise in ATRP systems as a way to overcome this limitation.[2−4] Disadvantages of these systems, as compared to traditional ATRP conditions, are higher molecular weights than predicted, broader molecular weight distributions, and longer reaction times. A possible explanation for these sluggish reaction rates is the heterogeneous conditions that cause slow diffusion of the polymer chain to the silica or polystyrene bead surface. Recently, Zhu and co-workers[5] reported using silica-supported multidentate amine ligands in ATRP to afford low polydispersity and good molecular weight control for PMMA to about 80% conversion. Zhu and co-workers have also used polyethylene and polyethylene−poly(ethylene glycol) supports for ligand supports for ATRP.[6,7] An immobilized/soluble hybrid catalyst system for ATRP that overcomes the diffusion limitation of heterogeneous catalyst systems was developed by Matyjaszewski and co-workers.[8,9] In our group, we have investigated polyethylene[10] and “precipitons”[11] functionalized with ATRP ligands to achieve homogeneous reaction conditions combined with ease of catalyst removal. As an extension of our work, we hope to use a solid supported catalyst to polymerize a wider variety of monomers under various conditions.

In this work, we present the use of JandaJel resins as solid supports for ATRP. As compared to divinylbenzene cross-linked resins, JandaJels have increased homogeneity, organic solvent compatibility, and site accessibility due to the flexible cross-linker.[12] For immobilized catalyst systems, the major factor controlling the polymerization is the deactivation step, which is affected by the mobility of the immobilized catalyst particles and the diffusion of the polymer chains in the reaction mixture. A bulky support hinders diffusion to the catalyst site and may become rate determining. We speculated that JandaJel resins functionalized with nitrogen ligands for ATRP would behave more like a homogeneous system and would still allow for easy catalyst removal from ATRP reactions (since the ligand is insoluble). The synthesis and structures of the two JandaJel ligands that were used are shown in Figures 1 and 2. The precursors to these ligands are commercially available resins functionalized with −OH or $-NH_2$ (1.0 mmol functionality per gram).

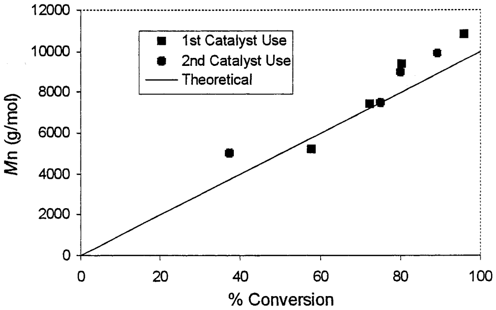

Figure 1. M_n vs conversion for ATRP of MMA using the JandaJel-imine ligand (**1**).

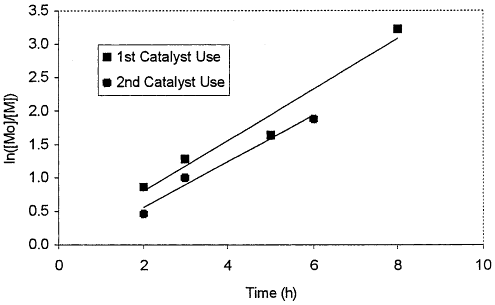

Figure 2. First-order kinetic plot for ATRP of MMA for first and second catalyst uses for JandaJel-imine ligand (**1**).

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Experimental Section

Materials. *N,N,N′,N′*-Tetraethyldiethylenetriamine (TEDETA, 90%) and 2-pyridinecarboxaldehyde were vacuum-distilled before use. JandaJel−NH$_2$ (100−200 mesh), JandaJel−OH (100−200 mesh), toluene, THF, acryloyl chloride, and triethylamine were all used as received from Aldrich. CuBr (98%) was purified as described in the literature.[13] Methyl methacrylate (MMA), styrene, and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were purchased from Aldrich and passed through basic alumina and were then stored under argon at 0 °C prior to use.

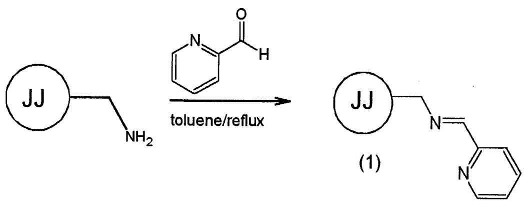
Preparation of JandaJel-Imine Ligand/CuBr Complex. JandaJel−NH$_2$ (typical loading 1.0 mmol N/g) was dispersed in toluene, and 2-pyridinecarboxaldehyde (2.0 mmol/g) was added. The dispersion was stirred vigorously at reflux for 24 h. The take-up of the aldehyde onto the support was monitored using ^{1}H NMR relative to an internal standard. The peak intensity at δ (ppm) 10.2 was used to determine the percent ligand supported onto the gel. 90% of the aldehyde reacted with the −NH$_2$ groups, resulting in supported ligands having functionality of 0.9 mmol/g. The insoluble gel was collected and washed with toluene 10 times and then dried in vacuo. For use in ATRP, CuBr and the supported ligand were thoroughly mixed in dry degassed toluene and extracted in a Soxhlet extractor for 48 h with toluene, dried in vacuo, and stored under an inert atomosphere.

Preparation of JandaJel−TEDETA Ligand. JandaJel−OH (typical loading of −OH functionality 1.0 mmol/g) was dispersed in anhydrous THF and cooled to 0 °C. Triethylamine (1.5 mmol/g) was added followed by dropwise addition of acryloyl chloride (1.5 mmol/g). The dispersion was stirred for 12 h, and the solids were collected by filtration and washed 10 times with water and 5 times with THF. The gel was dried in vacuo. The acrylate functional gel was dispersed in THF, and TEDETA (2.0 mmol/g) was added and the dispersion stirred for 48 h. The solids were collected, washed with THF, and dried in vacuo to afford supported TEDETA ligand. Elemental analysis indicated 2.5% N present (theoretical %N = 2.8%).

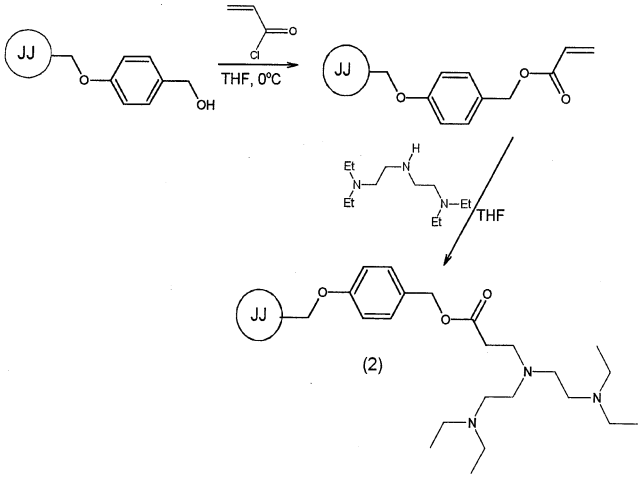
Characterization. ^{1}H NMR spectra were recorded on a Varian Gemini-300 spectrometer. Routine molecular weight analysis was performed by gel permeation chromatography (GPC) using a Waters 501 pump, a guard column, Waters HR2 and HR4 Styragel columns, a Waters 410 differential refractometer, and a Viscotek T60A dual detector. The eluent was THF, and the flow rate was 1.0 mL/min. M_n and M_w were determined using universal calibration. The copper content of the final polymer was determined by inductively coupled plasma optical emission spectroscopy by Galbraith Laboratories. The nitrogen content of the supported ligands was determined by elemental analysis by Galbraith Laboratories.

ATRP Procedure. A Schlenk flask was charged with CuBr (1 equiv) and JandaJel ligand (1.5 equiv), and the mixture was degassed with three vacuum/argon cycles. Via syringe, deoxygenated toluene (70:30, v/v toluene/monomer) and monomer (100 equiv, typical quantity monomer ~5 mL) were added. The solution was heated in an oil bath at the appropriate temperature: 100 °C for MMA and styrene; 60 °C for DMAEMA. Ethyl 2-bromoisobutyrate (1 equiv) was added, and the solution was heated at the reaction temperature until the reaction was complete. Aliquots were removed via syringe during the course of the reaction to determine percent conversion and molecular weight. Conversion was determined by placing a portion of the aliquot in an NMR tube with CDCl$_3$ and using ^{1}H NMR to compare peak intensity of monomer peaks to that of an internal standard (typically DMF or isobutyraldehyde). Molecular weight analysis was performed by diluting the sample with THF, filtering through a 0.4 μm filter to remove the insoluble ligand/CuBr complex, and removal of solvent to obtain the polymer sample which was subsequently used for GPC analysis. When the reaction was complete, the solution was cooled to room temperature and filtered using a coarse sintered glass filter to remove the catalyst complex. A sample of the decanted solution was used for UV−vis spectroscopic analysis for copper content. For elemental analysis for copper, the solvent was removed from the polymer solution in vacuo, and elemental analysis was performed on the unpurified polymer.

Scheme 1. Synthesis of JandaJel Ligand 1



Scheme 2. Synthesis of JandaJel Ligand 2



Preparation of PMMA-*b*-PDMAEMA Diblock. JandaJel ligand **1** (0.7 g, 6.3 × 10^{-4} mol ligand functionality) and CuBr (0.06 g, 4.2 × 10^{-4} mol) were complexed as described previously and placed in a Schlenk flask. The flask was degassed by three vacuum/argon cycles. Via syringe, deoxygenated toluene (10 mL) and monomer (4.2 g, 0.042 mol) were added. The solution was heated in an oil bath at 100 °C. Ethyl 2-bromoisobutyrate (0.08 mL, 4.2 × 10^{-4} mol) was added, and the reaction was allowed to proceed to 75% conversion (as determined by ^{1}H NMR relative to solvent). The solution was cooled to room temperature, and a sample was removed for molecular weight analysis. Volatiles (solvent and unreacted MMA) were removed by vacuum. Degassed DMAEMA (4.2 g, 0.027 mol) and toluene (10 mL) were added to the flask via syringe. The solution was heated to 60 °C, and samples were removed to determine conversion and molecular weight.

Results and Discussion

We first examined at ATRP of MMA using the JandaJel-imine ligand (**1**); the results are shown in Table 1 for the first and second catalyst uses. The polydispersity narrowed over the course of the ATRP reaction. Even though these PDIs are significantly higher than for a conventional ATRP of MMA, they are narrower than those for ATRP of MMA using ligands supported by DVB cross-linked PS resins (which were reported to be up to 10).[2] With a system such as this, we would expect a PDI higher than for a conventional reaction since there will be a diffusion effect on the deactivation reaction, which would not be present with a typical homogeneous ligand system. The reactions with the JandaJel ligands were reproducible.

Despite the broader polydispersity, these reactions proceeded with a linear increase of molecular weight with monomer conversion (Figure 1) and good control of molecular weight for both catalyst uses. At high conversions the molecular weights were higher than

Table 1. ATRP of MMA Using JandaJel-Imine Ligand (1)[a]

	time (h)	% conv	M_n(theo) (g/mol)	M_n(exp) (g/mol)	PDI
first catalyst use	2	58	5800	5200	1.40
	3	72	7200	7500	1.36
	5	80	8000	9400	1.32
	8	96	9600	10800	1.29
second catalyst use	2	37	3700	5000	1.81
	3	64	6400	7500	1.76
	5	71	7100	9000	1.52
	6	85	8500	9900	1.50

[a] Experimental conditions: [JandaJel ligand]:[ethyl 2-bromoisobutyrate initiator]:[CuBr]:[MMA] = 2:1:1:100; solvent = 3:1 v/v toluene/MMA; 100 °C. Conversion measured by ^{1}H NMR relative to an internal standard; M_n and M_w determined by GPC using universal calibration.

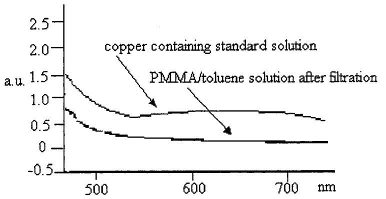


Figure 3. UV−vis spectrum for PMMA/toluene solution after ATRP reaction using the JandaJel-imine ligand (**1**).

predicted; this has been observed in the other reported heterogeneous ATRP systems. There was ~20% decreased activity (from the ratio of the slopes, k_{app}, of the first-order kinetic plots) for the second catalyst usage, which can be attributed to the presence of $CuBr_2$ (deactivator) due to oxidation of the catalyst, and the polydispersity was broader for the second catalyst usage. The first-order kinetic plot was linear for both the first use and for the recycled catalyst (Figure 2).

JandaJel ligands **1** and **2** were used for ATRP of MMA, DMAEMA, and styrene. After the reaction was complete, the solution was filtered to remove the solid catalyst/ligand complex. UV−vis spectroscopic analysis was done to analyze for copper in the polymer solution after filtration. Figure 3 shows that there is no copper detected in the polymer solution by UV analysis, as there is no absorbance at 680 nm where the copper/ligand complex absorbs.

The copper content of the resultant polymer was determined by elemental analysis. The copper content in the unpurified polymer samples ranged from 5 to 7% of the original copper used in the ATRP reaction. The polymer from this reaction required no purification other than simple decantation. For MMA and DMAEMA, the reactions were fast. The styrene reaction was sluggish and reached only 63% conversion and was not well controlled as evidenced by the broader polydispersities. The results are summarized in Table 2. The plot of M_n vs conversion (Figure 4) shows that M_n(exp) is in good agreement with M_n(theo) for all of the monomers. The reactions followed pseudo-first-order kinetics (Figure 5).

Data for the MMA polymerization with JandaJel ligand **2** are presented in Table 2 and indicate that both ligands behave similarly in ATRP reactions of MMA. The block copolymer PMMA-*b*-PDMAEMA was prepared by using PMMA−Br formed by ATRP using JandaJel ligand **1** to initiate polymerization of DMAEMA, indicating that the reaction by this supported CuBr catalyst results in polymer with active chain ends. The molecular weight of the PMMA block was 8000 g/mol at 75% conversion (M_n(theo) = 7500), and the resultant PMMA-*b*-PDMAEMA copolymer had M_n = 15 100 g/mol with the DMAEMA at 70% conversion; the GPC trace is shown in Figure 6.

Table 2. Polymerization of MMA, DMAEMA, and Styrene Homopolymers Using JandaJel Ligands 1 or 2

monomer (ligand)	time (h)	conv (%)	M_n(theo)[e] (g/mol)	M_n(exp)[e] (g/mol)	PDI
MMA (**1**)[a]	2	54	5400	4500	1.40
	4	74	7400	6400	1.36
	6	77	7700	9400	1.32
	9	93	9300	9900	1.29
MMA (**2**)[b]	2	30	3000	3200	1.25
	6	53	5300	5000	1.20
	8	75	7500	7600	1.15
	10	98	9800	9400	1.13
styrene (**1**)[c]	2	15	1500	1500	1.70
	6	29	2900	2400	1.62
	10	63	6300	5800	1.54
DMAEMA (**1**)[d]	0.5	37	5800	6000	1.85
	2	69	10800	9000	1.77
	3	84	13200	12500	1.54
	6	92	14400	14100	1.50

[a] [JandaJel ligand **1**]:[ethyl 2-bromoisobutyrate initiator]:[CuBr]:[MMA] = 2:1:1:100; solvent = 3:1 v/v toluene/MMA; 100 °C. [b] [JandaJel ligand **2**]:[ethyl 2-bromoisobutyrate initiator]:[CuBr]:[MMA] = 1.5:1:1:100; solvent = 3:1 v/v toluene/MMA; 100 °C. [c] Experimental conditions: [JandaJel ligand **1**]:[ethyl 2-bromoisobutyrate initiator]:[CuBr]:[styrene] = 2:1:1:100; solvent = 3:1 v/v toluene/styrene; 100 °C. [d] [JandaJel ligand **1**]:[ethyl 2-bromoisobutyrate initiator]:[CuBr]:[DMAEMA] = 2:1:1:100; solvent = 3:1 v/v toluene/DMAEMA; 60 °C. [e] Conversion measured by ^{1}H NMR relative to internal standard; M_n and M_w determined by GPC using universal calibration or reference to PMMA or PS standards.

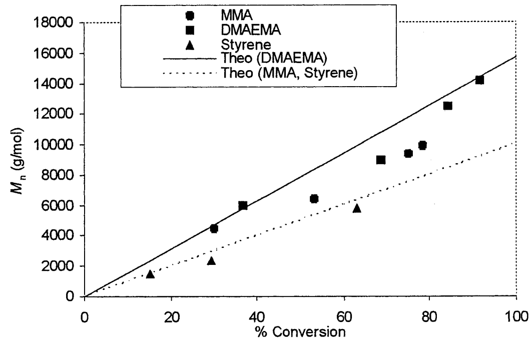


Figure 4. M_n vs conversion for ATRP of MMA, DMAEMA, and styrene using JandaJel ligand **1**.

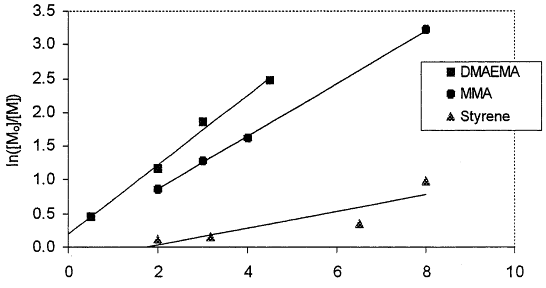


Figure 5. First-order kinetic plot for ATRP of MMA, DMAEMA, and styrene using JandaJel ligand **1**.

Conclusions

For immobilized catalyst systems, the major factor controlling the polymerization is the deactivation step, which is affected by the mobility of the immobilized catalyst particles and the diffusion of the polymer chains

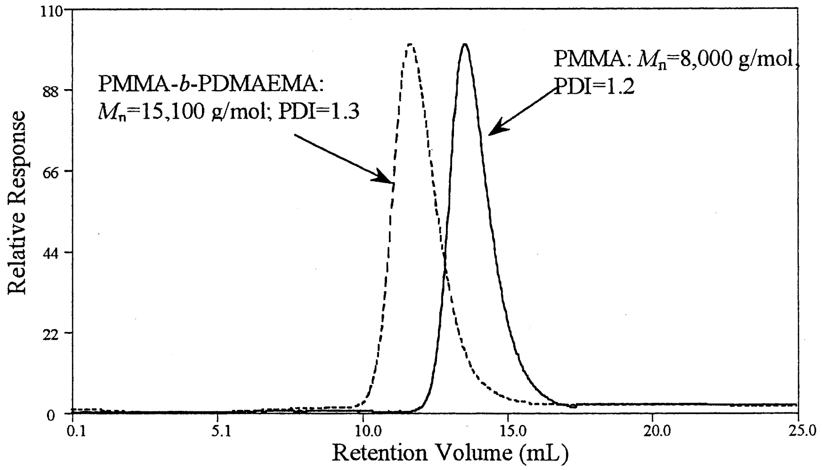


Figure 6. GPC trace of PMMA homopolymer and PMMA-*b*-PDMAEMA diblock copolymer.

in the reaction mixture. A bulky support hinders diffusion to the catalyst site and may become rate determining. The JandaJel ligands successfully mediated the ATRP of MMA, DMAEMA, and styrene and allowed for facile removal of the copper catalyst after simple filtration. For the more polar monomers, MMA and DMAEMA, the reactions were fast, possibly due to good compatibility of the monomer and growing polymer chain with the catalyst complex. A PMMA-*b*-PDMAEMA diblock was also synthesized, giving evidence for an active chain end using these systems. For MMA and DMAEMA, the polydispersities were lower than for many other heterogeneous systems. Styrene polymerizations were not as well controlled and did not proceed to high conversion. Catalyst reuse was possible using these ligands with a small decrease in catalyst activity for the second catalyst use. The JandaJel system does not remove copper as effectively as other copper removal systems such as the polyethylene supported ligand studied by our group[10] or the hybrid system developed by Matyjaszewski and co-workers.[9] However, compared to the polyethylene system, the JandaJel ligands have shorter reaction times and the system seems better suited for a larger variety of monomers. The JandaJel ligand catalyst system is an effective copper removal technique that combines heterogeneous reaction conditions (i.e., simple catalyst removal) with ability to control the ATRP reaction.

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