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Communications to the Editor

Atom Transfer Radical Polymerization of 4-Vinylpyridine

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Pyridine containing polymers have attracted much interest in recent years due to various applications such as water soluble polymers and coordination reagents for transition metals.[1] In contrast to 2-vinylpyridine (2VP),[2,3] the living polymerization of 4-vinylpyridine (4VP) has not been well studied until recently. Thus, the living anionic polymerization of 4VP was carried out in a mixture of THF/DMF[4] and later in a mixture of pyridine/THF.[5,6] Controlled/"living" radical polymerization is currently attracting much attention.[7] A variety of functional monomers can be readily polymerized, and reaction conditions can be very tolerant in a radical process. Recently, controlled radical polymerization of 4VP was reported using the 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) mediated stable free radical polymerization (SFRP) process.[8] Although a nearly linear increase of molecular weight along with an increase of conversion was observed, the polymerizations were carried out at high temperatures (130−145 °C), and the polydispersities of the obtained polymers were relatively high ($M_w/M_n \approx 1.2-1.5$).

Atom transfer radical polymerization (ATRP) is a relatively new and versatile method in the synthesis of polymers with controlled molecular weights and low polydispersities.[7] A large number of monomers can be polymerized in a well-controlled fashion. In this paper, we report the successful synthesis of well-defined poly(4-vinylpyridine) by copper-mediated ATRP.[9]

Polymerization of 4VP poses a very challenging problem for ATRP since both 4VP and P4VP are strong coordinating ligands that can compete for the binding of the metal catalysts in these systems. Since the monomer is normally present in large excess over the employed ligand, there is a possibility of the formation of pyridine-coordinated metal complexes in the polymerization solution. Pyridine-coordinated copper complexes are not effective catalysts for ATRP. For example, addition of 5 vol % pyridine to the polymerization solution of styrene catalyzed by CuBr complexed by 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) significantly slowed the polymerization rate.[10] When polymerization of 4VP was carried out using 1-phenylethyl bromide (PEBr) as the initiator and CuBr complexed by 2,2′-bipyridine (bpy) as the catalyst in 2-propanol, a very slow polymerization rate was observed. Under the conditions of $[4VP]_0 = 4.55$ M, $[4VP]_0/[PEBr]_0 = 95$, and $[PEBr]_0/[CuBr]_0/[bpy]_0 = 1/1/2$, a monomer conversion of 10% was reached after 25 h at 40 °C, presumably due to the significant coordination of the monomer to the catalyst.

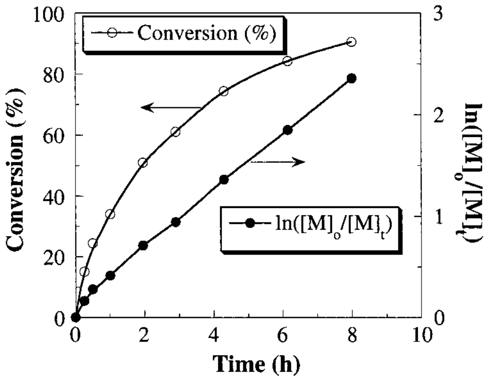

Figure 1. Kinetic plot for the copper-mediated ATRP of 4VP in 2-propanol. Reaction conditions: 40 °C; $[4VP]_0 = 4.55$ M; $[4VP]_0/[PECl]_0 = 95$; $[PECl]_0/[CuCl]_0/[Me_6TREN]_0 = 1/1/1$.

If a stronger binding ligand, such as the tridentate *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), was used, faster polymerization rates were observed. However, the competitive coordination of 4VP monomer to copper was evident. Under similar conditions as when bpy was used as the ligand, a PMDETA to CuBr ratio of 6:1 was needed to maintain a relatively fast polymerization rate and to obtain a monomer conversion of 50% after 4 h. In contrast, at a PMDETA to CuBr ratio of 1:1, the polymerization was approximately 4 times slower. The polymer solutions were green after passing through the alumina columns with CuBr/PMDETA as the catalyst, suggesting the complexation of P4VP with copper. Polymerization using 1-phenylethyl chloride (PECl) as the initiator and CuCl/PMDETA as the catalyst under similar conditions generated less colored polymer solutions when purified by passing through alumina columns. However, the reaction was slower than when bromine was used as the halogen, presumably due to the lower activation/deactivation equilibrium constant of alkyl chloride and CuCl/PMDETA.

When the polymerization of 4VP was carried out in 2-propanol using PECl as the initiator and CuCl complexed by tris[2-(dimethylamino)ethyl]amine[11] (Me_6TREN) at 40 °C, the polymerization was greatly improved.[12] The reaction solution was green and homogeneous. A linear plot of $\ln([M]_0/[M]_t)$ vs time was obtained, indicating that the number of propagating species remained constant (Figure 1). The slight decrease of the initial rate of polymerization can be ascribed to radical termination reactions due to the presence of a large concentration of radicals at the beginning of the reaction. All polymer samples were purified by passing through alumina columns before characterization by size exclusion chromatography (SEC)

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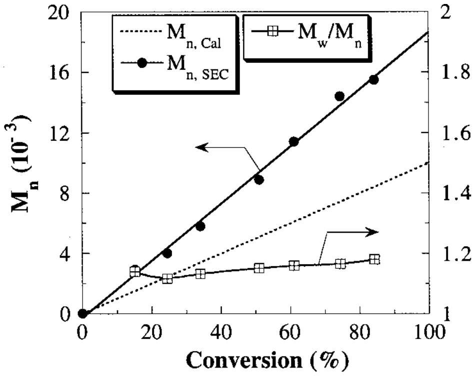

Figure 2. Dependence of molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) on monomer conversion. See Figure 1 for conditions.

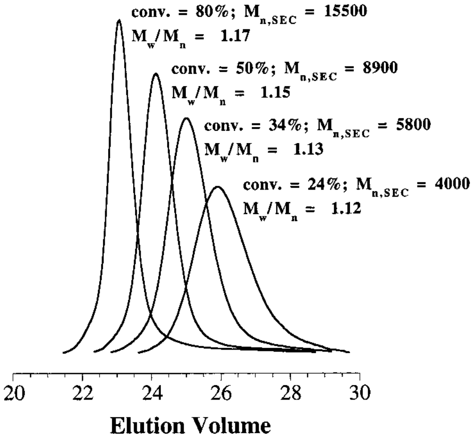

Figure 3. SEC chromatograms of P4VP prepared using ATRP. See Figure 1 for conditions.

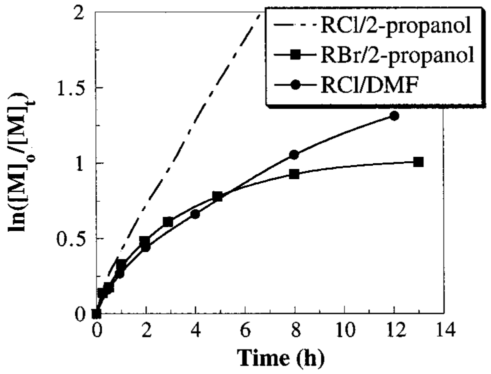

Figure 4. Effect of halogen and solvent on kinetics for the ATRP of 4VP. Reaction conditions are as follows. For RCl/2-propanol: see Figure 1. For RBr/2-propanol: 40 °C; $[4VP]_0 = 4.55$ M; $[4VP]_0/[PEBr]_0 = 95$; $[PEBr]_0/[CuBr]_0/[Me_6TREN]_0 = 1/1/1$. For RCl/DMF: 40 °C; $[4VP]_0 = 4.55$ M; $[4VP]_0/[PECl]_0 = 95$; $[PECl]_0/[CuCl]_0/[Me_6TREN]_0 = 1/1/1$.

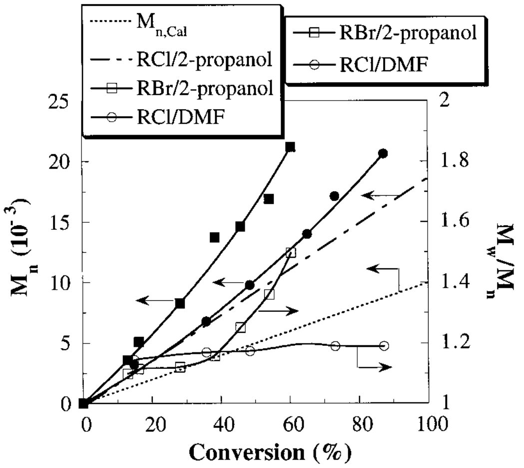

Figure 5. Effect of halogen and solvent on molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) for the copper-mediated ATRP of 4VP. See Figures 1 and 4 for reaction conditions.

using DMF with added Bu_4NBr (0.1% w/v) as the eluent. Significantly, the polymer solutions were almost colorless after passing through alumina columns, suggesting a strong coordination between copper and the Me_6TREN ligand. The linear increase of molecular weights (M_n) with conversion as shown in Figure 2 indicates a "living" nature of the polymerization. The polydispersities of the resulting polymers remained quite low throughout the polymerization ($M_w/M_n \approx 1.1-1.2$), indicative of a fast exchange between the active sites and the dormant species. Representative SEC traces of the polymerization are shown in Figure 3.

Several factors in the polymerization merit further discussion. The use of Cl as the halogen has many advantages. The strong C−Cl bond balances the activation/deactivation by the $CuCl/Me_6TREN$ complex for a suitable concentration of the active radicals. In addition, the inferior ability of chlorine atom as the leaving group renders it less susceptible for S_N2 type nucleophilic attack of pyridine molecules on the terminal and initiating alkyl halide headgroups, a probable side reaction in the system. In contrast, the use of Br as the halogen and $CuBr/Me_6TREN$ as the catalyst of 4VP resulted in a significant amount of termination reactions. This was demonstrated by the fact that the conversion of 4VP leveled off around 60% (Figure 4) with a sharp increase of polydispersities (Figure 5). The SEC chromatograms of samples taken at higher conversions showed significant tailing leading to the large increase of polydispersity. Moreover, the polymerization solution employing Br showed much darker color than that with Cl, indicating a higher concentration of copper(II) present in the solution. The higher initiator efficiency, as defined by $M_{n,Cal}/M_{n,SEC}$, when Cl was used than that when Br was used (Figures 2 and 5), indicates less side reactions. The real values of molecular weights may, however, differ from those estimated using poly(methyl methacrylate) (PMMA) standards.

Carrying out the polymerization of 4VP in a protic solvent is important. 2-Propanol not only solubilizes P4VP but also reduces the coloring in the polymerization system possibly through hydrogen bonding to 4VP/P4VP, thus decreasing the contamination of the catalyst. Apparently, in the range of the experimental molecular weights, potential transfer to 2-propanol is not important. Polymerization can also be carried out in DMF which solubilizes both the monomer and polymer. Compared to the polymerization performed in 2-propanol using Cl as the halogen, a much slower rate of polymerization was observed (Figure 4), in part due to possible coordination of DMF to copper. In addition, the rate of polymerization decreased as the reaction proceeded, which can be attributed to the same termination reactions as those found in the RBr/2-propanol system. The polymerization carried out in DMF afforded a similar profile of molecular weight vs conversion and polydispersities as those in 2-propanol (Figures 2 and 5); however, the measured molecular weights showed a progressive deviation from linearity as a result of

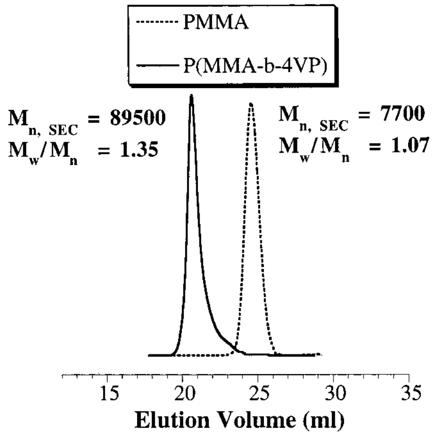

Figure 6. SEC chromatograms of PMMA macroinitiator and PMMA-*b*-P4VP copolymer. Reaction conditions: 50 °C; $[4VP]_0 = 4.62$ M; $[4VP]_0/[PMMA-Cl]_0 = 710$; $[PMMA-Cl]_0/[CuCl]_0/[Me_6TREN]_0 = 1/2/2$.

termination reactions.

The synthesis of block copolymers containing P4VP was also successfully carried out. Figure 6 shows the formation of an amphiphilic PMMA-*b*-P4VP copolymer using a PMMA macroinitiator made by ATRP.[13] By ^{1}H NMR, the block copolymer had 87 wt % of P4VP and a molecular weight of $M_{n,NMR} = 62\,500$, which was in good agreement with the calculated value ($M_{n,Cal} = 63\,800$ at 84% monomer conversion) assuming quantitative cross-propagation and the absence of any chain-breaking reactions. However, the molecular weight determined by SEC with PMMA standards was much higher ($M_{n,SEC} = 89\,500$).

In summary, ATRP has been successfully carried out to obtain well-defined poly(4-vinylpyridine). The linear increase of molecular weights with conversion has been observed, and polymers with low polydispersities ($M_w/M_n \approx 1.1-1.2$) were obtained. Several factors pertinent to the polymerization, such as the choice of ligand, exchanging halogen, and solvent, have been optimized and discussed. The best result was obtained using PECl as the initiator and CuCl/Me_6TREN as the catalyst in an alcohol solvent such as 2-propanol at 40 °C.

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(12) All materials were purified using standard procedures. In a typical polymerization, a dry round-bottom flask with a stir bar was charged with copper halide. The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed solvent, amine ligand, and monomer were then added using degassed syringes. The flask was immersed in an oil bath held by a thermostat at the desired temperature. Initiator was then added and timing was started. At timed intervals, samples were withdrawn from the flask using degassed syringes and added to DMF. Monomer conversion was determined from the concentration of residual monomer using gas chromatography. Molecular weights and polydispersities were measured by size exclusion chromatography using DMF with added Bu_4NBr (0.1% w/v) as the eluent. Poly(MMA) standards were used to calibrate the columns.

(13) The PMMA−Cl macroinitiator was prepared according to the reported procedure,[14] recovered by precipitation in methanol, and dried under vacuum to a constant weight. The block copolymer was synthesized in the following manner. A dry glass tube with a stir bar was charged with CuCl (2.6 mg), the PMMA−Cl macroinitiator ($M_{n,\,SEC} = 7700$, $M_w/M_n = 1.06$, 100 mg), DMF (0.5 mL), Me_6TREN (7.1 μL), and 4VP (1.0 mL). Three freeze−pump−thaw cycles were performed, and the tube was sealed under vacuum and placed in an oil bath held at 50 °C. After 3.0 h, the tube was opened, and the contents were dissolved in DMF. Monomer conversion and SEC measurements were performed on the reaction mixture, similar to those for P4VP.[12] For the ^{1}H NMR analysis, the block copolymer was recovered by removing the solvent under reduced pressure, redissolving the polymer in chloroform, passing the polymer solution through an alumina column to remove the metal-containing residues, and precipitation in cold hexane. The polymer was dried at 80 °C under vacuum for 48 h.

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