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Synthesis of Block and Random Copolymers of 3-Vinylpyridine by Nitroxide-Mediated Radical Polymerization

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Nitroxide-mediated free radical polymerization (NMP) of 3-vinylpyridine (3VP) as well as random copolymerization of 3VP and styrene (St) were proved to proceed in a pseudo-living manner in the presence of urethane-functionalized alkoxyamine unimolecular initiator, providing polymers with controlled molecular weight and narrow polydispersities. A linear relationship between molecular weight and conversion was confirmed. The effects of polar urethane group on initiator, reaction temperature, and feed ratio of monomers on polymerization rate, molecular weight, and polydispersity of the synthesized polymers were investigated at bulk condition. Diblock copolymers of St and 3VP with defined block lengths and low polydispersities could also be obtained by the use of alkoxyamine-terminated polystyrene as macroinitiator.

Key words: Nitroxide-mediated free radical polymerization (NMP), 3-vinylpyridine, random copolymers, block copolymers, alkoxyamine

1. INTRODUCTION

Polymers and copolymers with complex, yet well-defined architectures are drawing attention in the search for novel materials with unconventional and/or improved properties.[1] During decades, the field of "living", or pseudo-living, free radical polymerizations has witnessed explosive growth due to the great promise shown by these synthetically robust and simple procedures.[2,3] One of the most widely studied approaches to "living" free radical polymerizations involves the nitroxide-mediated free radical polymerization (NMP) procedures. However, NMP was limited to a few monomers, mainly styrene and styrenic derivatives, recent development of NMP has permitted the polymerization of a wide variety of monomer families, with a level of structural control approaching traditional anionic polymerization procedures. On the other hand, the poorly defined nature of the initiating species in bimolecular initiating system prompted the development of single molecular initiating system. The advantage of the unimolecular initiator approach is that the structure of polymers prepared can be controlled to a much greater extent. The unimolecular initiator can also be functionalized to permit the controlled introduction of functional groups at the chain ends of macromolecules.

Poly(vinylpyridine)s (PVP) exhibit interesting properties as a result of the presence of the nitrogen atom. PVP are particularly important in applications as polyelectrolytes, polymeric reagents, catalysts and so on. The homopolymerization of the 4-,[4,5] 3-,[6] and 2-vinylpiridine[7] by NMP process with 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO)-based bimolecular initiation system has already been reported. The authors report herein the polymerization of 3-vinylpiridine (3VP) along with the preparation of block and random copolymer of 3VP and styrene (St) with TEMPO-based unimolecular initiator.

2. EXPERIMENTAL

2.1 Measurements

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic measurements were carried out at 25 °C with a JEOL JNM-EX400 spectrometer using tetramethylsilane as an internal standard in chloroform-*d*. IR spectra were obtained with a Perkin Elmer Spectrum One infrared spectrometer as thin film on NaCl. Monomer conversion was determined by ^{1}H NMR of the crude reaction mixtures. Number and weight average molecular weights (M_n and M_w, respectively) as well as polydispersity (M_w/M_n) of the samples were estimated by size exclusion chromatography (SEC) at 40 °C using tetrahydrofuran (THF) with 5% v/v tetramethylethylenediamine as the eluent, at a flow rate of 0.8 $\mathrm{mL{\cdot}min^{-1}}$. Measurements were performed on a TOSOH HLC-8120GPC high performance liquid chromatography (HPLC) system equipped with a polystyrene gel column [Shodex GPC KF-804L column (300 × 8.0 mm)]. Sample detection was done with a refractive index (RI) detector. The system was calibrated against 6 standard polystyrene samples (M_n = 800-152000; M_w/M_n = 1.03-1.10).

2.2 Materials

TEMPO-based unimolecular initiator **1**[8] and **2**[9] were prepared by the method reported previously (Figure 1). 3-Vinylpyridine (3VP) was prepared and purified as previously reported.[6] Commercially obtained styrene (St) (Wako, 99%) was distilled under vacuum over CaH_2 immediately prior to use. Other reagents were purchased

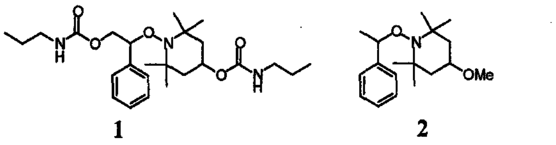

Figure 1. Structure of the alkoxyamine unimol ecular initiator

from Aldrich, Kanto Chemicals or Wako Pure Chemical Industries and were used as received without purification.

2.3 Synthesis

General Procedure for Polymerization of 3VP; Preparation of Poly(3VP).

A mixture of the desired alkoxyamine 1 (23.2 mg, 0.05 mmol) and 3VP (1.08 mL, 10 mmol) was charged into a round-bottom flask containing a magnetic stirring bar, and degassed by three freeze-pump-thaw cycles. The mixture was incubated at 125 °C under argon for 1.5 h, and after dilution with chloroform the solution was poured into hexane. The resulting polymer precipitated was collected by filtration and dried in vacuo to give the purified polymer as a white powder (698 mg, 65 % yield). $M_n = 11500$, $M_w/M_n = 1.28$

General Procedure for Block Copolymer Formation; Preparation of Poly(St)-b-poly(3VP)

A mixture of alkoxyamine-terminated poly(St) (M_n = 3900, M_w/M_n = 1.10, 110 mg) and 3VP (1.08 mL, 10 mmol) was charged into a round-bottom flask containing a magnetic stirring bar, and degassed by three freeze-pump-thaw cycles. The mixture was incubated at 125 °C under argon for 1.5 h, and after dilution with chloroform the solution was poured into methanol. The resulting polymer precipitated was collected by filtration and dried in vacuum (673 mg, 58 % yield). M_n = 21600, M_w/M_n = 1.38

3.RESULTS AND DISCUSSION

3.1 Influence of Initiator

First, the influence of unimolecular initiator structure on polymerization rate was investigated. The comparison of $\ln([M]_0/[M]_t)$ vs. time plots for the polymerization of 3VP with urethane functionalized initiator 1 and unfunctionalized initiator 2 is shown in Figure 2. Compared with styrene, the rate of the polymerization is surprisingly fast. In NMP, the polymerization rate mainly depends on the strength of C-TEMPO bond, because the equilibrium between active and domant species is influenced by the dissociation energy.[2,10] Hence, it is considered, on account of electronic distribution on the pyridine ring, along with resonance effects, that the terminal C-TEMPO bond on 3VP has quite low dissociation energy compared with that on styrene. On the other hand, the use of 1 exhibit the higher polymerization rate compared with 2. As was already reported, the intramolecular hydrogen bond between urethane bond and oxygen on alkoxyamine moiety leads to a change in mediating ability.[2,3] Consequently, the use of 1 affords the rate enhancement effect. The nearly linear relationships between $\ln([M]_0/[M]_t)$ and time were observed on both systems, indicating that the number of active species is almost constant throughout the polymerization.

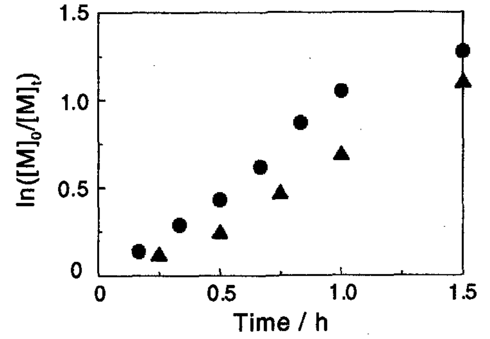

Figure 2. The $\ln([M]_0/[M]_t)$ vs. time plots for polymerization of 3VP at 125 °C with (●) alkoxyamine derivative 1 and (▲) alkoxyamine derivative 2 as initiators.

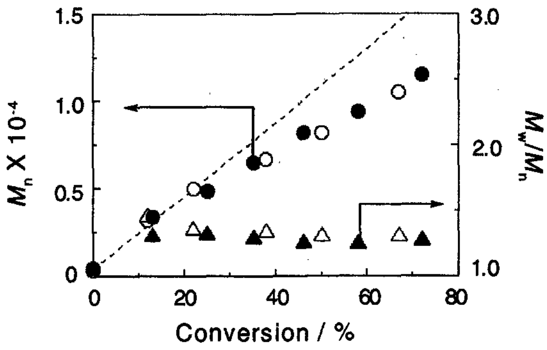

Figure 3. Evolution of M_n (circle) and M_w/M_n (triangle) with conversion for polymerization of 3VP at 125 °C with (●, ▲) alkoxyamine derivative 1 and (○ , △) alkoxyamine derivative 2 as initiators. The calculated molecular weights are shown in a dashed line.

One feature of living free radical polymerizations is the linear increase of the molecular weight versus conversion. M_n and M_w/M_n are plotted as a function of conversion in Figure 3. Although M_ns are not in agreement with theoretical M_n at high conversion, M_n increased with increasing conversion. The M_w/M_n were slightly higher than those of styrene, however, M_w/M_n values decreased with conversion to about 1.28, which is regarded as relatively low value. The decrease of M_w/M_n as monomer conversion is another indication of the living character of the polymerization. Interestingly, initiator 1 affords the higher molecular weight control than 2. This phenomenon is probably caused by the high polymerization rate triggered by intramolecular hydrogen bond.[8,11] It has been shown that the autoinitiation of styrene-based monomers at elevated temperature can be a significant problem leading to loss of the 'living' character of the polymerization process.[12] Long reaction times result in the increase of the contribution of autoinitiation process. Hence, high polymerization rate prevents the loss of the 'living' character.

3.2 Influence of Temperature

The influence of temperature was studied with experiments conducted at 110, 125, and 138 °C in the

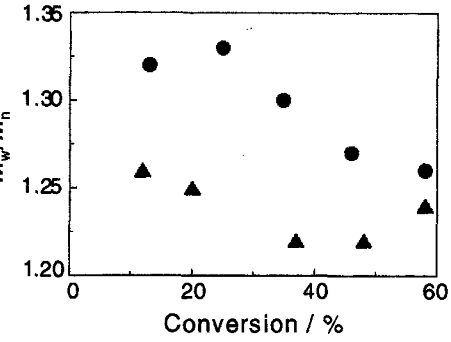

Figure 4. Evolution of molecular weight distribution with conversion for copolymerization of St and 3VP in the presence of 1 as an initiator at (●) 125°C and (▲) at 138 °C.

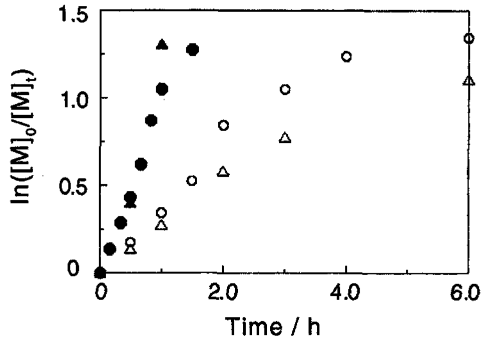

Figure 5. The $\ln([M]_0/[M]_t)$ vs. time plots for copolymerization of St and 3VP at 125 °C in the presence of 1 as an initiator (●St:3VP = 0:10; ▲St:3VP = 5:5; ○St:3VP = 8:2; △St:3VP = 9:1).

presence of 1 as an initiator. A decrease in temperature induced a decrease in the slope of the $\ln([M]_0/[M]_t)$ vs. time plot, that is, in the polymerization rate. According to previous work, polymerization of 3VP with NMP in bimolecular initiation system, that is to say, polymerization conducted in the presence of benzoyl peroxide and TEMPO, is controlled even at 110 °C that is regarded too low for NMP on St.[6] Contrary to the feature, in the case of unimolecular initiating system, when the polymerization conducted at 110°C, the significant peak derived from initiator was observed on SEC profile throughout polymerization, and molecular weight of resulting polymer was not controlled. On the other hand, polymerization was well controlled at higher temperature. As shown in Figure 4, at the initial stage of polymerization, M_w/M_n revealed low value in 138 °C than 125 °C. Further, in contrast to the polymerization at 125 °C, M_w/M_n increased at the high conversion in that at 138 °C. As was already mentioned, the difference of dissociation energy induced the temperature effect. Compared with 3VP-TEMPO bond, St-TEMPO bond needs high temperature to dissociate enough to initiate polymerization quantitatively. Once 3-VP-TEMPO terminal group is generated, the polymerization proceeds by the dissociation-termination cycle of alkoxyamine even at 110 °C. From these perspectives, it can be inferred that the polymerization of 3VP on styrene-based unimolecular initiating system is controlled at the temperatures that are enough to accomplish quantitative initiation of styrene-based alkoxyamine unit. However, the excessive temperature results in acceleration of autoinitiation, and poor control of what at high conversion.

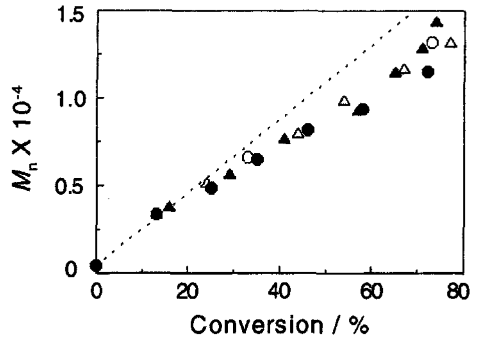

Figure 6. Evolution of M_n with conversion for copolymerization of St and 3VP at 125 °C in the presence of 1 as an initiator (●St:3VP = 0:10; ▲ St:3VP = 5:5; ○ St:3VP = 8:2; △ St:3VP = 9:1). The calculated molecular weights are shown in a dashed line.

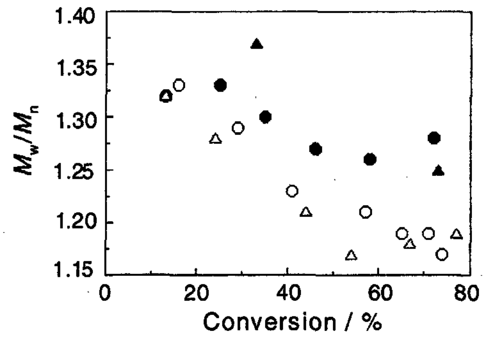

Figure 7. Evolution of molecular weight distribution with conversion for copolymerization of St and 3VP at 125 °C in the presence of 1 as an initiator (●St:3VP = 0:10; ▲St:3VP = 5:5; ○St:3VP = 8:2; △St:3VP = 9:1).

3.3 Preparation of Random Copolymers of St and 3VP

The copolymerizations of 3VP and St at different 3VP/St ratios were performed using 1 as an initiator at 125 °C. The comparison of $\ln([M]_0/[M]_t)$ vs. time plots is shown in Figure 5. A linear behavior of $\ln([M]_0/[M]_t)$ on reaction time is clearly observed on each condition at the initial stage of polymerization. However, the long reaction time provided deviation from the linear relationship, indicating some inactivation of propagating radicals. The rate of polymerization was slower than that of homopolymerization of 3VP, and increased with an increasing 3VP content. As shown in Figure 6, a better polymerization control can be accomplished with an increasing St content in the feed mixture. Dependence of M_w/M_n on conversion is shown in Figure 7. In all cases, the polydispersity index revealed relatively narrow values, and decreased with an increasing St content. It should also be mentioned that the M_w/M_n are almost same at low conversion. Figure 7 also demonstrates that

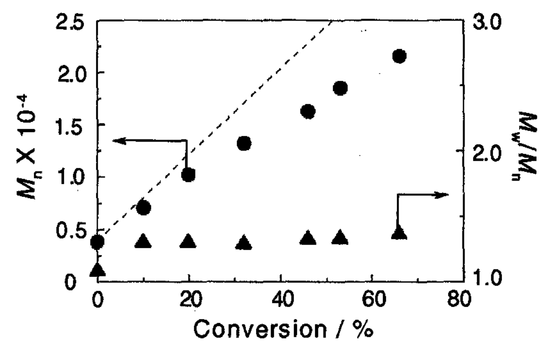

Figure 8. Evolution of M_n and M_w/M_n with conversion for polymerization of 3VP at 125 °C with alkoxyamine-terminated poly(St) prepared from 1 (M_n = 3900, M_w/M_n = 1.10) as macroinitiator. The calculated molecular weights are shown in a dashed line.

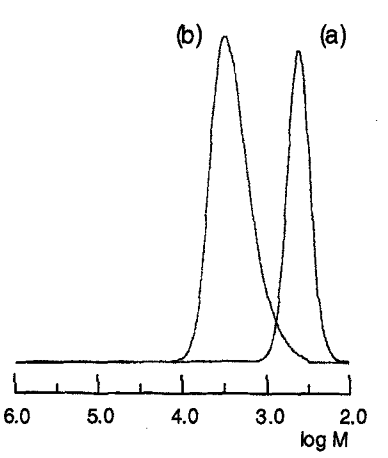

Figure 9. Comparison of GPC profiles for (a) alkoxyamine terminated poly(St) (M_n = 3900, M_w/M_n = 1.10) and (b) poly(St)-*b*-poly(3VP) diblock copolymer (M_n = 21600, M_w/M_n = 1.38)

the M_w/M_n decreased with increasing conversion. These findings indicate that there were some potential termination or decomposition of C-TEMPO bond and autoinitiation of the 3VP.

3.4 Preparation of Block Copolymers of St and 3VP

Block copolymers of 3VP and St were also synthesized. Poly(St) end-capped with alkoxyamine unit synthesized from 1 was dissolved in 3VP, and the mixture was heated at 125 °C under argon. M_n and M_w/M_n are plotted as a function of conversion in Figure 8. Similarly with the homopolymerization of 3VP, there is a slight difference between experimental M_n and theoretical one, but M_ns increased linearly with conversion. M_w/M_n values maintained relatively low value throughout polymerization. Furthermore, the linear evolution of $\ln([M]_0/[M]_t)$ as a function of time was established. Figure 9 shows the SEC profiles of poly(St) macroinitiator and poly(St)-*b*-poly(3VP) block copolymer. SEC profiles revealed that the symmetric unimodal peak of postpolymer shifted from that of macroinitiator toward the higher molecular weight region, and more importantly, leaving no significant shoulder peak at the elution position of macroinitiator, indicating that most of the macroinitiators initiated polymerization.

4. CONCLUSION

Nitroxide-mediated free radical polymerization of 3VP proceeds in a pseudo-living manner by the use of alkoxyamine compound as unimolecular initiator. Consequently, it is possible to control the features of the final poly(3VP) macromolecules. Molecular weights increase linearly with conversion and polydispersities remain narrow. Block and random copolymers also successfully prepared in a controlled manner. This permits novel well-defined amphiphilic copolymers to be readily prepared in the minimum number of steps under synthetically nondemanding conditions. In comparison with bimolecular initiation system, single molecule initiating system represents a dramatic improvement in the design of macromolecular architecture and chain end functionalization.[13]

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