

# Nitroxide-Mediated Homopolymerization and Copolymerization of 2-Vinylpyridine with Styrene

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**ABSTRACT:** Homopolymerization and copolymerization of 2-vinylpyridine (2VP) with styrene (S) at 125°C in the presence of 2,2,6,6-tetramethyl piperidin-1-yloxy (TEMPO) radicals have been studied. The homopolymerization was carried out with 2,2'-azobis(isobutyronitrile) (AIBN) as a thermal initiator or without AIBN in the initial reaction mixture. In the copolymerization initiated with AIBN, the molar fraction of 2VP in the feed,  $F_{2VP}$ , varied in the range of 0.1–0.9;  $F_{2VP} = 0.65$  was found to be the azeotropic composition. The linear semilogarithmic time–conversion plots demonstrated a pseudoliving nature of the polymerizations under study. The molecular weight–conversion dependences indicated the participation of side reactions, diminishing the number of TEMPO-terminated polymer chains. The synthesized homopolymers and copolymers were characterized using size-exclusion chromatography (SEC), nitrogen analysis, and NMR spectroscopy. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2024–2030, 2001

**Key words:** nitroxide-mediated polymerization; pseudoliving mechanism; 2-vinylpyridine polymers; azeotropic copolymerization

## INTRODUCTION

In the last 2 decades, new radical polymerization techniques were developed that make it possible to synthesize polymers with controlled architectures and properties. Typical representatives of these procedures are the iniferter technique,<sup>1,2</sup> stable free radical polymerization,<sup>3,4</sup> atom transfer radical polymerization,<sup>5–8</sup> and, quite recently, radical polymerization with reversible addition and fragmentation chain transfer.<sup>9</sup> Each of these methods has its specificity, its advantages, and drawbacks. However, one feature is common for all of them. The control of the polymerization is achieved by reversible end-capping of growing

polymer chains. At higher temperatures, usually above 100°C, the reversibly terminated, i.e., potentially active chains undergo thermal homolysis. In this process, polymer radicals and terminating fragments are regenerated. The polymer radicals can add the monomer present in the reaction mixture and then be again terminated with the released terminating fragments. The cycle, i.e., the homolytical splitting of polymer chains, propagation, and reversible termination can repeat until the monomer is consumed. Bimolecular, irreversible termination reactions, typical of a conventional free radical polymerization, are substantially reduced by decreasing the number of active chain ends. As a result, a pseudoliving polymerization proceeds.

A widely studied approach to the radical pseudoliving polymerizations involves the use of stable nitroxide free radicals, such as TEMPO.<sup>3,4,10–23</sup> Nitroxide-based systems for the controlled polymerization have some important advantages: (a) ni-

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**Table I Homopolymerization of 2-Vinylpyridine (2VP) in Presence of TEMPO**

Polymer	AIBN $\times 10^4$ (mol)	TEMPO $\times 10^4$ (mol)	Time (h)	Conversion (%)	$M_n \times 10^{-3}$	$M_w/M_n$
H1	1	1.5	0.5	36.8	10.1	1.14
H2	1	2	1	8.2	3.6	1.23
H3	1	2	2	30.9	9.2	1.35
H4	1	2	2.5	36.8	9.5	1.41
H5	0.5	1.5	2	13.0	5.6	1.29
H6	0.5	1.5	3	18.1	8.0	1.42
H7	0.5	1.5	4	24.8	8.9	1.46
H8	—	1.5	4.5	12.9	10.7	1.25
H9	—	1.5	6.5	24.2	11.2	1.26

The homopolymerization was at 125°C with  $5 \times 10^{-2}$  mol 2VP and 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator.

troxyl radicals do not initiate, they only terminate, thus enhancing the possibility to obtain polymers of a narrow molecular weight distribution (MWD); (b) a relatively labile bond between the chain and the terminal nitroxyl group is favorable to the polymerization process; (c) the absence of an added metal complex, which is a necessary component of an initiating system in atom transfer radical polymerization, results in tolerance to the presence of functional groups and easy purification of products.

Originally, the nitroxide-mediated radical polymerization has been successfully applied to styrene, its derivatives, and comonomer mixtures. The method, however, progressively expanded to other monomers.<sup>24–30</sup> Of potential monomers, 2- and 4-vinylpyridines are attractive compounds. Polymers containing vinylpyridine structural units exhibit interesting properties due to the presence of the basic nitrogen atom, making possible a variety of reactions, such as quaternization, reaction with acids, and complexation of metals.<sup>31</sup> Vinylpyridine polymers and their ionic derivatives can be used as polyelectrolytes, polymer reagents, and in electrical applications. The controlled radical polymerization of vinylpyridines, however, was not investigated. Only recently, nitroxide-mediated polymerization of 4-vinylpyridine has been reported.<sup>25,26,29</sup> The present study is focused on the homopolymerization and copolymerization of 2-vinylpyridine with styrene in the presence of TEMPO radicals. The aim was to synthesize nitroxide-terminated functional macroinitiators with narrow molecular weight distributions, which are intended for our further research concerning related block copolymers.

## EXPERIMENTAL

### Materials

All the chemicals used were from Fluka. The 2VP (bp 48°C/1.56 kPa) and S (36°C/1.56 kPa) were distilled prior to use. AIBN (m.p. 105°C) was recrystallized from ethanol. The TEMPO radical (m.p. 36–39°C) was a commercial product. The solvents were of analytical grade.

### Synthesis of TEMPO-Terminated Poly(2-Vinylpyridine)s

Homopolymerization of 2VP using an initiating system AIBN–TEMPO and autopolymerization in the presence of TEMPO were carried out in sealed glass ampoules in an inert atmosphere at 125°C. The total amount of 2VP was  $5 \times 10^{-2}$  mol, the amounts of AIBN and TEMPO in the system were  $0.5 \times 10^{-4}$  or  $1 \times 10^{-4}$  mol and  $1.5 \times 10^{-4}$  or  $2 \times 10^{-4}$  mol, respectively. In the autopolymerization,  $1.5 \times 10^{-4}$  mol TEMPO was in the feed. After a predetermined time, the resulting TEMPO-terminated homopolymers were precipitated from the reaction mixtures and reprecipitated from chloroform solutions with hexane. They were dried under vacuum (6.6 Pa) at room temperature. The reaction conditions, conversions, molecular weights, and MWDs for homopolymers H1–H9 are given in Table I.

### Synthesis of TEMPO-Terminated 2-Vinylpyridine–Styrene Copolymers

A mixture of 2VP and S ( $5 \times 10^{-2}$  mol total),  $1 \times 10^{-4}$  mol AIBN, and  $1.5 \times 10^{-4}$  mol TEMPO was heated in a glass ampoule in an inert atmosphere at

**Table II Copolymerization of 2-Vinylpyridine (2VP) and Styrene (S) Initiated with 2,2'-Azobis(isobutyronitrile) (AIBN) in the Presence of TEMPO**

Copolymer	$F_{2VP}$	$f_{2VP}$	Conversion (%)	$M_n \times 10^{-3}$	$M_w/M_n$
C1 <sup>a</sup>	0.1	0.17	15.2	9.8	1.07
C2	0.2	0.34; 0.30 <sup>b</sup>	5.2	7.7	1.06
C3 <sup>c</sup>	0.3	0.39	28.7	13.9	1.12
C4	0.4	0.47; 0.50 <sup>b</sup>	23.3	12.2	1.13
C5	0.5	0.58	28.2	13.3	1.17
C6	0.6	0.64; 0.67 <sup>b</sup>	30.0	13.3	1.17
C7	0.7	0.66	37.5	15.1	1.24
C8	0.8	0.78	40.6	13.6	1.25
C9	0.9	0.82	42.3	15.4	1.29

$F_{2VP}$  and  $f_{2VP}$  are the molar fractions of 2VP in the feed and in the copolymer, respectively. The copolymerization was at 125°C for 1 h with  $5 \times 10^{-2}$  mol total comonomers,  $1 \times 10^{-4}$  mol AIBN, and  $1.5 \times 10^{-4}$  mol TEMPO.

<sup>a</sup> 3 h.

<sup>b</sup> From <sup>1</sup>H-NMR.

<sup>c</sup> 2 h.

125°C. The molar fraction of 2VP in the feed,  $F_{2VP}$ , varied in the range of 0.1–0.9. After 1 h, or at  $F_{2VP}$  equal to 0.2 and 0.3 h after 3 h and 2 h, copolymers of 2VP and S were isolated and treated in the same way as the above-mentioned homopolymers. The reprecipitated copolymers C1–C9 were dried under vacuum (6.6 Pa) at 60°C for 2 days. Table II summarizes yields, compositions, molecular weights, and MWDs of the copolymers.

In Table III, the results of the 2VP–S copolymerization at the azeotropic feed composition,  $F_{2VP} = 0.65$ , are presented. The initial reaction mixture contained  $4 \times 10^{-2}$  mol total comonomers,  $0.5 \times 10^{-4}$  mol AIBN, and  $1 \times 10^{-4}$  mol TEMPO. The 0.5-h, 1-h, 1.5-h, and 2-h copolymerizations were performed at 125°C.

### Measurements

The yields of homopolymers and copolymers were determined gravimetrically. The compositions of

copolymers of 2VP and S were found from nitrogen analyses or <sup>1</sup>H-NMR measurements. The molecular weights and MWDs of polymer products were evaluated using size-exclusion chromatography (SEC).

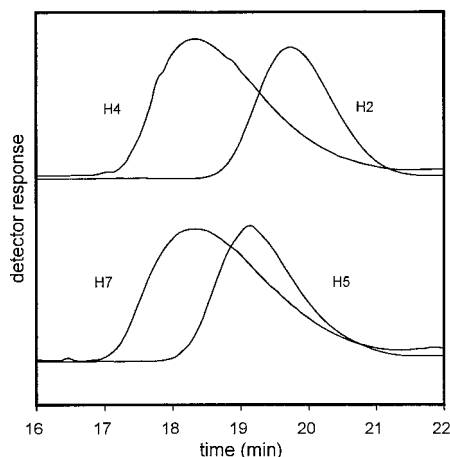
### Determination of Molecular Weights

The SEC measurements for evaluation of number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) were carried out on a PSS SDV 10,000 column (8 × 600 mm, Polymer Standard Service, Germany), filled with 5- $\mu$ m sorbent particles. Tetrahydrofuran served as a mobile phase. The chromatographic data from refractometric and UV (254 nm) detectors were treated using the Data-Monitor system (Watrex, Czech Republic). A universal calibration equation calculated from the data on polystyrene standards (Merck, Germany) was used for the determination of molecular weights.

**Table III Copolymerization of 2-Vinylpyridine (2VP) and Styrene (S) Initiated with 2,2'-Azobis(isobutyronitrile) (AIBN) in the Presence of TEMPO at the Azeotropic Feed Composition; ( $F_{2VP}$ )<sub>A</sub> = 0.65**

Copolymer	Reaction Time (h)	Conversion (%)	$M_n \times 10^{-3}$	$M_w/M_n$
C <sub>A</sub> 1	0.5	9.7	6.0	1.43
C <sub>A</sub> 2	1	22.2	13.0	1.50
C <sub>A</sub> 3	1.5	28.9	13.6	1.50
C <sub>A</sub> 4	2	36.4	16.5	1.53

( $F_{2VP}$ )<sub>A</sub> is the molar fraction of 2VP in the feed corresponding to the azeotropic composition. The copolymerization was at 125°C with  $4 \times 10^{-2}$  mol total comonomers,  $0.5 \times 10^{-4}$  mol AIBN, and  $1 \times 10^{-4}$  mol TEMPO.



**Figure 1** SEC curves of poly(2-vinylpyridine)s H2, H4, and H5, H7 (Table I).

### NMR Measurements

$^1\text{H-NMR}$  spectra (300.13 MHz) of 10% w/w copolymer solutions in  $\text{CDCl}_3$  were measured at 295 K with a Bruker Avance DPX 300 spectrometer and hexamethyldisiloxane as the internal standard. The relative contents of 2VP and S units were found by comparing intensities of the signals in the respective aromatic groups.

## RESULTS AND DISCUSSION

### TEMPO-Mediated Homopolymerization of 2-Vinylpyridine

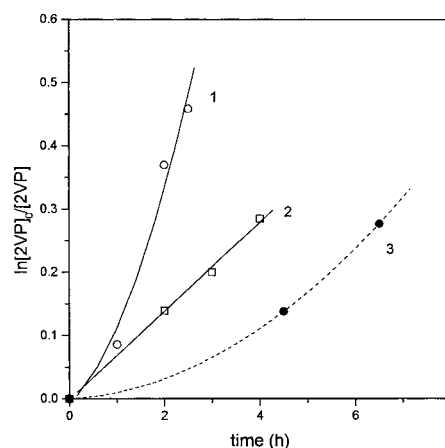
Table I summarizes the results on homopolymerization of 2VP at  $125^\circ\text{C}$  in the presence of TEMPO with AIBN or without any thermal initiator in the reaction mixture. The molar ratios TEMPO/AIBN were 1.5/1, 2/1, and 3/1. As expected, at TEMPO/AIBN = 1.5/1, the homopolymerization proceeded most rapidly (36.8%/0.5 h), while, in the absence of AIBN, conversion of 2VP reached 24.2% after 6.5 h. The molecular weights of the obtained homopolymers increased with conversion (the latter is given in parentheses): from  $3.6 \times 10^3$  (8.2%, H2) to  $9.5 \times 10^3$  (36.8%, H4) at a molar ratio TEMPO/AIBN = 2/1, and from  $5.6 \times 10^3$  (13.0%, H5) to  $8.9 \times 10^3$  (24.8%, H7) at TEMPO/AIBN = 3/1. In Figure 1, the SEC curves of the corresponding homopolymers are depicted. Almost identical molecular weights were found for homopolymers H8 and H9 ( $10.7 \times 10^3$  and  $11.2 \times 10^3$ , respectively) at conversions 12.9% (H8) and 24.2% (H9). The  $M_w/M_n$  values were fairly

low, in particular those of homopolymers, which were prepared in the presence of AIBN during 0.5 h (1.14, H1), 1 h (1.23, H2), and 2 h (1.29, H5) or by autopolymerization (1.25 and 1.26, H8 and H9). However, a broadening in MWDs of homopolymers H3, H4 ( $M_w/M_n = 1.35, 1.41$ ) and H6, H7 ( $M_w/M_n = 1.42, 1.46$ ) was observed.

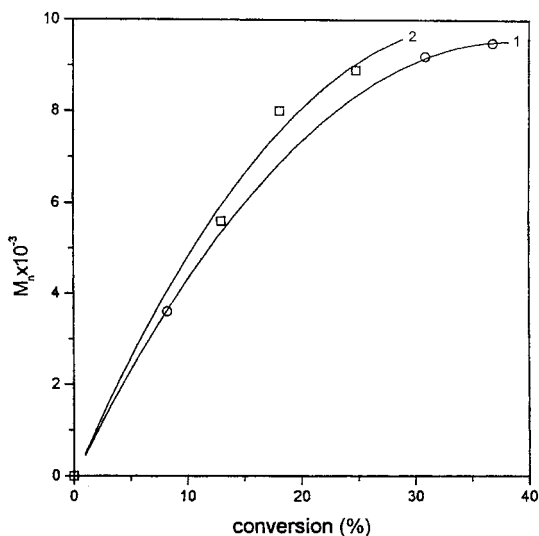
In an effort to gain a deeper insight into the polymerization process, semilogarithmic time-conversion plots (Fig. 2) were constructed. The dependences showed a linear course (line 1, after about 1 h, at TEMPO/AIBN = 2/1, and line 2 at TEMPO/AIBN = 3/1). Evidently, in eq. (1) for the rate of polymerization,  $R$ ,

$$R = -d[2VP]/dt = k_p[C^*][2VP] \quad (1)$$

where  $[2VP]$  and  $[C^*]$  are, respectively, molar concentrations of 2VP and initiating centers, both active and latent,  $t$  is time, and  $k_p$  is the rate constant of propagation), the  $[C^*]$  is approximately constant under given experimental conditions, and, hence, the pseudoliving polymerization proceeds. A slight initial increase in the case of curve 1 can be associated with an increase in the number of initiating centers due to the formation of *in situ* unimolecular initiators. These initiators are generated by the trapping reaction of radical species from autopolymerization of 2VP with TEMPO. A similar course can be assumed for homopolymerization in the absence of AIBN (the dotted curve 3).

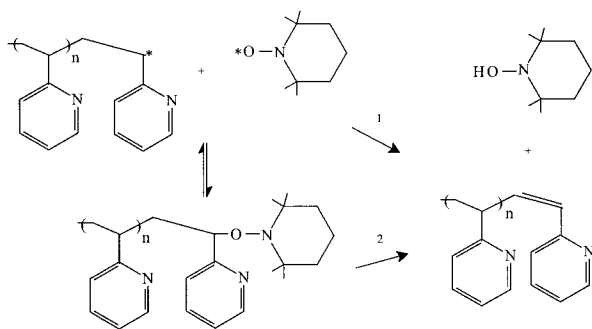


**Figure 2** The semilogarithmic time-conversion plots for the homopolymerization of 2VP at a molar ratio TEMPO/AIBN = 2/1 (1), 3/1 (2), and without AIBN (3) (Table I).  $[2VP]_0$  and  $[2VP]$  are initial and current monomer concentrations, respectively.

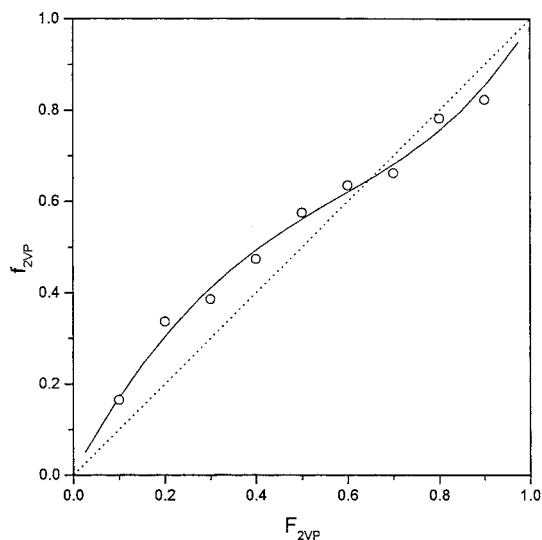


**Figure 3** The  $M_n$  conversion dependences for the homopolymerization of 2VP at a molar ratio TEMPO/AIBN = 2/1 (1) and 3/1 (2) (Table I).

Figure 3 shows dependences of  $M_n$  on conversion. The observed curvatures indicate that the number of TEMPO-terminated chains decreases during the polymerization. According to the literature,<sup>27–29</sup> this phenomenon might occur due to a disproportionation reaction between a poly(2VP) radical and TEMPO, and/or because of thermal decomposition of the  $\omega$ -(TEMPO)poly(2VP) (Scheme 1). As a result,  $\omega$ -unsaturated polymer chains are generated, and TEMPO is deactivated giving a hydroxylamine; the latter can take part in the termination of polymer radicals, thus shortening the polymer chains. These reactions might also account for the found broader MWDs of homopolymers H3, H4, and H6, H7 at TEMPO/AIBN = 2/1 and 3/1, respectively, as well as for tailing at lower molecular weights in SEC curves for H4 and H7 (Fig. 1).



**Scheme 1**



**Figure 4** The dependence of the copolymer composition ( $f_{2VP}$ ) on the feed composition ( $F_{2VP}$ ) in the 2VP–S copolymerization in the presence of TEMPO (Table II).

### TEMPO-Mediated Copolymerization of 2-Vinylpyridine and Styrene

Similarly to the homopolymerization of 2VP, the copolymerization of 2VP with S in the presence of TEMPO affords polymers of narrow MWDs (Table II). At molar fractions  $F_{2VP} = 0.1$  and  $0.2$ , the  $M_w/M_n$  values of the 2VP–S copolymers (C1, C2) were even lower than 1.1. The rate of copolymerization increased with the increasing content of 2VP in the initial reaction mixture. After 1 h, conversions were 23.3 and 42.3% at  $F_{2VP} = 0.4$  and  $0.9$ , respectively. However, molecular weights of the corresponding copolymers C4 and C9 increased only slightly, from  $12.2 \times 10^3$  to  $15.4 \times 10^3$ . Obviously, the above-mentioned reactions leading to the reduced number of TEMPO-terminated chains in the homopolymerization of 2VP take place also in the 2VP–S copolymerization.

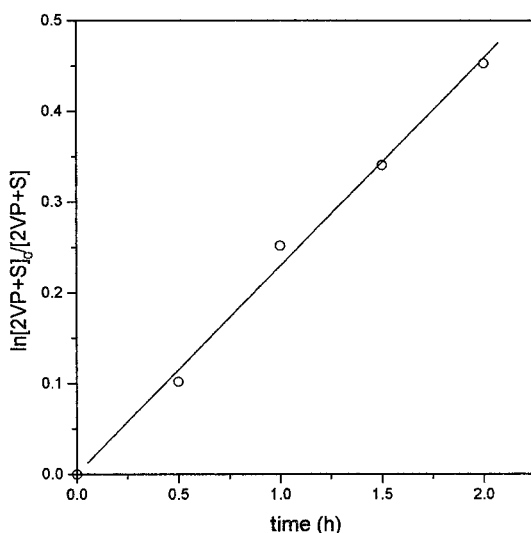
As known from the literature,<sup>32,33</sup> the conventional radical copolymerization of 2VP with S initiated with AIBN proceeds in an azeotropic manner. The monomer reactivity ratios ( $r$ ) were found to be 0.75 for 2VP ( $r_{2VP}$ ) and 0.46 for ( $r_S$ ). Hence, the calculated azeotropic composition,  $F_{2VP} = 1/[1 + (r_{2VP} - 1/r_S - 1)]$ , is 0.68. In Figure 4, the dependence of the composition of the 2VP–S copolymers prepared in the presence of TEMPO ( $f_{2VP}$ ) on the feed composition ( $F_{2VP}$ ) is presented. The azeotropic course was also observed and the azeotropic composition,  $(F_{2VP})_A = 0.65$ , close to that in the absence of nitroxide, was found.



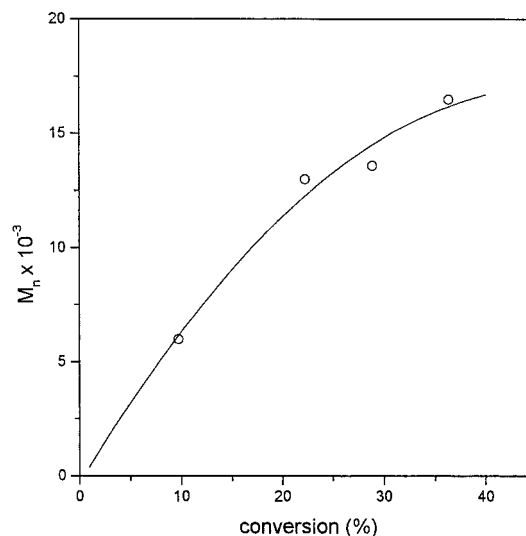
Table III presents the results on the TEMPO-mediated copolymerization of 2VP with S at  $(F_{2VP})_A = 0.65$ . The molar fractions of 2VP in the obtained copolymers  $C_{A1}$ – $C_{A4}$  were approximately the same as that in the feed. Within the reaction times of 0.5–2 h, the respective conversions and molecular weights increased from 9.7% and  $6.0 \times 10^3$  up to 36.4% and  $16.5 \times 10^3$ . MWDs were about 1.5, probably due to the irreversible termination reactions occurring to a larger extent using  $4 \times 10^{-2}$  mol of total comonomers,  $0.5 \times 10^{-4}$  mol AIBN, and  $1 \times 10^{-4}$  mol TEMPO in the initial reaction mixtures. The linear semilogarithmic time–conversion plot for the copolymerization yielding  $C_{A1}$ – $C_{A4}$  (Fig. 5) demonstrates the “livingness” of the process and the  $M_n$  vs. conversion dependence in Figure 6 suggests the occurrence of TEMPO-deactivating side reactions (cf. the previous section).

## CONCLUSIONS

Thermal radical homopolymerization and copolymerization of 2VP with S at 125°C in the presence of stable nitroxyl radicals (TEMPO) yielded narrow-polydispersity polymers. The azeotropic 2VP–S copolymerization was found to proceed. The azeotropic composition,  $(F_{2VP})_A = 0.65$ , did not differ substantially from that in the conven-



**Figure 5** The semilogarithmic time–conversion plot for the 2VP–S copolymerization in the presence of TEMPO at a molar fraction of 2VP in the feed  $F_{2VP} = 0.65$  (Table III).  $[2VP + S]_0$  and  $[2VP + S]$  are initial and current comonomer concentrations, respectively.



**Figure 6** The  $M_n$  conversion dependence for the 2VP–S copolymerization in the presence of TEMPO at a molar fraction of 2VP in the feed  $F_{2VP} = 0.65$  (Table III).

tional copolymerization in the absence of a nitroxide in the reaction mixture (0.68). Under the studied experimental conditions, a pseudoliving polymerization process was observed. The molecular weights of both the homopolymers and copolymers increased with increasing conversion, although the increase is limited, obviously due to the side reactions reducing the number of TEMPO-terminated polymer chains.

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