

Synthesis of Hydroxyl-Terminated Copolymer of Styrene and 4-Vinylpyridine via Nitroxide-Mediated Living Radical Polymerization

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ABSTRACT: The random copolymers of styrene (St) and 4-vinylpyridine (4-VP) with hydroxyl end group and low polydispersities were synthesized by nitroxide-mediated living radical polymerization initiated by azobisisobutyronitrile (AIBN) and 4-hydroxyl-2,2,6,6-tetramethylpiperidine-oxyl (TEMPO-OH). The experimental results have shown that all synthesized copolymers have narrow molecular weight distribution. The conversion of monomers and the molecular weight of copolymer increased with polymerization time. The copolymerization rate is affected by molar

ratios of HTEMPO to AIBN. ¹H-Nuclear magnetic resonance spectra shows that one end of copolymers was capped by TEMPO-OH moiety. The use of this method permits the copolymer with hydroxyl chain end and controllable molecular weight and molecular weight distribution. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1842–1847, 2004

Key words: nitroxide-mediated living radiated polymerization; copolymers of styrene and 4-vinylpyridine; molecular weight distribution

INTRODUCTION

Recently, accurate control of polymerization processes to prepare well-defined molecular weight, low polydispersity, and end-functionalized polymers has become a highlight of polymer chemistry¹ since the end-functionalized polymers are capable of forming networks, producing various types of block copolymers,² and anchoring to a solid surface to adjust the surface characteristics of a substrate.³ Conventionally, the homopolymers or random copolymers with functional chain ends and narrow polydispersities used to be prepared by anionic,⁴ cationic,¹ or group transfer polymerization techniques.^{5,6} While these procedures are surely successful, they do have some drawbacks, such as rigorous synthetic requirements and incompatibility with a variety of functional groups.⁷

In 1993, Georges et al. reported the pseudoliving free radical polymerization in the synthesis of polystyrene by nitroxide-mediated radical polymerization.⁸ Then, a number of homopolymers, block copolymers, and random copolymers with low polydispersities were prepared by the nitroxide-mediated radical polymerization technique.⁹

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The homopolymer and copolymer that contain a pyridine group have attracted much interest in very recent years due to various applications, such as water-soluble polymer and coordination reagents for transition metal.¹⁰ Usually, poly(4-vinylpyridine) (P4VP) and its copolymer with controllable molecular weight and narrow molecular weight distribution were synthesized by anionic polymerization. However, this technique is limited by the poor solubility of P4VP with certain molecular weight in the common solvent, tetrahydrofuran (THF), in anionic polymerization. More recently, the synthesis of poly(4-vinylpyridine) was reported by using 2,2,6,6-tetramethylpiperidine-oxyl (TEMPO)-mediated free radical polymerization.^{11,12} However, the synthesis of random copolymers of styrene and 4-vinylpyridine with low polydispersity, controllable molecular weight, and functional end group hasn't been reported.

For functionalization of the chain end of polymers with nitroxide-mediated polymerization, Turro et al. has reported a method that is to first synthesize TEMPO-capped polymers as the precursors in nitroxide-mediated polymerization, followed by a nitroxide exchange with 4-hydroxyl- or 4-carboxyl-substituted TEMPO at 125°C in a high boiling point solvent. However, a complete exchange of chain end does not occur.¹³

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In this paper, we report the direct synthesis of hydroxyl-terminated copolymers of styrene (St) and 4-vinylpyridine (4-VP) with low molecular weight polydispersity by nitroxide-mediated radical polymerization using an initiation system, TEMPO-OH and azobisisobutyronitrile (AIBN).

EXPERIMENTAL SECTION

Materials

Commercially obtained 4-VP (Aldrich), St (Shanghai 1st Factory of Chemicals, China, 99%), calcium hydride (Shanghai 1st Factory of Chemicals), AIBN (Shanghai 4th Factory of Chemicals, 99%), 4-hydroxyl-2,2,6,6-tetramethylpiperidine (Beijing Huashan Auxiliary Factory), 30% hydrogen peroxide (Shanghai Chemistry and Chemical Engineering Ltd Co, China), sodium tungstate (Guangdong Liushan Chemistry and Chemical Engineering Factory, China), and ethylenediaminetetraacetic acid (Chemical Factory, Jiangsu Huakang Science and Technology Company, China) were purchased. 4-VP and St were dried with calcium hydride and then distilled under reduced pressure before use. AIBN was purified by recrystallization with absolute methanol. TEMPO-OH was prepared by oxidation of 4-hydroxyl-2,2,6,6-tetramethylpiperidine with 30% hydrogen peroxide using sodium tungstate and ethylenediaminetetraacetic acid as catalyst.¹⁴

Synthesis

Hydroxyl-terminated copolymer of styrene and 4-vinylpyridine (P(St-*r*-4VP)-OH)

The typical synthesized process was described below: after a 25-mL single-necked flask was treated with three freeze-pump-thaw cycles, 5.25 g of 4-VP (0.05 mol), 5.20 g of St (0.05 mol), 28.5 mg of AIBN (0.2 mmol), and 67.4 mg of TEMPO-OH (0.36 mmol) were added to the single-necked flask and stirred with magnetic stirrer, the single necked flask was placed into an oil bath at 100°C for 2 h to allow the decomposition of AIBN, and then was heated up to 130°C under Ar atmosphere. The polymerization was stopped by cooling the reaction system to -20°C. The copolymer was purified through dissolving it in mixed solvent of ethanol and toluene (1/1, v/v), and precipitating in *n*-hexane. This step was repeated three times.

Two-step copolymerization of P(St-*r*-4VP)-OH with styrene and 4-vinylpyridine

The process of the two-step copolymerization of P(St-*r*-4VP)-OH with St and 4-VP was similar to that of random copolymerization of St and 4-VP. First, the low molecular weight P(St-*r*-4VP)-OH was prepared

in the feed ratio of St to 4VP of 7/3 at the polymerization time of 5 h. The copolymer with lower molecular weight (1.0 g) then was dissolved in 7.3 g, (0.07 mol) of St and 3.2 g (0.03 mol) of 4-VP. The mixture was allowed to react for 19 h at 130 ± 2°C, in the absence of AIBN and TEMPO-OH.

Measurements

Infrared spectra were recorded on Nicolet 170SX FTIR spectrometer. ¹H-Nuclear magnetic resonance measurement (¹H-NMR) was performed on a Bruker MSL-300 spectrometer with CDCl₃ or DMSO-d₆ as the solvent. The molecular weight (M_n , M_w) and distribution index (M_w/M_n) were determined with a Waters 244 gel permeation chromatograph (GPC) employed with ultraviolet detector. For the samples for which the molar fraction of 4-VP was higher than 0.6, *N,N*-dimethylformamide (DMF) was used as elution solvent, and for other samples tetrahydrofuran (THF) was used as elution solvent. Monodisperse polystyrene (PS) samples were used as standards for calibration.

RESULTS AND DISCUSSION

Synthesis of P(St-*r*-4VP)-OH

Table I summarizes the data related to total conversion of monomers, molecular weights, and polydispersities of samples obtained using TEMPO-OH-mediated living radical polymerization at 130°C with different polymerization times. The molar ratio, TEMPO-OH/AIBN, was 1.8/1. As expected, the polydispersity was in the range of 1.1 to 1.3. The molecular weights of copolymers somewhat increased with styrene concentration in system.

Figure 1 shows $\ln([M]_0/[M])$ as a function of polymerization time for the copolymerization system with feed molar ratios of styrene to 4-vinylpyridine of 1, 7/3, 5/5, 3/7, and 0, respectively. The linear dependence of $\ln([M]_0/[M])$ on polymerization time suggests first-order kinetics with respect to the total monomer concentration, which is accordance with Baumann and Schmidt-Naake's result.¹² Comparing the slope of these lines, it is obvious that the polymerization rate of 4-VP is lower than that of St, and the copolymerization rate of St and 4-VP increases with increasing St concentration. In conventional free radical polymerization, 4-VP is known to be somewhat more active than St;¹⁵ herein, the lower polymerization rate of 4-VP in the presence of TEMPO-OH may be because the polarity of 4-VP is higher than that of St, which makes the C-ON bonds attaching to 4-VP more stable.

Figure 2 shows the number average molecular weight versus conversion plots for copolymerization of St and 4-VP at 130°C in the presence of TEMPO-OH

TABLE I
Copolymerization Data for Styrene and 4-Vinylpyridine

Reaction Time (h)	Total Conversion (%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	St/4-VP (Mole Ratio) ^a
5	17.0	0.97	1.11	1.14	7/3
8	26.2	2.37	2.82	1.19	
12	37.2	3.25	3.94	1.21	
16	46.3	4.79	5.60	1.17	
24	56.7	5.58	6.30	1.13	
5	13.0	0.81	0.94	1.16	5/5
8	21.0	1.79	2.2	1.2	
12	30.7	2.84	3.44	1.21	
16	38.4	3.86	4.79	1.24	
24	47.0	4.73	6.14	1.30	
5	9.1	0.6	0.7	1.17	3/7
8	14.5	1.5	1.7	1.13	
12	22.3	2.46	3.03	1.23	
16	31.0	3.29	4.18	1.27	
24	42.0	4.12	5.03	1.22	

^a Determined in feed molar ratio of St to 4-VP.

and AIBN at the feed molar ratios of 7/3, 5/5, and 3/7 (St/4-VP), respectively. The linear dependence of M_n on conversion was observed (Fig. 2, dashed line), exhibiting the basic character of "living" radical polymerization. The calculation of the theoretical values (Fig. 2, solid line) is larger than experimental values, which accounts for the presence of spontaneous autopolymerization in the copolymerization.

¹H-NMR spectrum of copolymer

Figure 3 shows the ¹H-NMR spectra of copolymer with a feed molar ratio of 5/5 (St/4-VP) and 26 kg/mol M_n . As seen in Figure 3, the peak near δ 8.3 corresponds to the third and fifth protons in pyridine rings; the peak near δ 7.2 belongs to the third, fourth,

and fifth protons in styrene rings; the peak near δ 6.7 is attributed to the second and sixth protons in pyridine rings and styrene rings;¹⁶ while the multiple peaks near δ 1.0 correspond to the methylene protons of the piperidine moiety and the resonance near δ 4.0 is attributed to the methine proton in neighborhood to the TEMPO-OH group. These results indicate that the chemical structure of synthesized copolymer is consistent with that of the random copolymer of styrene and 4-vinylpyridine, and the TEMPO-OH is capped at the one end of the copolymer chains.¹⁷

From the ¹H-NMR spectra of random copolymers of St and 4-VP, the content of 4-VP in copolymer can be determined through dividing the area of signal at 8.3 ppm corresponding to the third and fifth protons in pyridine rings by the area of signal at 6.6 ppm corre-

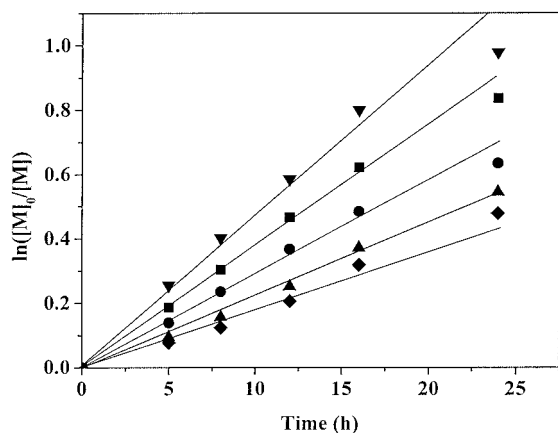


Figure 1 $\ln([M]_0/[M])$ as a function of polymerization time in different feed ratios of St to 4-VP, (∇) St, (\blacksquare) St/4-VP = 7/3, (\bullet) St/4-VP = 5/5, (\blacktriangle) St/4-VP = 3/7, (\blacklozenge) 4-VP, [HTEMPO] = 3.6×10^{-4} mol/L, [AIBN] = 2×10^{-4} mol/L, [Total monomer] = 0.36 mol/L.

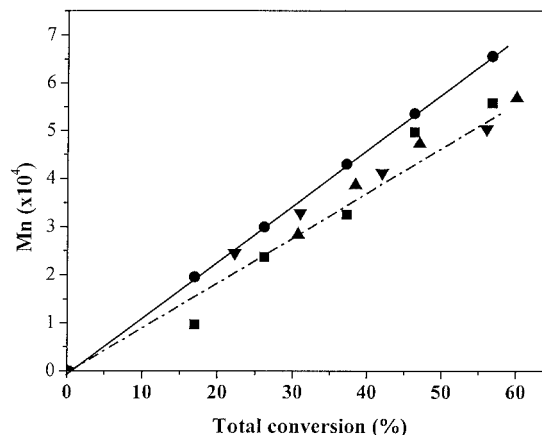


Figure 2 \bar{M}_n as a function of total conversion at different feed ratios (\blacksquare) St/4-VP = 7/3, (∇) St/4-VP = 5/5, (\blacktriangle) St/4-VP = 3/7, (\bullet) theoretical values. [HTEMPO] = 3.6×10^{-4} mol/L, [AIBN] = 2×10^{-4} mol/L, [Total monomer] = 0.36 mol/L.

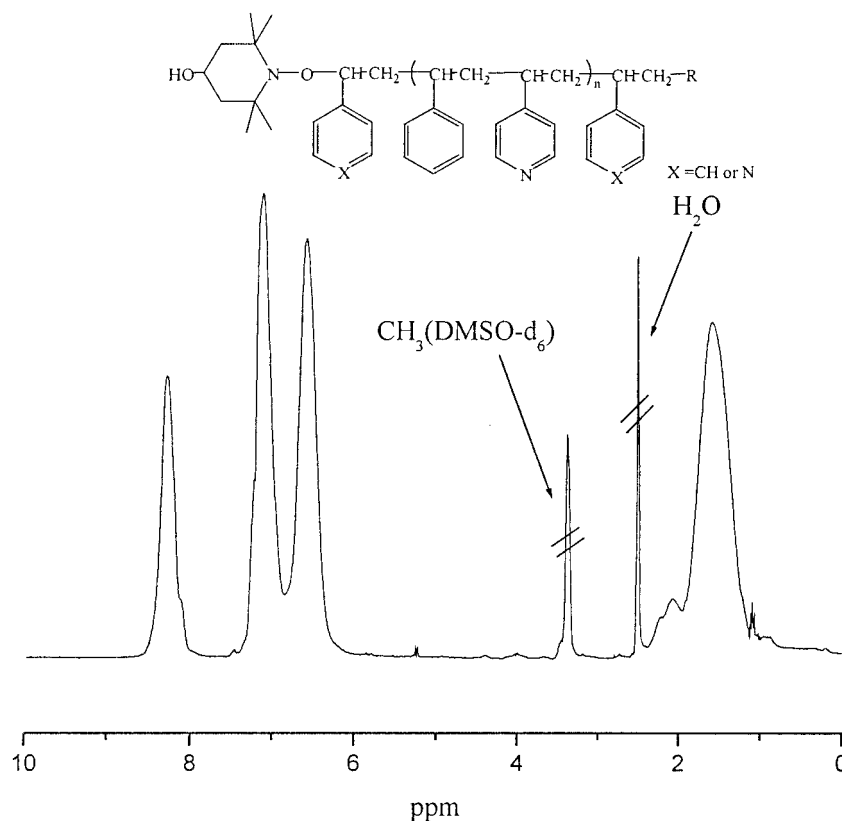


Figure 3 $^1\text{H-NMR}$ spectra of copolymer of styrene and 4-vinylpyridine, with feed molar ratio of 5/5 (St/4-VP) and M_n 26 g/mol.

sponding to the second and sixth protons in styrene rings and pyridine rings, respectively.¹⁶ The composition of copolymers calculated from $^1\text{H-NMR}$ spectra is listed in Table II.

Figure 4 shows the effective molar fraction of 4-VP in copolymers determined (F_{4VP}) by $^1\text{H-NMR}$ as a function of feed molar fraction of 4-vinylpyridine in the presence of AIBN and TEMPO-OH at 130°C for a polymerization time of 5 h. The monomer reactivity ratios were calculated according to Kelen-Tüdö's method,¹⁸ r_{St} and r_{4VP} are equal to 0.66 ± 0.03 and 1.12 ± 0.2 , respectively, for the copolymerization of St and 4-VP in the presence of AIBN and TEMPO-OH at 130°C.

Two-step copolymerization of P(St-*r*-4VP)-OH with St and 4-VP

It was found that, at 40 and 60% conversion, approximately 90 and 80% of chains, respectively, were still

TABLE II
Glass Transition Temperature

f^a	0.00	0.20	0.28	0.43	0.52	0.58	0.66	1.00
M_n (10^{-4})	2.53	2.60	2.51	2.59	2.63	2.74	2.70	2.82
T_g ($^{\circ}\text{C}$) ^b	122	114	112	108	106	105	102	90

^a Styrene fraction f calculated from $^1\text{H-NMR}$ spectra.

^b The T_g from DSC measurements.

active and carried an alkoxyamine end group in the TEMPO-mediated polymerization.¹⁹ To investigate the living nature of the chain end group in our system, the two-step copolymerization was carried out. Initially, the precursor copolymer, P(St-*r*-4VP)-TEMPO-OH, with low molecular weight, was prepared by using an initiation system, TEMPO-OH and AIBN. The copolymerization of precursor copolymer with St and 4-VP then was performed in the absence of AIBN

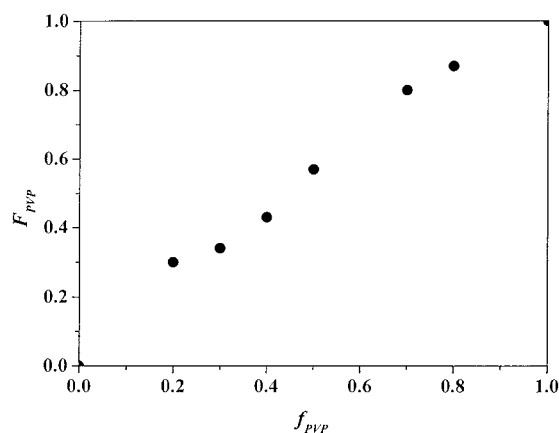


Figure 4 the effective 4-vinylpyridine mole fraction in copolymer (F_{4VP}) as function of initial mole fraction of 4-vinylpyridine in feed (f_{4VP}) at 130°C for 5 h.

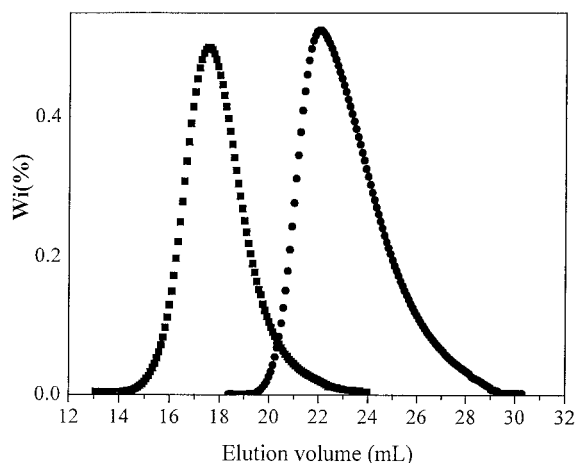


Figure 5 GPC curves of copolymers prepared by two step copolymerization (feed ratio St/4-VP = 7/3), (●) precursor copolymer, $M_n = 9.7$ k, $M_w/M_n = 1.13$, (■) The resultant copolymer, $M_n = 56$ k, $M_w/M_n = 1.2$.

and TEMPO-OH. Figure 5 displays the GPC curves of the precursor copolymer ($M_n = 9.7$ k, $M_w/M_n = 1.13$) and the resultant copolymer ($M_n = 56$ k, $M_w/M_n = 1.2$). It shows that the molecular weight of copolymer increases after the second step of polymerization, which indicates that TEMPO-OH ends possess the "living" nature and the ability to prepare the block copolymer.

Effect of molar ratio of TEMPO-OH to AIBN

Figure 6 presents the dependence of $\ln([M]_0/[M])$ versus polymerization time for the copolymerization of St and 4-VP at the feed ratio of 7/3 (St/4-VP, molar ratio) and molar ratios of TEMPO-OH to AIBN of 1.8 and 2.5, respectively. It shows that the copolymerization rate decreased with an increase of the ratio of

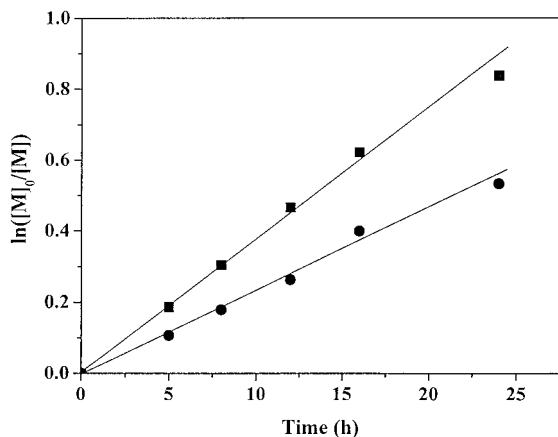


Figure 6 $\ln([M]_0/[M])$ as a function of polymerization time with two ratios of HTEMPO to AIBN at 130°C. (■) $[HTEMPO]/[AIBN] = 1.8/1$, (●) $[HTEMPO]/[AIBN] = 2.5/1$.

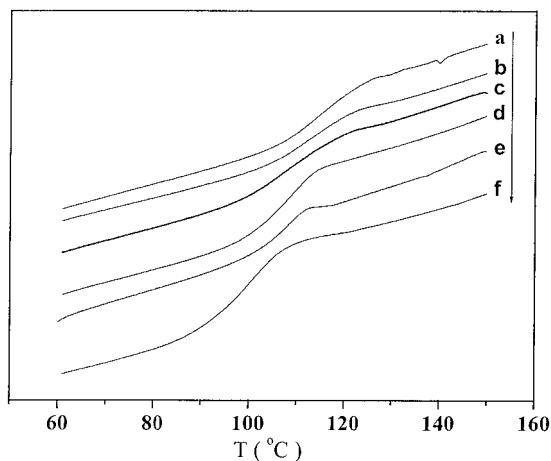


Figure 7 the DSC Curves of synthesized copolymers: (a) $f = 0.2$. (b) $f = 0.28$. (c) $f = 0.43$. (d) $f = 0.52$. (e) $f = 0.58$. (f) $f = 0.66$.

TEMPO-OH to AIBN. For higher concentrations of TEMPO-OH, the polymer chain radicals can be trapped very rapidly by HTEMPO and the propagation of copolymer chain was predominately carried out through nitroxide-mediated living radical polymerization. On other hand, for lower concentrations of TEMPO-OH, the spontaneous autocopolymerization may be dominant at the initial polymerization stage; consequently, the polymerization rate was higher compared to that with a higher concentration of TEMPO-OH.

Glass transition temperature (T_g) of copolymers

To investigate the copolymer chain structure, the T_g may provide some clues about the structure of copolymer. The T_g was determined by using differential scanning calorimetry (DSC) measurement. To avoid the effect of molecular weight of polymer on T_g , the polymer with similar average molecular weight (in the range of 25 to 28 kg/mol) was selected during DSC measurement. As shown in Figure 7 and Table 2, the results from DSC indicate that all synthesized copolymers having only one glass transition ranged from 90 to 120°C and T_g of copolymer increases with increasing P4VP fraction in the copolymer, indicating that all synthesized copolymers are random and homogeneous.

CONCLUSION

The random copolymerization of St and 4-VP initiated by AIBN and TEMPO-OH in bulk was investigated. It shows that hydroxyl terminated copolymers with various St fraction can be obtained by TEMPO-OH-mediated polymerization. The conversion of monomers and the molecular weight of copolymer increased with

polymerization time. The conversion and polymerization rate were affected by molar ratio of HTEMPO to AIBN. The synthesized copolymers have low polydispersities ($\overline{M}_w/\overline{M}_n = 1.13\sim 1.3$). $^1\text{H-NMR}$ spectra suggested that the end of the copolymer is capped by the TEMPO-OH moiety; DSC measurement shows that each of synthesized copolymers exhibits one glass transition, and the T_g of copolymers increases with the decrease of St fraction in the copolymer.

Although we have focused on the synthesis of hydroxyl-terminated copolymers by TEMPO-OH-mediated polymerization in this paper, the potential application of this method is broader; for example, we have successfully used such hydroxyl-terminated polymers to initiate ring-opening polymerization of caprolactone and lactide at temperatures below 100°C . Thus, the synthesis of the block copolymers with polycaprolactone or polylactide as one block and polystyrene or poly(4-vinylpyridine) as another block becomes simple.

References

1. Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. *Macromolecules* 1996, 29, 3050.
2. Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. *Science* 1997, 275, 1458.
3. Quirk, R. P.; Lynch, T. *Macromolecules* 1993, 26, 1206.
4. Fréchet, J. M. *J Science* 1994, 263, 1710.
5. Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* 1987, 20, 1473.
6. Xia, J.H.; Zhang, X.; Matyjaszewski, K. *Macromolecules* 1999, 32, 3531.
7. Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* 1993, 26, 2145.
8. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987.
9. Yoshida, E.; Sugita, A. *Macromolecules* 1996, 29, 6422.
10. Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC Press: Boca Raton, FL, 1984; vol. 2.
11. Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* 1996, 29, 2686.
12. Baumann, M.; Schmidt-Naake, G. *Macromol Chem Phys* 2000, 201, 2751.
13. Turro, N. J.; Lem, G.; Zavarine, I. S. *Macromolecules* 2000, 33, 9782.
14. Kurosaki, T. K.; Lee, W.; Okawara, M. *J Polym Sci Polym Chem Ed* 1972, 10, 3295.
15. Bohrisch, J.; Wendler, U.; Jaeger, W. *Macromol Rapid Comm* 1997, 18, 975.
16. Bossè, F.; Schreiber, H. P.; Eisenberg, A. *Macromolecules* 1993, 26, 6447.
17. Howell, B. A.; Priddy, I. Q.; Li, P. B.; Smith, P. E. *Polym Bull* 1996, 37, 451.
18. Kelen, T.; Tüdö, F. *J Macromol Sci* 1975, A9, 1.
19. Dorota, G. K.; Matyjaszewski, J. *Macromolecules* 1996, 29, 7661.