

Synthesis of Diblock Copolymers Comprising Poly(2-vinylpyridine-*co*-acrylonitrile) and Polystyrene Blocks by Nitroxide-Mediated Radical Polymerization

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ABSTRACT: Nitroxide-mediated radical copolymerization of 2-vinylpyridine (2VP) with acrylonitrile (AN) at various mole fractions of 2VP in the feed at 125°C was studied. An alkoxyamine containing the diethoxyphosphoryl group (MAMA-SG1) or a two-component system of 2,2'-azobis(isobutyronitrile) or dibenzoyl peroxide in combination with nitroxyl radicals TEMPO were used for the initiation; in addition, spontaneous thermal radical copolymerization of both the comonomers was performed in the presence of a nitroxide. The obtained nitroxide-terminated 2VP-AN copolymers showed a low polydispersity ($M_w/M_n \sim 1.2$). They initiated polymerization of styrene (S) giving poly(2VP-*co*-AN)-*block*-polyS diblock copolymers; however, in dependence on the used macroinitiator, the resulting

products might be markedly contaminated with inactive polymer chains. On the other hand, the 2VP-AN copolymerization, which was initiated at 125°C with a TEMPO-terminated polyS, proved to be an efficient synthetic route for the preparation of diblock copolymers comprising blocks of polyS and poly(2VP-*co*-AN). The synthesized copolymers were characterized by NMR spectroscopy and size-exclusion chromatography. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1616–1622, 2007

Key words: 2-vinylpyridine-acrylonitrile copolymers; nitroxide-mediated radical copolymerization; chain extension; diblock copolymers

INTRODUCTION

The development of new radical polymerization techniques in the last 2 decades opened the way to the synthesis of polymers with controlled and complex architectures. Among other methods, the radical polymerization in the presence of a nitroxide stable radical, such as 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO), offers the possibility to prepare a wide range of different, well-defined polymer materials.^{1–15} In the course of the polymerization, the nitroxide prevents irreversible bimolecular termination of macroradicals by trapping them under formation of thermally unstable *N*-alkoxyamines. At temperatures above 100°C, the C—ON bond of the *N*-alkoxyamine undergoes dissociation to regenerate both the polymer and nitroxyl radicals. The polymer radical adds more monomer units and is trapped again by the nitroxyl. Due to the fast initiation and the reversible trapping reaction, the growth of the polymer chains proceeds in a quasili-

ing manner. As a result, molecular weights of the resulting polymers increase with increasing conversion and have a narrow distribution. However, some side reactions can also occur in the polymerization impairing its quasili- nature. Their typical representatives are the deactivation of the nitroxyl radical by a termination reaction with the growing polymer chain or the decomposition of the *N*-alkoxyamine leading to an ω -unsaturated copolymer and a hydroxylamine derivative.^{8–10}

Initially, two-component systems consisting of a thermal radical initiator, as a rule dibenzoyl peroxide, in combination with nitroxyl radicals were used in the initiation of controlled radical polymerizations.¹ Later on, unimolecular initiators based on an alkoxyamine structure were developed.^{3,6,14} They contain both a latent initiating group and nitroxide in the 1 : 1 stoichiometry. The success of the controlled radical polymerization process depends on the strength of the C—ON bond in the initiators. Styrene (S)-based monomers as well as structurally similar vinylpyridine and some of their comonomer mixtures polymerize in the controlled manner even without any added initiator.^{5,16,17} The relatively high temperatures, at which the polymerizations in the presence of a nitroxide are conducted, result in a spontaneous formation of primary radicals. They are terminated with the nitroxide to give

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in situ unimolecular initiators; thus, a controlled auto-polymerization can proceed.

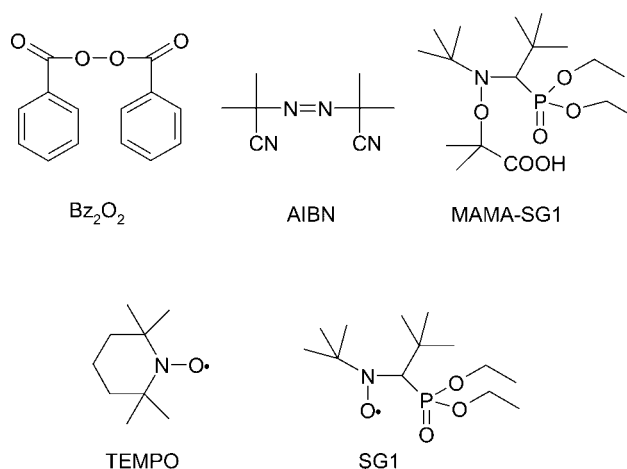
The obtained nitroxide-terminated polymers can be isolated, purified, and stored. They are widely used as precursors of block copolymers in chain extension reactions. A number of new interesting diblock copolymers comprising random copolymer blocks were described by Fukuda et al.⁴ Their properties can be extensively modified by changing the nature, amount, and ratio of comonomer units. For example, through copolymerization of an azeotropic mixture of styrene and acrylonitrile (AN) in the presence of TEMPO-terminated polyS, polyS-*block*-poly(S-*co*-AN) diblock copolymers were prepared and characterized.^{4,18,19} In our recent work,²⁰ first we have synthesized TEMPO-terminated azeotropic S-AN copolymers, which served as precursors of poly(S-*co*-AN)-*block*-polyS diblock copolymers. A tri-block copolymer of the A-B-A type was also prepared. These block copolymers showed promising properties as membrane materials for the separation of nitrogen/oxygen mixtures.

The purpose of the present study was to synthesize analogous block copolymers containing 2-vinylpyridine (2VP) structure units. The presence of the vinylpyridine units with nucleophilic nitrogen makes possible a variety of modifying reactions, such as quaternization, reaction with acids, and complexation of metals. Vinylpyridine polymers and their ionic derivatives can be used as polyelectrolytes, polymer reagents, membranes, and in electrical applications.²¹ So, the 2VP-AN copolymerization in the presence of TEMPO-capped polyS was conducted. Similarly to our work,²⁰ we have also prepared nitroxide-terminated copolymers of 2VP with AN and employed them as macroinitiators in the polymerization of styrene. Copolymerizations of 2VP-AN mixtures at various mole ratios of the comonomers and under different initiating conditions were performed; then, chain extension of the resulting polymer products with styrene was carried out. Both the synthetic routes, i.e., with polyS or the 2VP-AN copolymer precursor containing reversibly bound terminal nitroxyl groups, afforded film-forming block copolymers composed of polyS and poly(2VP-*co*-AN) blocks. A study of chemical modifications of the prepared functional block copolymers and their properties is in progress.

EXPERIMENTAL

Materials

2,2'-Azobis(isobutyronitrile) (AIBN) (Fluka, Switzerland) (mp 105°C) was recrystallized from ethanol. Dibenzoyl peroxide (Bz₂O₂) (Fluka) (mp 104°C) was reprecipitated from a chloroform solution with methanol. 2-((*tert*-Butyl)[1-(diethoxyphosphoryl)-2,2-dimethyl-



Scheme 1 The initiators and nitroxides used in the copolymerization of 2-vinylpyridine with acrylonitrile.

propyl]amino)oxy)-2-methylpropanoic acid (MAMA-SG1) (mp 125°C) and {*tert*-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino}oxyl radical (SG1) (purity 86.6%) were supplied by Atofina, France. The TEMPO radical (mp 36–39°C) was a commercial product of Fluka. (Chemical formulae of these initiators and nitroxides are given in Scheme 1.) 2VP (Fluka) (bp 48°C/1.56 kPa), AN (Fluka) (bp 78°C/101.2 kPa), and styrene (Kaučuk Group, Kralupy, Czech Republic) (bp 36°C/1.56 kPa) were distilled prior to use. The solvents used were of analytical grade.

Synthesis of nitroxide-terminated polymer precursors

TEMPO-terminated polyS

The polyS precursor was prepared according to the procedure described earlier²²: A mixture of S (25 mL), Bz₂O₂ (1×10^{-2} mol L⁻¹), and TEMPO (1.5×10^{-2} mol L⁻¹) was heated in a glass ampoule in an inert atmosphere at 125°C for 20 h. The resulting polyS (PS-TEMPO) (about 75% conversion) was precipitated with ethanol from a chloroform solution. It was dried under vacuum (6.6 Pa) at room temperature. $M_n = 3.86 \times 10^4$, $M_w/M_n = 1.08$.

Nitroxide-terminated 2VP-AN copolymers

A mixture of 2VP, AN (5×10^{-2} mol of comonomers), and *N*-alkoxyamine MAMA-SG1 (1×10^{-4} mol) was heated at 125°C in a sealed glass ampoule in nitrogen atmosphere. Mole fractions of 2VP, F_{2VP} , varied in the range 0.2–0.9. After 1 h, the resulting SG1-terminated 2VP-AN copolymer was precipitated from the reaction mixture with excess hexane and dried under vacuum (6.6 Pa) at 60°C. The yields, compositions, molecular weights, and molecular weight distributions (MWD) of copolymers A2,

TABLE I
Copolymerization of 2-Vinylpyridine (2VP) with Acrylonitrile in the Presence of Alkoxyamine MAMA-SG1 at 125°C

Copolymer	F_{2VP}	f_{2VP}^a	Yield (wt %)	M_n (10^{-4}) ^b	M_w/M_n
A2	0.2	0.34	47.3	10.22	1.49
A5	0.5	0.55	34.3	6.94	1.23
A6	0.6	0.60	23.7	5.16	1.19
A7	0.7	0.65	24.8	5.44	1.25
A8	0.8	0.73	25.3	4.88	1.24
A9	0.9	0.86	27.0	5.68	1.20

Reaction conditions: 5×10^{-2} mol of total comonomers; 1×10^{-4} mol of MAMA-SG1; 1 h.

F_{2VP} and f_{2VP} are the mole fractions of 2VP in the feed and in the copolymer, respectively.

^a From ¹H NMR.

^b Polystyrene-equivalent, SEC.

A5–A9 are given in Table I. Table II summarizes the results on the synthesis of 2VP-AN copolymers A6-1 (A6-4 at $F_{2VP} = 0.6$ under various reaction conditions using the nitroxide SG1 or TEMPO).

Chain extension of nitroxide-terminated polymer precursors

According to the type of the precursor Scheme 2, the chain extension reaction proceeded as follows:

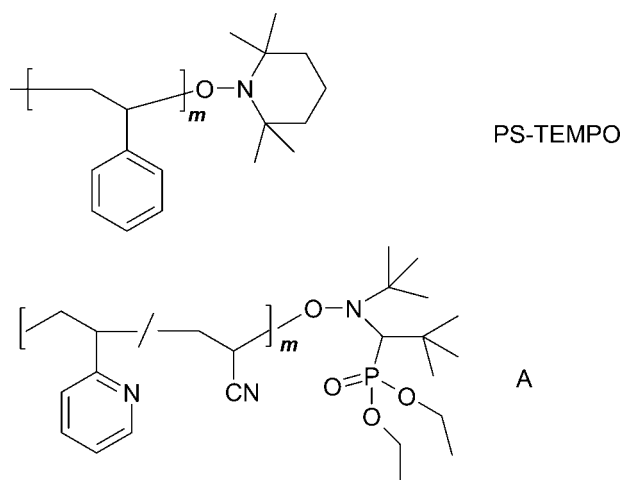
The PS-TEMPO (0.2 g), 2VP, and AN (5×10^{-2} mol total) in a glass ampoule were heated at 125°C in nitrogen atmosphere for 40 min. The mixture contained 20, 50, or 80 mol % of 2VP. The precipitation with an excess of hexane yielded a diblock copolymer. It was dried under vacuum (6.6 Pa) at 60°C.

In a similar way, using the SG1-terminated 2VP-AN copolymer A2, A5, or A8 (0.2 g) as a macroinitiator, the chain extension with styrene (5 mL) took place under formation of the diblock copolymer composed of poly(2VP-*co*-AN) and polyS blocks.

Table III presents some characteristics of the prepared block copolymers Scheme 3.

Characterization of the copolymers

The yields of copolymers were determined gravimetrically, their compositions from ¹H-NMR measure-



Scheme 2 The nitroxide-terminated polymer precursors used in the synthesis of block copolymers comprising poly(2-vinylpyridine-*co*-acrylonitrile) and polystyrene blocks.

ments. The molecular weights and MWDs were evaluated by size-exclusion chromatography (SEC).

NMR measurements

¹H-NMR spectra of 10% (w/w) copolymer solutions in deuterated chloroform were measured at 300.13 MHz with a Bruker Avance DPX 300 spectrometer at 330 K. Hexamethyldisiloxane was used as internal standard. The relative contents of comonomer units (in parentheses) were expressed by the integrated intensities of corresponding signals for 2VP-AN copolymers (I_A) and for diblock copolymers with polyS and poly(2VP-*co*-AN) blocks (I).

2VP-AN copolymers

$$(2VP) = I_{A(2VP)}/4$$

$$(AN) = [I_{A(2VP+AN)} - 3I_{A(2VP)}/4]/3;$$

$I_{A(2VP)}$ and $I_{A(2VP+AN)}$ refer to the signals of four aromatic protons in the 2VP ring and of 3 + 3 aliphatic protons in 2VP+AN units, respectively.

TABLE II
Copolymerization of 2-Vinylpyridine (2VP) with Acrylonitrile (AN) in the Presence of a Nitroxide SG1 or TEMPO at 125°C^a

Copolymer	Initiator (10^4 mol)	Nitroxide (10^4 mol)	Time (h)	Yield (wt %)	M_n (10^{-4}) ^b	M_w/M_n
A6-1	–	SG1: 1	2	12.8	9.59	1.26
A6-2	–	TEMPO: 1.5	3.5	7.6	7.54	1.37
A6-3	AIBN: 1	TEMPO: 1.5	1	33.7	5.63	1.37
A6-4	Bz ₂ O ₂ : 0.5	TEMPO: 0.75	1	27.5	9.56	1.36

Reaction conditions: 3×10^{-2} mol (60 mol %) of 2VP; 2×10^{-2} mol (40 mol %) of AN.

^a The copolymers contained about 60 and 40 mol % of 2VP and AN units, respectively, as determined by ¹H NMR.

^b Polystyrene-equivalent, SEC.

TABLE III
Chain Extension of Nitroxide-Terminated Polymer Precursors (0.2 g of Precursor, 125°C, 40 min)

Resulting polymer	Precursor ^a	Monomer(s)	$(f_S)_T$	$(f_{2VP})_T$	f_{2VP}	M_n (10^{-4}) ^b	M_w/M_n
B2	PS-TEMPO	2VP-AN ^c	0.26	0.30	0.41	8.86 (11.68)	1.54
B5	PS-TEMPO	2VP-AN ^d	0.21	0.47	0.60	11.83 (15.58)	1.72
B8	PS-TEMPO	2VP-AN ^e	0.35	0.49	0.75	8.62 (10.77)	1.68
C2	A2	S ^f	0.60	0.12	0.30	18.19	1.70
C5	A5	S ^f	0.63	0.18	0.49	g	2.03
C8	A8	S ^f	0.65	0.20	0.58	g	1.94

$(f_S)_T$ and $(f_{2VP})_T$ are the mole fractions of incorporated S and 2VP units, respectively, in the resulting polymer; f_{2VP} is the mole fraction of 2VP units in the incorporated 2VP-AN copolymer, as determined by ¹H NMR.

^a The molecular weight of the polystyrene precursor (PS-TEMPO) is 3.86×10^4 , $M_w/M_n = 1.08$; the characteristics of the precursors A2, A5, and A8 are given in Table I.

^b Polystyrene-equivalent, SEC; the values in parentheses were calculated from both the M_n of the precursor and the composition of the block copolymer.

^c 20 mol % (1×10^{-2} mol) of VP, 80 mol % (4×10^{-2} mol) of AN.

^d 50 mol % (2.5×10^{-2} mol) of VP, 50 mol % (2.5×10^{-2} mol) of AN.

^e 80 mol % (4×10^{-2} mol) of VP, 20 mol % (1×10^{-2} mol) of AN.

^f 5 mL of styrene.

^g A bimodal SEC curve.

The mole fractions of incorporated 2VP units, f_{2VP} , were calculated from eq. (1) (Tables I and II):

$$f_{2VP} = (2VP)/[(2VP) + (AN)] \quad (1)$$

Block copolymers comprising polyS and poly(2VP-co-AN) blocks

$$(2VP) = I_{(2VP)}$$

$$(S) = [I_{(2VP+S)} - 3I_{(2VP)}]/5$$

$$(AN) = \{I_{(2VP+S+AN)} - 3[I_{(2VP+S)} - 3I_{(2VP)}]/5 - 3I_{(2VP)}\}/3;$$

$I_{(2VP)}$ refers to the signals of 1 aromatic proton adjacent to nitrogen in the 2VP ring, $I_{(2VP+S)}$ refers to

the signals of 3 remaining aromatic protons in the 2VP ring + 5 aromatic protons in the S unit, and $I_{(2VP+S+AN)}$ to the signals of 3 + 3 + 3 aliphatic protons in 2VP+S+AN units.

An example of the ¹H-NMR spectrum of a synthesized block copolymer is given in Figure 1.

The mole fractions of incorporated S units, $(f_S)_T$, were calculated from eq. (2) (Table III):

$$(f_S)_T = (S)/[(S) + (2VP) + (AN)] \quad (2)$$

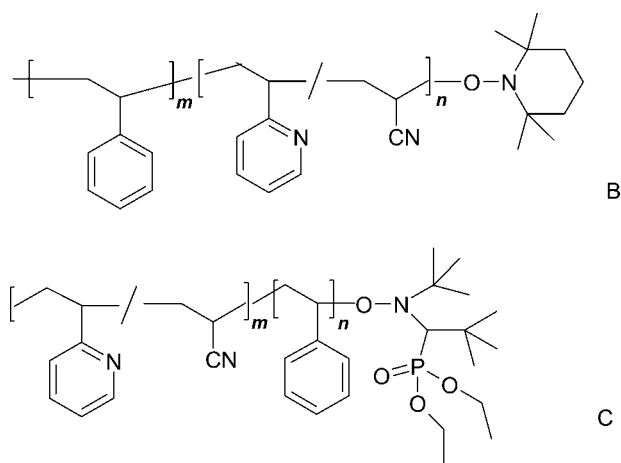
Determination of molecular weights

The SEC measurements for evaluation of number- and weight-average molecular weights (M_n and M_w) were carried out on a Biospher GM 1000 column (8×500 mm²; Labio, Czech Republic) filled with 10- μ m sorbent particles. Distilled *N,N*-dimethylacetamide (Fluka) served as a mobile phase. The data from refractive index detector were collected and treated using CSW 1.7 software (Data Apex, Czech Republic). For the determination of molecular weights, a universal calibration equation calculated from the data on polyS standards (Merck, Germany) was used.

RESULTS AND DISCUSSION

Nitroxide-terminated 2VP-AN copolymers

Table I presents the results on the copolymerization of 2VP with AN at various mole ratios of the comonomers, initiated with alkoxyamine MAMA-SG1 at 125°C. The highest yield (47.3%) was reached at 20 mol % of 2VP in the feed; the obtained copolymer A2 also exhibited the highest molecular weight ($M_n = 10.22 \times 10^4$) and the broadest polydispersity



Scheme 3 The synthesized block copolymers comprising poly(2-vinylpyridine-co-acrylonitrile) and polystyrene blocks.

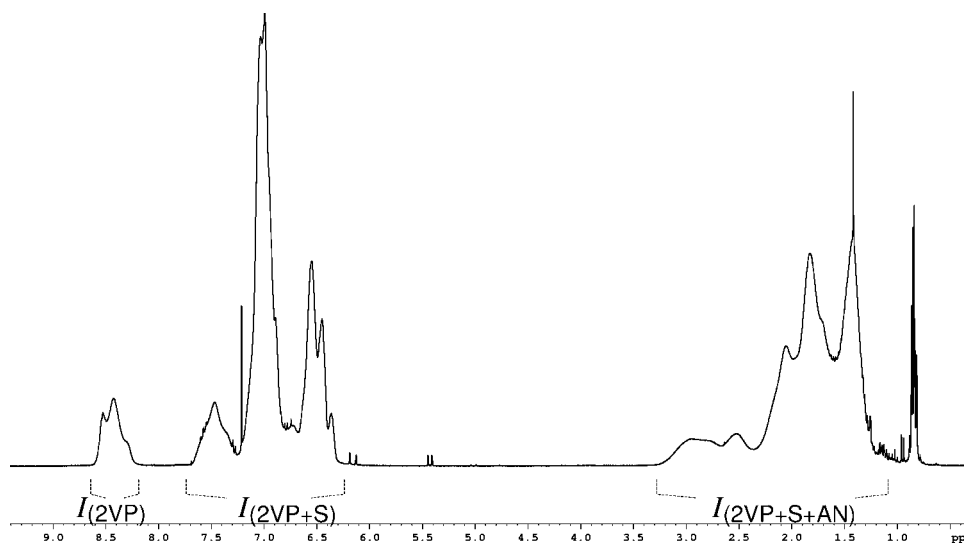


Figure 1 ^1H NMR spectrum of diblock copolymer B2. $I_{(2VP)}$, $I_{(2VP+S)}$, and $I_{(2VP+S+AN)}$ are the integrated intensities of signals of one aromatic proton adjacent to nitrogen in the 2VP ring, three remaining aromatic protons in the 2VP ring + 5 aromatic protons in the S unit, and $3 + 3 + 3$ aliphatic protons in 2VP+S+AN units, respectively.

($M_w/M_n = 1.49$). The latter value indicates that the largest extent of deactivation of growing polymer chains resulting in broadening of MWD can be assumed at the mole fraction $F_{2VP} = 0.2$. The other copolymers, A5–A9, exhibited a very narrow MWD ($M_w/M_n \sim 1.2$), typical of a quasiling polymerization mechanism. Their compositions (f_{2VP} values) were in good accordance with the f_{2VP} – F_{2VP} dependence (dotted curve in Fig. 2), which was observed in the conventional radical 2VP-AN copolymerization; the curve was calculated using the published monomer reactivity ratios (r), namely, $r_{2VP} = 0.47$ for 2VP and $r_{AN} = 0.11$ for AN.²³ A deviation of the f_{2VP} value at $F_{2VP} = 0.2$ from the depicted dependence is evidently due to a high conversion of the comonomers under given reaction conditions. The 2VP-AN copolymerization proceeds in an azeotropic manner with the preferential incorporation of 2VP into polymer chains at the mole fraction F_{2VP} within 0–0.6. The calculated azeotropic composition, $F_{2VP} = (1 - r_{AN}) / (2 - r_{AN} - r_{2VP})$, is equal to 0.63.

At $F_{2VP} = 0.6$, the 2VP-AN copolymerization was also carried out in the presence of stable radicals SG1 or TEMPO without any added initiator (Table II). Thermal nitroxide-mediated radical copolymerization took place giving copolymers A6-1 and A6-2 with a low polydispersity ($M_w/M_n = 1.26$ and 1.37). The copolymers A6-2, A6-3, and A6-4, which were prepared in the presence of TEMPO alone or together with the thermal initiator AIBN or BZ_2O_2 , showed a slightly broader molecular-weight distribution ($M_w/M_n \sim 1.37$) than the SG1-terminated 2VP-AN copolymers ($M_w/M_n \sim 1.23$) (Tables I and II). In comparison with the TEMPO-terminated polymer chains, those containing terminal SG1

groups are obviously more susceptible to the quasiliving process.

PolyS-*block*-poly(2VP-co-AN) diblock copolymers

The 2VP-AN copolymerization was also readily initiated with a nitroxide-terminated polyS. On heating at 125°C, a mixture of the comonomers containing

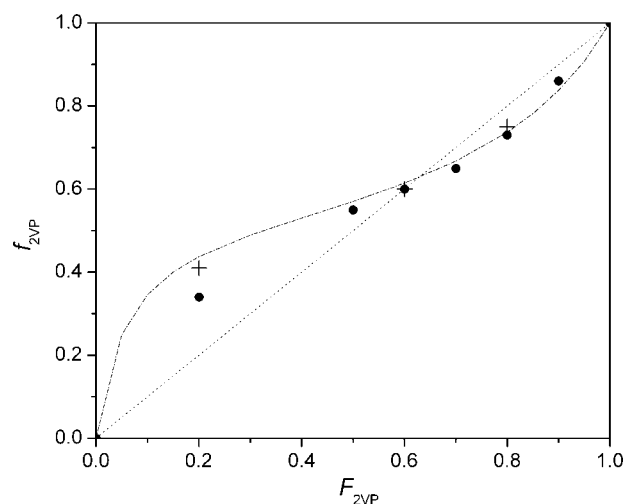


Figure 2 The dependence of the copolymer composition on the feed composition in the 2-vinylpyridine (2VP)–acrylonitrile (AN) copolymerization. F_{2VP} and f_{2VP} are mole fractions of 2VP in the feed and in the copolymers, respectively. Dotted curve was calculated from the monomer reactivity ratios for the conventional radical 2VP-AN copolymerization ($r_{2VP} = 0.47$, $r_{AN} = 0.11$), circles and crosses correspond to values obtained using, respectively, MAMA-SG1 (Table I) and PS-TEMPO (Table III) as initiators.

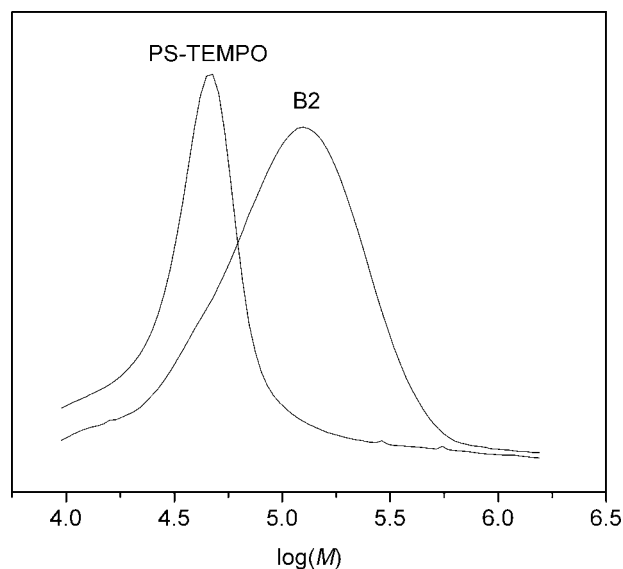


Figure 3 SEC curves of the nitroxide-terminated polystyrene PS-TEMPO and related diblock copolymer B2 with polystyrene and poly(2-vinylpyridine-*co*-acrylonitrile) blocks.

20, 50, or 80 mol % of 2VP and the synthesized PS-TEMPO yielded a diblock copolymer, in which the formed 2VP-AN copolymer blocks were attached to the polyS blocks. This was confirmed by the unimodal eluogram indicating complete incorporation of the macroinitiator by an increased molecular weight and by the composition of the resulting polymer. In comparison with the original PS-TEMPO, broadening of MWDs appeared, probably due to concomitant irreversible termination reactions. Figure 3 illustrates the SEC curves of the polyS macroinitiator and related diblock copolymer B2. In the prepared diblock copolymers B2, B5, and B8 (Table III), the fractions of the 2VP-AN copolymer blocks were found to be three to four times higher than those of polyS. A somewhat lower content of the incorporated 2VP-AN copolymer (65 mol %) in B8 than in B2 (74 mol %) and B5 (79 mol %) can be related to a slower copolymerization of the comonomers containing 80 mol % of 2VP (cf. Table I). In accordance with this feature, copolymer B5 had a higher molecular weight ($M_n = 11.83 \times 10^4$) than B8 ($M_n = 8.62 \times 10^4$). However, no significant difference was observed in the M_n values of B8 and B2 ($M_n = 8.86 \times 10^4$), even though, according to Table I, the rate of copolymerization at $F_{2VP} = 0.2$ was almost double than at $F_{2VP} = 0.8$ using alkoxyamine MAMA-SG1 as the initiator. So, the determined molecular weights indicate that the structure of terminal nitroxyl groups in polymer chains plays an important role in the copolymerization; this was already observed in experiments given in Table II. The SG1- and TEMPO-terminated polymer chains evidently differ in reactions influencing the final chain length.

The same conclusion can be drawn taking into account the calculated M_n values of the diblock copolymers B2, B5, and B8. Considering the unimodal SEC curves of the copolymers and, consequently, the complete consumption of the precursor PS-TEMPO ($M_n = 3.86 \times 10^4$), the corresponding M_n was calculated using eq. (3):

$$M_n = 3.86 \times 10^4 \{1 + [(f_{2VP})_T \times M_{2VP}] / [(f_S)_T \times M_S] + [(f_{AN})_T \times M_{AN}] / [(f_S)_T \times M_S]\}; \quad (3)$$

$(f_{2VP})_T$, $(f_S)_T$, $(f_{AN})_T$ and M_{2VP} , M_S , M_{AN} are the mole fractions and molecular weights, respectively, of the individual comonomer units.

The more correct M_n values were obtained in this way; the SEC method provided only polyS-equivalent molecular weights due to its inability to distinguish the different nature of the incorporated comonomers. Nevertheless, both the determined and calculated M_n values follow the same order: M_n of B5 > M_n of B2 > M_n of B8.

Table III also presents the mole fractions of 2VP in the 2VP-AN copolymer blocks (f_{2VP}); the values were plotted in Figure 2. As expected, they corresponded to the same f_{2VP} - F_{2VP} dependence as for the 2VP-AN copolymerization initiated with the alkoxyamine MAMA-SG1 or for conventional radical copolymerization of both the comonomers.

The obtained polyS-*block*-poly(2VP-*co*-AN) diblock copolymers are white powders. Films can be prepared from them by casting chloroform solutions and subsequent evaporation of the solvent.

Chain extension of nitroxide-terminated 2VP-AN copolymers with styrene

The results on the polymerization of styrene initiated with the SG1-terminated 2VP-AN copolymers A2, A5, and A8 demonstrate that 60–65 mol % of S was incorporated in the resulting polymers C2, C5, and C8 (Table III) under given reaction conditions. In C2, the determined content of 2VP in the incorporated 2VP-AN copolymer was rather close to that in the original A2 ($f_{2VP} = 0.30$ versus 0.34) and a unimodal SEC curve was observed (Fig. 4); thus, the prepared C2 can be regarded as a diblock copolymer. The obtained polymers C5 and C8, however, showed a distinct difference in the f_{2VP} values, which were found for the corresponding original and incorporated 2VP-AN copolymers A5 ($f_{2VP} = 0.55$ versus 0.49) or A8 ($f_{2VP} = 0.73$ versus 0.58) (cf. Tables I and III). At the same time, bimodal SEC curves of C5 and C8 (Fig. 4) indicated that an appreciable amount of polymer chains was excluded from the chain extension. The unequal mole ratios and compositions

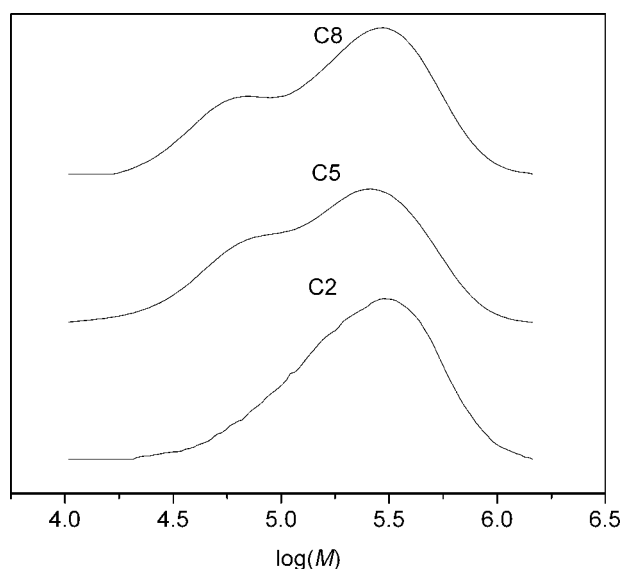


Figure 4 SEC curves of copolymers C2, C5, and C8, which were synthesized by chain extension with styrene of nitroxide-terminated 2-vinylpyridine-acrylonitrile copolymers A2, A5, and A8, respectively.

of the generated diblock copolymer and a concomitant inactive polymer fraction, resulting in the preferential precipitation of long polymer chains, i.e., the diblock copolymer, might account for the observed f_{2VP} differences. Thus both the bimodal eluograms and the discrepancy between the f_{2VP} values revealed that, along with the formation of diblock copolymers derived from A5 and A8, deactivated polymer chains arose to a large extent, probably due to side reactions such as thermal decomposition or disproportionation termination.⁸⁻¹⁰

CONCLUSIONS

The copolymerization of 2VP with AN, initiated with an alkoxyamine MAMA-SG1, thermally in the presence of SG1 or TEMPO radicals or with a system AIBN (Bz_2O_2) - TEMPO at 125°C yields the nitroxide-terminated 2VP-AN copolymers of a narrow polydispersity. The copolymerization course exhibits an azeotropic copolymer at the mole fraction of 2VP in the feed, F_{2VP} , equal to 0.6; this value is virtually identical with that found for the conventional radical copolymerization of both the comonomers ($F_{2VP} = 0.63$).

The SG1-terminated 2VP-AN copolymers initiate chain extension with styrene. Diblock copolymers

poly(2VP-*co*-AN)-*block*-polyS are generated; however, according to the used macroinitiator, they can contain a considerable amount of inactive polymer chains.

The diblock copolymers with blocks of polyS and poly(2VP-*co*-AN) can be readily synthesized by the 2VP-AN copolymerization in the presence of TEMPO-terminated polyS. The compositions of the incorporated 2VP-AN copolymer blocks are in accordance with the process, characterized by the monomer reactivity ratios $r_{2VP} = 0.47$ and $r_{AN} = 0.11$.

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