

Synthesis of Block Copolymer from Dissimilar Vinyl Monomer by Stable Free Radical Polymerization

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ABSTRACT: Controlled polystyrenes with different molar mass values were synthesized starting from benzoyl peroxide and TEMPO (2,2,6,6-tetramethylpiperidiny-1-oxy). The polystyrene homopolymers served as macroinitiators for the block copolymerizations of the dissimilar vinyl monomers butyl methacrylate (BMA), ethyl methacrylate (EMA), methyl methacrylate (MMA), octyl methacrylate (OMA), vinyl acetate (VAc), *N,N*-dimethylacrylamide (DMA), and 2-(dimethylamino)ethyl acrylate (DAEA). Polystyrene–polymethacrylate diblock copolymers with well-defined structures as well as controlled and narrow molar mass distribution were obtained from the lower-mass polystyrene macroinitiator. Contrary to methacrylates, VAc and DAEA are not readily initiated by the polystyrene macroinitiator. Block copolymer formation was confirmed by ^1H NMR and GPC measurements. On the basis of the ^1H NMR investigation, there is strong evidence for the presence of TEMPO-terminated copolymers. The TEMPO-mediated polymerization is suitable for the synthesis of polystyrene–polymethacrylate diblock copolymers from vinyl monomers.

Introduction

Accurate control of polymerization processes to give well-defined polymers and copolymers is an increasingly important aspect of polymer chemistry.¹ Living polymerizations provide the maximum amount of control of the synthesis of well-defined copolymers.² However, many of the traditional methods for controlling polymeric structure, such as anionic,³ cationic,⁴ and group transfer procedures,⁵ are not well suited for the preparation of well-defined block copolymers from dissimilar vinyl monomers, such as styrenics and acrylates. To expand the scope of complex macromolecular architectures, the concept of a living free radical polymerization process has long been a goal of synthetic polymer chemists. Although many systems have been proposed, the two most widely used are nitroxide-mediated polymerizations and atom transfer radical polymerizations (ATRP).⁶ The use of a stable organic free radical such as a nitroxide to endcap propagating styryl radicals enables the synthesis of polystyrenes with narrow molecular weight distribution and controlled M_n at elevated temperatures over prolonged reaction time in the absence of solvent.^{7–14} Benefits of this procedure are that the initiating system is extremely stable and the reaction conditions require no solvent or rigorous experimental and purification techniques. Saban¹⁵ has also shown that living free radical polymerizations do not suffer from the gel effect, which may be beneficial for industrial-scale production.

Nitroxide-mediated polymerizations can be successfully used for making block copolymers based on styrene and derivatives.^{16–19} This restricts the versatile use of this highly simple and attractive technique to control free radical polymerization. In the beginning, Yoshida et al.²⁰ prepared an aminoxy-terminated polystyrene, and used it to initiate the radical polymerization of methyl, ethyl, and butyl acrylate to afford the corresponding block copolymers. Fukuda et al.¹⁷ synthesized a block copolymer of styrene and acrylonitrile to produce

a random copolymer with narrow polydispersity by carrying out the free radical polymerization in the presence of nitroxide stable free radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Lokaj et al.²¹ prepared polystyrene–poly(2-(dimethylamino)ethyl methacrylate) block copolymers by stable free radical polymerization. Listigovers et al.²² synthesized low molecular weight polyacrylate homopolymers as well as polystyrene–polyacrylate diblocks, polyacrylate–polyacrylate diblocks, and polyacrylate–polyacrylate–polyacrylate triblocks via nitroxide-mediated living polymerization. Steenbock et al.²³ attempted to initiate living radical polymerization of MMA using PS having a TEMPO end group as a macroinitiator by the addition of camphor-sulfonic acid (CSA) and found that the copolymer was contaminated with high levels of homo-PS. Recently, Burguiere et al.²⁴ synthesized ω -unsaturated poly(styrene-*b*-*n*-butyl methacrylate) block copolymers using TEMPO-mediated controlled radical polymerization with low monomer conversions.

The purpose of this work is to synthesize well-defined block copolymers from dissimilar vinyl monomers. The free radical polymerization of *n*-butyl methacrylate (BMA), ethyl methacrylate (EMA), methyl methacrylate (MMA), octyl methacrylate (OMA), vinyl acetate (VAc), *N,N*-dimethylacrylamide (DMA), and 2-(dimethylamino)ethyl acrylate (DAEA) were initiated by polystyrene macroinitiators with terminal TEMPO groups to produce a wide range of hard–soft, hydrophilic–hydrophobic, and other block copolymers containing various functionality.

Experimental Section

Materials. All reagents were purchased from Aldrich, TEMPO (98%) was used as received without purification. Monomers were distilled immediately prior to use.

Polymer Characterization. The structures of the block copolymers were analyzed by ^1H NMR spectroscopy. The ^1H NMR spectra were recorded on a Varian Unity Plus-500 spectrometer for 5% (w/v) polymer solution in CDCl_3 at 298

Table 1. Change of Molecular Weight and Polydispersity (PDI) with Time and Conversion for a Bulk Free Radical Polymerization of Styrene

reaction time (h)	convn (%)	$10^{-4}M_n(\text{theor})$	$10^{-4}M_n(\text{exptl})$	PDI
4	19	0.57	0.52	1.21
8	42	1.26	1.15	1.16
12	65	1.96	1.85	1.19
18	87	2.62	2.43	1.22
28	92	2.77	2.67	1.25

^a Styrene (10 mL, 0.087 equiv) at 130 °C using a 1:1.2 molar mixture of BPO (0.073 g, 0.0003 equiv) and TEMPO (0.057 g, 0.00036 equiv).

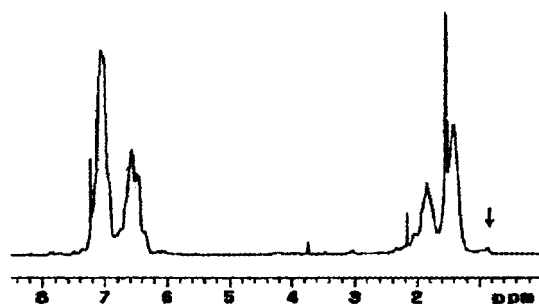
K, and tetramethylsilane was used as internal standard. The number- and weight-average molecular weights of the polymers were evaluated by gel permeation chromatography (GPC) at 25 °C using a Varian 5000 Liquid Chromatograph equipped with four Waters Ultrasytragel columns of pore size 10^4 , 2×500 , and 100 Å. Polystyrene standards were used for calibration, and tetrahydrofuran (THF) was used as the mobile phase with a flow rate of 0.8 mL/min.

Synthesis of Polystyrene Macroinitiators. A mixture of styrene (S, 4.45 g), dibenzoyl peroxide (BPO, 0.347 g) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO, 0.269 g) radical (molar ratio of TEMPO/BPO = 1.2) was preheated in a round-bottom flask in an argon atmosphere at 95 °C for 3 h to allow BPO to decompose completely. Then the system was heated at 130 °C for 24 h to yield polystyrene macroinitiator. The resulting polystyrene was precipitated with methanol (400 mL) from a THF (40 mL) solution. The resulting solid was then collected by vacuum filtration and dried to give the TEMPO-terminated polystyrene macroinitiator, PS-2, as a buff solid (3.96 g). Yield: 89%; M_n = 3400 and PDI = 1.15. ^1H NMR (500 MHz, CDCl_3): δ 0.16, 0.20, 0.86, 0.88 (each br s, 12H, CH_3), δ 1.4 (m, 2H, CH_2), δ 1.9 (m, 1H, CH), δ 6.4–7.2 (m, 5H, ArH), δ 7.3–7.9 (m, 5H, ArH). Under the same condition, the homopolymerization of BMA, EMA, DMA, and DAEA initiated by BPO in the presence of TEMPO yielded only a small amount of polymer (about 1% conversion).

Polymerization of BMA, EMA, MMA, OMA, VAc, DMA and DAEA Initiated by Polystyrene Macroinitiators. The polystyrene macroinitiator (PS-2, 0.1 g, 0.029 mmol) was dissolved in MMA (0.94 g, 9.4 mmol). The solution was placed in an ampule, and the contents were degassed, sealed, and heated at 130 °C under argon for 5 h. The polymerization mixture, which solidified after ca. 3 h, was then dissolved in tetrahydrofuran (20 mL) and precipitated into methanol (200 mL). The resulting solid was then collected by vacuum filtration and dried to give the TEMPO-terminated polystyrene-poly(methyl methacrylate) diblock copolymer, copolymer **11**, as a white solid (1.0 g). Yield: 96%; M_n = 31100 and PDI = 1.23. ^1H NMR (500 MHz, CDCl_3): δ 0.06, 0.08, 0.70–0.75, (each br s, 12H, CH_3), δ 1.0–1.3 (m, 3H, CH_3), δ 1.6–2.1 (m, 2H, CH_2), δ 3.6 (s, 3H, OCH_3), δ 6.4–7.2 (m, 5H, ArH), δ 7.3–7.9 (m, 5H, ArH). The homopolymerization of the protic monomer due to self-initiation was negligible.

Results and Discussion

Polystyrene Macroinitiators. As expected, the polymerization of styrene initiated by BPO in the presence of TEMPO afforded TEMPO-terminated polystyrene with narrow polydispersities (PDI) (1.1–1.3). Samples were removed from the reaction mixture over the course of the reaction, and their molecular weight data are summarized in Table 1. In agreement with the results of Georges et al.,⁷ the polydispersities of all of the polymers were low and well below the theoretical limiting polydispersity of 1.5 for a conventional free radical process. The molecular weight of the polymer gradually increased with time and maintained a very narrow molecular weight distribution. The molecular weight evolves in a nearly linear fashion with increasing

**Figure 1.** 500 MHz ^1H NMR spectrum of PS-2-TEMPO macroinitiator (PS-2, Table 2).**Table 2. Results of the Polymerization of Styrene**

entry	S/BPO	<i>t</i> (h)	convn (%)	$10^{-4}M_n(\text{theor})$	$10^{-4}M_n(\text{exptl})$	reaction time (h)
PS-1	25	16	75	0.26	0.28	1.09
PS-2	30	24	89	0.31	0.34	1.15
PS-3	54	24	83	0.56	0.53	1.13
PS-4	86	45	90	0.89	0.76	1.15
PS-5	182	45	86	1.89	1.84	1.19
PS-6	323	45	92	3.36	3.18	1.24
PS-7	1141	60	91	11.87	9.80	1.30
PS-8	1485	60	90	15.44	11.73	1.41
PS-9	2084	60	87	21.67	15.18	1.56

^a Styrene (5 mL, 0.043 equiv) at 130 °C using a 1:1.2 molar mixture of BPO and TEMPO.

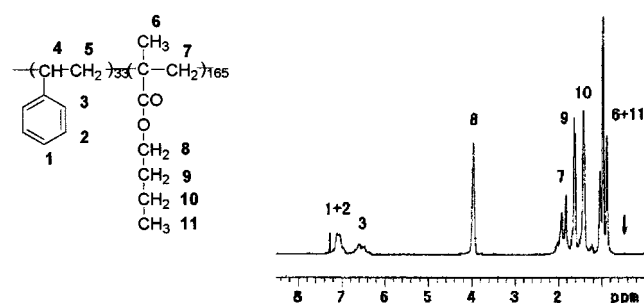
conversion. This linear relationship is characteristic of living polymerizations and the nitroxide-mediated free radical polymerizations of styrene. Figure 1 shows the 500 MHz ^1H NMR spectrum of a typical low molecular weight (M_n = 3400) polystyrene polymerized in bulk in the presence of BPO and TEMPO. The relative intensities of the resonances attributable to benzoyloxy and TEMPO end groups and the styrene units adjacent to them are consistent with a benzoyloxy:TEMPO ratio of ~1:1. The intensities of all of these resonances are inversely proportional to the polymer molecular weight (M_n).

Furthermore, high molecular weight resins with narrow polydispersities can be obtained, as summarized in Table 2. The experimental molecular weights of the polymers prepared using BPO/TEMPO are close to the theoretical molecular weight calculated from the ratio of styrene to BPO. At molecular weights below 5×10^4 , the agreement is excellent. As the molecular weight increases, this difference increases distinctly at molecular weights above 1×10^5 , and the polydispersity also increases. The polymerizations are difficult to control at molecular weights above 1×10^5 using the 1:1.2 mixture of BPO/TEMPO initiating system. For the BPO/TEMPO initiating system, the initial step is decomposition of the benzoyl peroxide, followed by reaction of benzoyloxy radical with a styrene monomer and subsequent trapping of this species with TEMPO. Previously, Moad²⁵ showed that this reaction is complicated by a variety of side reactions that decrease the initiator efficiency and generate unwanted side products. This results in higher polydispersities and less control over molecular weights.

Block Copolymerization. A particularly useful advantage of most living free radical polymerization systems for the preparation of AB block copolymers is the ability to isolate, purify, and store the stable free radical terminated resins.²² The end groups of the polystyrene macroinitiator are generally stable to pro-

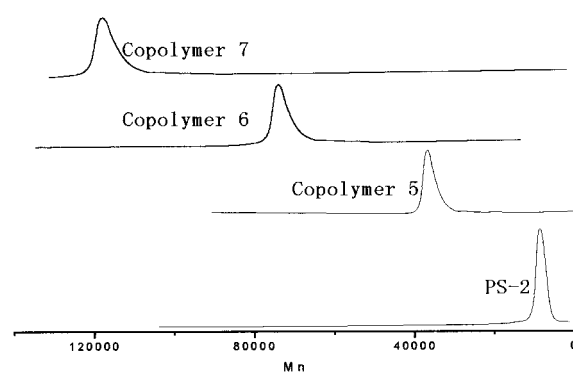
Table 3. Polymerization of the Polar Monomers Initiated by Polystyrene Macroinitiators

copolymer	monomer (mmol)	initiator (μ mol)	time (h)	convn (%)	$10^{-4}M_n(\text{theor})$	$10^{-4}M_n(\text{exptl})$	PDI
1	BMA (9.4)	PS-2 (29.4)	2	24	1.31	1.44	1.21
2	BMA (9.4)	PS-2 (29.4)	5	52	2.46	2.69	1.26
3	BMA (20)	PS-5 (27.2)	2	19	3.83	4.26	1.29
4	BMA (20)	PS-5 (27.2)	5	44	6.44	6.89	1.38
5	EMA (32)	PS-2 (29.4)	2	36	3.02	3.58	1.20
6	EMA (32)	PS-2 (29.4)	3.5	66	7.19	7.69	1.31
7	EMA (32)	PS-2 (29.4)	5	90	10.46	11.77	1.37
8	EMA (20)	PS-5 (27.2)	5	70	7.69	7.25	1.41
9	MMA (9.4)	PS-2 (29.4)	2	48	1.71	1.80	1.21
10	MMA (9.4)	PS-2 (29.4)	3.5	86	2.82	2.67	1.18
11	MMA (9.4)	PS-2 (29.4)	5	96	3.11	3.34	1.23
12	MMA (38)	PS-5 (27.2)	5	92	14.57	16.47	1.28
13	OMA (4.5)	PS-2 (29.4)	8	94	2.91	3.47	1.42
14	OMA (18)	PS-2 (29.4)	16	87	9.92	11.86	1.57
15	DAEA (10)	PS-2 (29.4)	90	9	1.15	0.97	1.25
16	DAEA (20)	PS-4 (65.8)	85	24	1.92	1.48	1.41
17	DAEA (20)	PS-6 (15.7)	55	30	5.87	4.93	1.64
18	DMA (14.5)	PS-2 (29.4)	15	90	4.03	4.76	1.41
19	DMA (39)	PS-4 (65.8)	15	78	5.31	6.34	1.54
20	VAc (27)	PS-1 (35.7)	72	4	0.62	0.51	1.31

**Figure 2.** 500 MHz ^1H NMR spectrum of PSt-PBMA copolymer (copolymer 2, Table 3).

longed exposure to light, air, and moisture.¹³ The thermal lability of the TEMPO chain end is also good, and the polystyrene produced by this TEMPO process shows a 10% weight loss at 360 °C.¹³ Thus, we first prepared and isolated a stable free radical-terminated A block (polystyrene macroinitiator) of molecular weight (M_n) from 2600 to 33 600. A variety of B block was added to the A block by changing the identity or amount of the monomer used for the B block to produce a series of AB block copolymers in which the structure, molecular weight, and polydispersity of the A block is identical for all members of the series. These resins could then be used to study the effect of changes of the B block on the performance of the block copolymers.

The results of polymerization of the protic monomers using the polystyrene macroinitiator are presented in Table 3. Figure 2 shows the ^1H NMR spectrum of copolymer 2. Copolymer 2 has a ca. 1:3 molar ratio of styrene to butyl methacrylate units. This, coupled with the molecule's weight increase from $M_n = 3290$ (PDI = 1.15) to 26 900 (PDI = 1.26), indicates that block copolymers have been achieved using a polystyrene macroinitiator having a TEMPO chain end, and that relatively narrow polydispersities and defined block lengths have been obtained. In block copolymerizations of BMA, EMA, and MMA initiated by a polystyrene macroinitiator, the GPC plots of the macroinitiator (PSt) and final copolymer (PSt-PBMA, PSt-PEMA and PS-MMA) show a shifting of the GPC peak of the starting material to higher molecular weight. No traces of the remaining polystyrene macroinitiator were found after 2 h reaction time, indicating complete initiation and formation of block copolymers. No shoulder is evident

**Figure 3.** GPC profiles of polystyrene macroinitiator PS-2 and block copolymers obtained by reacting EMA and PS-2 at 130 °C for 2 h (copolymer 5), 3.5 h (copolymer 6), and 5 h (copolymer 7).

in the GPC plot (see Figure 3), which suggests that no new chain formation due to autopolymerization occurs, indicating that the new products are derived from the macroinitiators. MMA produces block copolymers with no detectable homopolymer impurity (<5%) at an acceptable rate of polymerization. The molecular weights of the copolymers (copolymers 5, 6, and 7) increase with reaction time and conversion, which indicates the polymerization is living. However, the increase in polydispersity with the block copolymers is consistent with some chain termination. The GPC curves of the copolymers suggest that they are mostly block copolymers of styrene and the polar monomers and contain only small amounts of homopolymers of the polar monomers generated by chain-transfer and thermal polymerization.

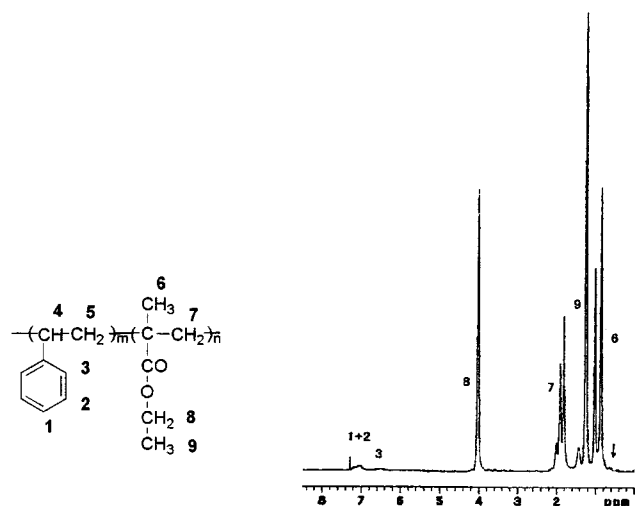
Figure 3 also shows a typical GPC profile of the product obtained upon polymerization of EMA. Comparison of copolymers 5 ($M_n = 35\,800$, PDI = 1.20), 6 ($M_n = 76\,900$, PDI = 1.31), 7 ($M_n = 117\,700$, PDI = 1.37), with the starting material, PS-2 ($M_n = 3400$, PDI = 1.15), shows that the growth is controlled with no evidence of homopolymer contamination. The SEC curves shift toward lower elution volumes as the reaction time increases. The polydispersity remained low. However, there was a substantial amount of a low molecular weight shoulder when high molecular weight starting polystyrene blocks ($M_n > 50\,000$) were used.

Functional block copolymers having pendant dimethylamino groups were also obtained by the polym-

Table 4. Difference in the Chemical Shifts of TEMPO Moiety Attached to the PSt Macroinitiator and Copolymer

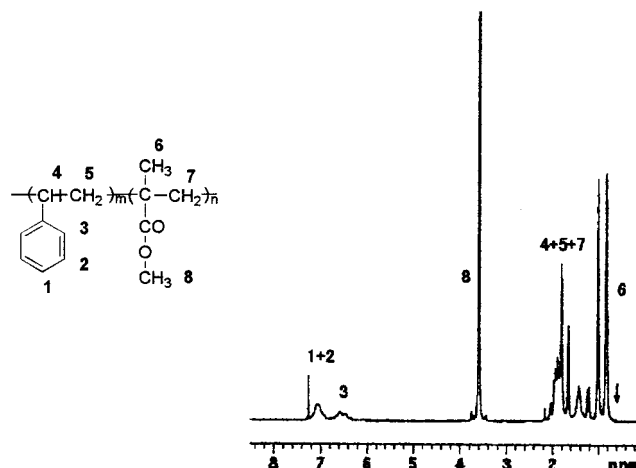
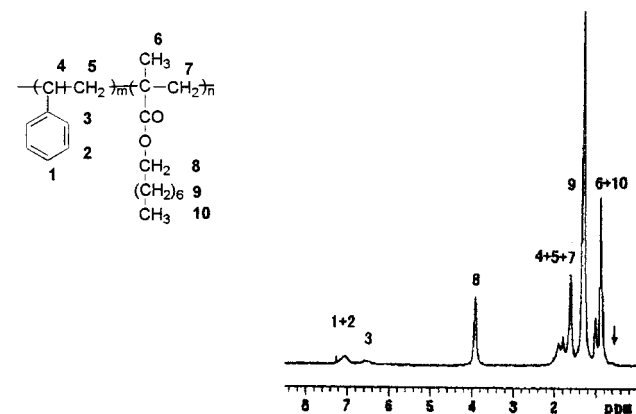
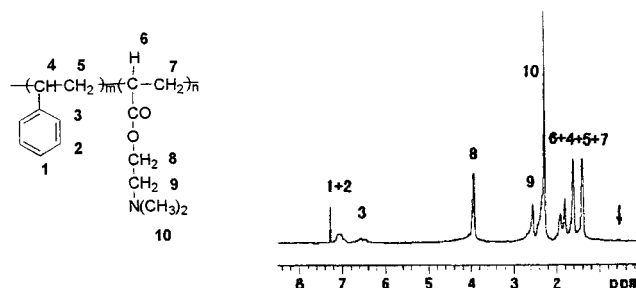
polymer	high-field methyl resonances ^a of TEMPO (ppm)				benzoyloxy:TEMPO
PSt-TEMPO (PS-2)	0.88	0.86	0.20	0.16	1.04
PSt-PBMA-TEMPO (copolymer 2)	0.65	0.57	0.16	0.12	0.91
PSt-PEMA-TEMPO (copolymer 5)	0.65	0.55	0.17	0.14	0.93
PSt-PMMA-TEMPO (copolymer 9)	0.72	0.61	0.08		1.95
PSt-POMA-TEMPO (copolymer 13)	0.65	0.58	0.09		0.89
PSt-PDAEA-TEMPO (copolymer 15)	0.95	0.88	0.15	0.07	1.16
PSt-PDMA-TEMPO (copolymer 18)	0.93	0.88	0.14	0.07	1.11
PSt-PVAc-TEMPO (copolymer 20)	0.85	0.80	0.15	0.08	0.86

^a From the enlarged ¹H NMR signals of the PSt macroinitiator and copolymers (Figures 1–8).

**Figure 4.** 500 MHz ¹H NMR spectrum of PSt-PEMA copolymer (copolymer 5, Table 3).

erization of DMA and DAEA monomers using a polystyrene macroinitiator. Similar to the methacrylates, DMA has an acceptable rate of polymerization and can reach 90% conversion after 15 h using a lower-mass polystyrene macroinitiator (PSt-2, $M_n = 3400$), but with higher polydispersity. Contrary to the methacrylates, DAEA is not readily initiated by the polystyrene macroinitiator. Using identical reaction conditions, DAEA after 90 h reaches only 9% conversion (copolymer 15). It is difficult to achieve higher than 40% conversion. VAc is also very difficult to polymerize using a polystyrene macroinitiator.

Block copolymer formation was also confirmed by ¹H NMR in CDCl₃. The ¹H NMR spectra of the copolymers show a series of peaks (Figures 2 and 4–9) between 0.07 and 0.95 ppm which have previously been assigned²⁶ to the methyl resonances of the chain-capping TEMPO moiety indicated by an arrow in the NMR spectra. The appearance of four different methyl peaks for the TEMPO moiety is due to two diastereotopic axial methyl groups and two diastereotopic equatorial methyl groups in the TEMPO fragment. The high field methyl resonances of the TEMPO moiety shift some what upfield or downfield after attachment to the copolymer moiety, relative to attachment to the styryl moiety (Table 4). This complex pattern, which arises from a combination of polymer microstructure and TEMPO conformational effects,²⁶ is clear evidence that the all copolymers reported here were obtained by the nitroxide-mediated stable free radical mechanism. Further confirmation is provided by the presence of a benzoyloxy initiating moiety (7.3–7.9 ppm) in the approximate benzoyloxy:TEMPO ratio of ~1:1 (Table 4). On the basis of the ¹H

**Figure 5.** 500 MHz ¹H NMR spectrum of PSt-PMMA copolymer (copolymer 9, Table 3).**Figure 6.** 500 MHz ¹H NMR spectrum of PSt-POMA copolymer (copolymer 13, Table 3).**Figure 7.** 500 MHz ¹H NMR spectrum of PSt-PDAEA copolymer (copolymer 15, Table 3).

NMR investigation, there is a strong evidence for the presence of TEMPO-terminated copolymers.

While this work was in progress, similar work has recently been demonstrated by Benoit et al.²⁷ using a different nitroxide that can also be used to prepare

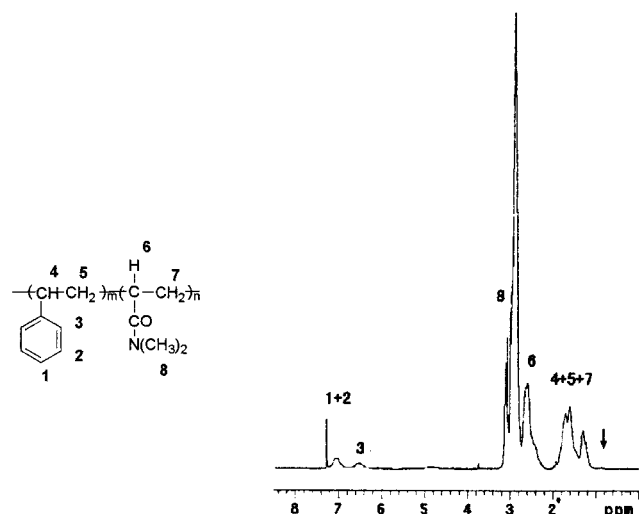


Figure 8. 500 MHz ^1H NMR spectrum of PSt-PDMA copolymer (copolymer **18**, Table 3).

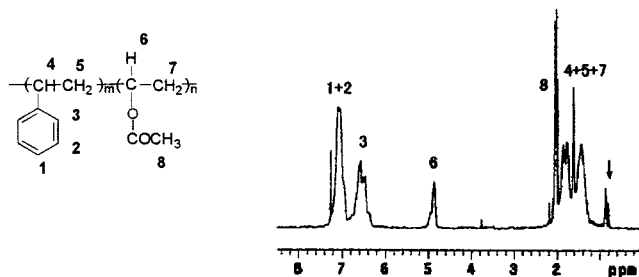


Figure 9. 500 MHz ^1H NMR spectrum of PSt-PVAc copolymer (copolymer **20**, Table 3).

acrylate starting blocks follow by styrene blocks. The examples discussed here demonstrate that the TEMPO-mediated polymerization is suitable for the synthesis of polystyrene-polymethacrylate diblock copolymers from dissimilar vinyl monomers.

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