Synthesis of Polystyrene−Poly(2-(dimethylamino)ethyl methacrylate) Block Copolymers by Stable Free-Radical Polymerization

Jan Lokaj,* Petr Vlček, and Jaroslav Kříž

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic

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Introduction. Recently, new approaches in the free-radical polymerization processes were developed that make it possible to synthesize polymers usually obtainable only by ionic polymerization. The pseudoliving propagating chains are formed due to their reversible termination using convenient initiating systems, such as iniferters,[1−11] stable free radicals along with peroxides or alone at elevated temperatures,[12−19] or organometallic complexes in association with stable radicals or with peroxides.[19,20] In comparison with the anionic, cationic, and group-transfer polymerizations, however, the free-radical process is noted for an easy and economical performance and can be carried out in the presence of water, as in an emulsion or suspension polymerization.

Special attention is paid to the methods offering the possibility of making polymer materials with narrow polydispersities, well-defined chain lengths, and complex architecture. Among other techniques, the stable free-radical polymerization seems to be a promising means for obtaining polymers with desired properties. Thus, the polymerization of styrene initiated by the system dibenzoyl peroxide−2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) radical at various molar ratios and temperatures of 123−150 °C yields low-polydispersity polystyrenes, the molecular weights of which can be adjusted to the required values.[12] Low-polydispersity polystyrenes were also formed in the absence of peroxide.[19] Random copolymers with low polydispersities and controlled molecular weights were obtained by copolymerization of various comonomers mediated by TEMPO radicals.[14,21−23] Free-radical polymerization in the presence of nitroxide radicals has been also applied to the preparation of block copolymers.[21−25] In principle,[14] a nitroxide-terminated macroinitiator is synthesized and then a mixture of the macroinitiator and monomer is heated at a temperature above 120 °C. By heating, the relatively weak bond between the macroinitiator chain and the nitroxide end group is broken and the monomer adds to the polymer chain end; the propagating macroradical is reversibly terminated with the liberated nitroxide radical. These reactions can repeat until the monomer is consumed. Due to the fast dissociation of the macroinitiator, all the growing chains are initiated at about the same time and, consequently, polymers with narrow polydispersities are obtained.

The aim of this study was the preparation of block copolymers comprising hydrophobic polystyrene blocks on the one hand and hydrophilic blocks of poly(2-(dimethylamino)ethyl methacrylate) on the other. Such functional copolymers of amphiphilic nature could be useful, for instance, in the micelle formation or as potential permselective membrane materials. The free-radical polymerization of 2-(dimethylamino)ethyl methacrylate (DAMA) was initiated by the prepared polystyrene macroinitiators with terminal TEMPO groups, and the molecular weights, polydispersities, and compositions of synthesized polymer products were evaluated.

Experimental Section. Synthesis of Macroinitiators. A mixture of styrene (S) (25 mL), dibenzoyl peroxide (BPO) (0.0605 g, 0.010 mol L^{-1}), and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) radical (0.0585 g, 0.015 mol L^{-1}) (molar ratio of TEMPO/BPO = 1.5) was heated in a glass ampule in an inert atmosphere at 125 °C for 22 h. The mixture gradually solidified. The resulting polystyrene PS-1 (18.4 g, 80.8% conversion) was precipitated with ethanol from a chloroform solution. In a similar way, from a mixture of S (25 mL), BPO (0.0605 g, 0.010 mol L^{-1}), and TEMPO (0.1170 g, 0.030 mol L^{-1}); i.e., at a molar ratio of TEMPO/BPO = 3.0, the polystyrene macroinitiator PS-2 was prepared. After 22 h at 125 °C, the macroinitiator was precipitated with ethanol from the viscous reaction mixture (16.0 g, 70.4% conversion) and reprecipitated from a chloroform solution.

Under the same conditions, the homopolymerization of DAMA initiated by BPO in the presence of TEMPO yielded only a small amount of poly(DAMA) (about 1% conversion).

Polymerization of Styrene Initiated by Polystyrene Macroinitiators (Chain-Extension Test). By heating 5 mL of styrene with 0.3 g of PS-1 or PS-2 in an inert atmosphere at 125 °C, 1.58 g (34.8% conversion) or 1.29 g (28.4% conversion) of polystyrene PS-3 or PS-4 was obtained after 3 h. The polystyrenes were reprecipitated from chloroform solutions.

Polymerization of 2-(Dimethylamino)ethyl Methacrylate Initiated by Polystyrene Macroinitiators. In each experiment, the polystyrene macroinitiator (0.3 g) was dissolved in DAMA (5 mL) and the solution was heated in a glass ampule in an inert atmosphere at 125 °C for 2, 4, 6 or 8 h. Then the ampule was opened, and the reaction mixture was poured into a 20-fold amount of hexane. Using PS-1 and PS-2, ca. 0.56 and 0.40 g, respectively, of polymer product was isolated, independently of reaction time. The polymer products were reprecipitated with hexane from chloroform solutions. Within 8 h at 125°C, the homopolymerization of DAMA due to the self-initiation was found to be negligible.

Polymer Characterization. The number- and weight-average molecular weights of synthesized polymers were evaluated by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as an eluent and toluene as an internal standard. For this purpose, the Czech apparatus Labora was used, the separation system of which consisted of two 300 × 8 mm columns (PSS, Germany) filled with Styragel (porosities 10^5 and 10^3 Å, respectively). The system was calibrated with poly(methyl methacrylate) standards, and eluograms were treated using the constants of the Mark−Houwink−Sakurada equation obtained for polystyrene/THF. The device was equipped with both refractometric and UV (260 nm) detectors; the molecular weight distribution (MWD) curves were calculated from the corresponding refractometric responses. The composition of polymer products from polymerizations of DAMA initiated by polystyrene macroinitiators were determined using both nitrogen elemental analysis and ^{1}H-NMR spectroscopy. ^{1}H NMR spectra (300 MHz) of 10% w/w polymer solutions in $CDCl_3$ were measured at 330 K with a Bruker Avance DPX 300 spectrometer, using hexamethyldisiloxane (δ = 0.05 ppm) as the internal standard. The relative contents of styrene and DAMA

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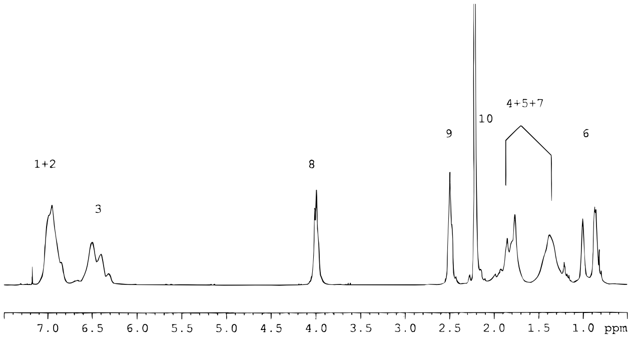


Figure 1. ^{1}H NMR spectrum of poly(S)−poly(DAMA) block copolymer (sample I, Table 2).

Table 1. Molecular Weights (M_n) and Polydispersities (PD) of Polystyrene Macroinitiators before (PS-1, PS-2) and after Chain Extension (PS-3, PS-4)

polystyrene	$10^{-4}M_n$[a]	PD[a]
PS-1	5.34	1.13
PS-2	2.81	1.10
PS-3	12.96 (28.12)[b]	1.49
PS-4	7.73 (12.08)[b]	1.36

[a] Determined by GPC. [b] Calculated from both the M_n of the macroinitiator and the conversion reached in a 3-h polymerization of styrene (5 mL) using macroinitiator (0.3 g) at 125 °C.

units were established by comparing integral intensities of the signals (1 + 2 + 3) with (8 + 9 + 6); see Figure 1.

Results and Discussion. Polystyrene Macroinitiators. In accordance with findings of Georges et al.,[12] the polymerization of styrene initiated by BPO in the presence of TEMPO afforded TEMPO-terminated polystyrenes PS-1 and PS-2 with narrow polydispersities (PD) (1.13 and 1.10, respectively) despite high monomer conversions (>70%) (Table 1). As expected, the molecular weight of PS-2 prepared at a molar ratio of TEMPO/BPO = 3 was lower than that of PS-1 (TEMPO/BPO = 1.5). Both PS-1 and PS-2 readily initiated the polymerization of styrene by extending their chains. The resulting PS-3 and PS-4 showed an increase in molecular weight and slightly broader distributions. Their molecular weights determined by GPC differed from those calculated from both M_n values of the initial macroinitiators and conversions under the assumption that styrene added only to the macroinitiator chains; the calculated values were higher. This demonstrates that, along with initiation by the polystyrene macroinitiator, spontaneous thermal initiation of styrene and recombination of chains take place.[19]

The molecular weights of PS-3 or PS-4 were several times larger than those of PS-1 or PS-2, and polydispersities did not exceed 1.5; i.e., they were markedly narrower than those at a conventional radical polymerization. For illustration, Figure 2 shows MWD curves of both PS-1 and the chain-extended PS-3. Neither PS-1 nor PS-2 were detected in PS-3 or in PS-4.

Contrary to styrene, DAMA is reluctant in the TEMPO-mediated polymerization. In this case, the termination reactions probably prevail and only a small amount of homopolymer is formed.

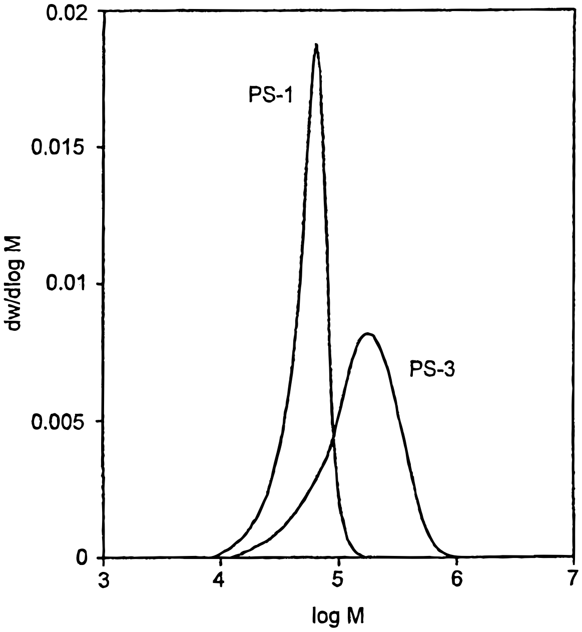


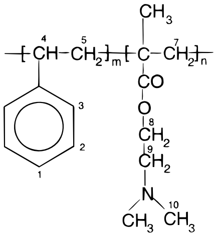
Figure 2. MWD curves of PS-1 and PS-3 (see Table 1).

Table 2. Polymerization of DAMA Initiated by Polystyrene Macroinitiators PS-1 (Copolymers I−IV) and PS-2 (copolymers V−VIII) (0.3 g of Macroinitiator, 5 mL of DAMA, 125 °C)

copolymer	time (h)	yield (g)	f_{DAMA}(copolymer)[a]		$10^{-4}M_n$			PD
			ex N	NMR	GPC	*b*	*c*	GPC
I	2	0.55	0.41	0.40	6.71	10.94	10.71	1.25
II	4	0.57	0.36		6.38	9.88		1.26
III	6	0.55	0.40	0.41	6.61	10.71	10.94	1.26
IV	8	0.58	0.39	0.39	6.71	10.50	10.50	1.29
V	2	0.42	0.29	0.26	3.40	4.54	4.30	1.28
VI	4	0.39	0.30	0.29	3.63	4.63	4.54	1.30
VII	6	0.39	0.27	0.25	3.49	4.38	4.22	1.26
VIII	8	0.42	0.29		3.66	4.54		1.25

[a] Mole fraction. [b] Calculated from both the M_n of the macroinitiator and the molar ratio of DAMA/S in the copolymer obtained from nitrogen elemental analysis. [c] Calculated from both the M_n of the macroinitiator and the molar ratio of DAMA/S in the copolymer as determined by NMR.

Polystyrene−Poly(2-(dimethylamino)ethyl methacrylate) Block Copolymers. The results of polymerization of DAMA using PS-1 and PS-2 macroinitiators are presented in Table 2. The amounts of isolated polymer products were approximately by 87 and 33% higher compared with the initial amounts of PS-1 and PS-2, respectively; they did not significantly change within 2−8 h of the reaction. GPC eluograms (see Figure 3) indicated the absence of polystyrene macroinitiators in the final products; if present, the residual macroinitiators should be seen as shoulders on the MWD curves. In particular, UV detection is very sensitive to the presence of pure polystyrene, which strongly absorbs at 260 nm. In Figure 1, the ^{1}H NMR spectrum of sample I is shown with signal assignment corresponding to



In this and all other cases, the spectra are clear superpositions of those of polystyrene and poly(DAMA), indicating thus, in particular with respect to the GPC results, that the products are poly(S)−poly(DAMA) block copolymers.

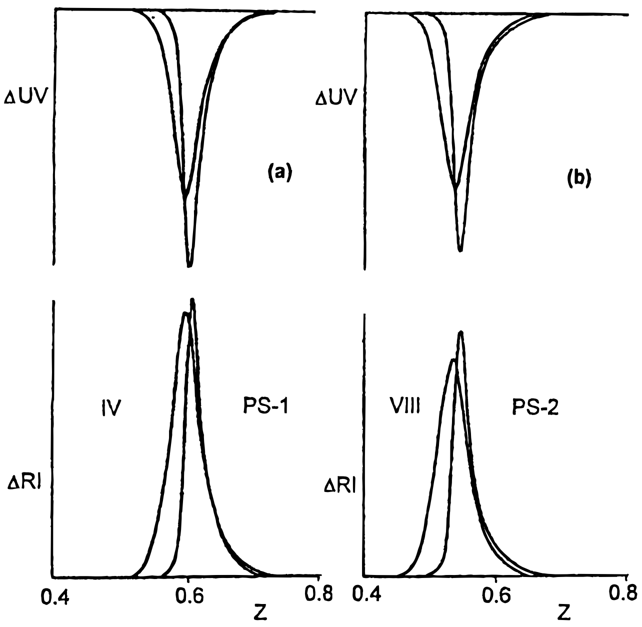


Figure 3. GPC eluograms of poly(S)−poly(DAMA) block copolymers and corresponding macroinitiators; copolymer IV and PS-1 (a); copolymer VIII and PS-2 (b) (see Tables 1 and 2). *Z*: Ratio of elution times of the polymer and toluene as an internal standard.

All the copolymers prepared with PS-1 contained approximately 40 mol % DAMA; those prepared with PS-2, 29 mol % DAMA. The DAMA contents determined by both nitrogen analysis and the ^{1}H NMR method were in good accordance. The higher DAMA content in the former copolymers is obviously associated with a lower termination rate in the polymerization process as a consequence of the lower molar concentration of PS-1 than PS-2.

The molecular weights of the copolymers were practically independent of the reaction time within 2−8 h. Considering the different nature of incorporated comonomers, the determination of M_n values based on calculation from both the M_n of the macroinitiator and the molar ratio of DAMA/S is more correct than that based on GPC measurements (cf. Experimental Section, Polymer Characterization). With regard to some weight losses in precipitation of the copolymers, the molar ratio of DAMA/S from NMR or nitrogen analysis was used and not that calculated from both the weight of incorporated DAMA and total yield. Polydispersities of the copolymers did not significantly differ from those of the initial macroinitiators and were lower than PDs of chain-extended polystyrenes PS-3 and PS-4. Contrary to the polymerization of styrene, in the copolymer formation under given conditions thermal self-initiation of DAMA was insignificant.

The very close yields and compositions of isolated copolymers I−IV or V−VIII as well as the found molecular weights revealed a limit for the growth reaction of DAMA initiated by polystyrene macroinitiators PS-1 or PS-2; within 2−8 h the chain propagation did not take place any longer. This indicates that after addition of a limiting amount of DAMA to the polystyrene radical, the irreversible chain termination proceeds. The explanation of this process, however, calls for a more detailed study, which is in progress.

Conclusion. The polymerization of DAMA initiated at 125 °C by polystyrene macroinitiators containing TEMPO end groups affords poly(S)−poly(DAMA) block copolymers of narrow polydispersities (1.25−1.30). The composition, molecular weights, and polydispersities of the block copolymers were evaluated using nitrogen elemental analysis, GPC, and ^{1}H NMR spectroscopy. The yields, compositions, and molecular weights depending on the chain length of the macroinitiator did not practically change with the reaction time within 2−8 h.

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