# Well-Defined Block Copolymers Comprising Styrene−Acrylonitrile Random Copolymer Sequences Synthesized by “Living” Radical Polymerization

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Recent years have witnessed remarkable success in synthesizing polymers with narrow polydispersity and well-defined chain-end structure by carrying out free-radical polymerization in the presence of nitroxide stable free radicals (SFRs) such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its derivatives.[1−12] According to Georges et al.,[1−6] the key to this success is the essentially simultaneous initiation and the reversible termination of the polymer radical with the SFR. The dissociation such as depicted in Figure 1 for the polystyrene (PS)−TEMPO adduct is known to occur in a limited number of systems (at high temperatures). This restricts the versatile use of this highly simple and attractive technique to control or “tame” free-radical polymerization. Another limitation would come, like in a usual free-radical system, from the irreversible bimolecular termination and transfer reactions.[13] Because of them, the structural and process control achievable by this technique would be limited to *relatively short*[14] chains. By this, the SFR-mediated polymerization is distinguished from genuine living ones and often referred to as pseudoliving or “living” radical polymerization. The notion of the “iniferter” polymerization proposed by Otsu et al.[15] some time ago shares a “living” character, but this approach has never obtained narrow polydispersities.

Although the number of monomers whose homopolymerizations have been successfully controlled by SFR may be limited to date, we have noted that the random (statistical) copolymerization of such a monomer with an SFR-uncontrollable monomer often gives an unexpectedly successful result.[16] For example, acrylonitrile (AN), methyl and ethyl acrylates (MA and EA), and 9-vinylcarbazole (VCz) gave no polymer (or no well-defined polymer), at least when their polymerization was attempted under the conditions used for the successful polymerization of styrene (S) with benzoyl peroxide (BPO) initiator and TEMPO (see below). However, their copolymerization with S under the same conditions proceeded in a “living” fashion, at least when the S composition in the feed was not too low, and gave narrow-polydispersity copolymers with fairly high molecular weights. Some examples are presented in Table 1. The $^{13}$C nuclear magnetic resonance (NMR) spectrum of the S−AN copolymer (PSAN) showed that its microstructure is the same as that of a conventional PSAN (Figure 2). At this time, it is not clear why the copolymerizations are controllable by TEMPO, but we suspect that the penultimate unit effect, which strongly affects the radical reactivity or stability in most systems,[17] may have something to do with the dissociation of the TEMPO adducts of the otherwise undissociative growing radicals.

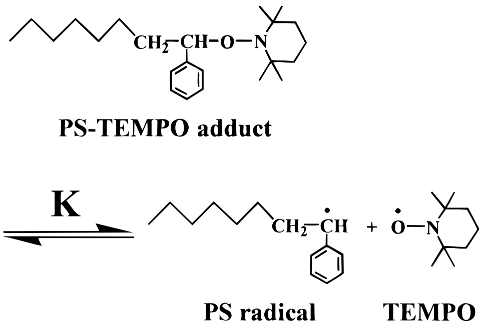

**Figure 1.** Scheme showing the reversible termination of the polystyryl radical with the TEMPO radical.

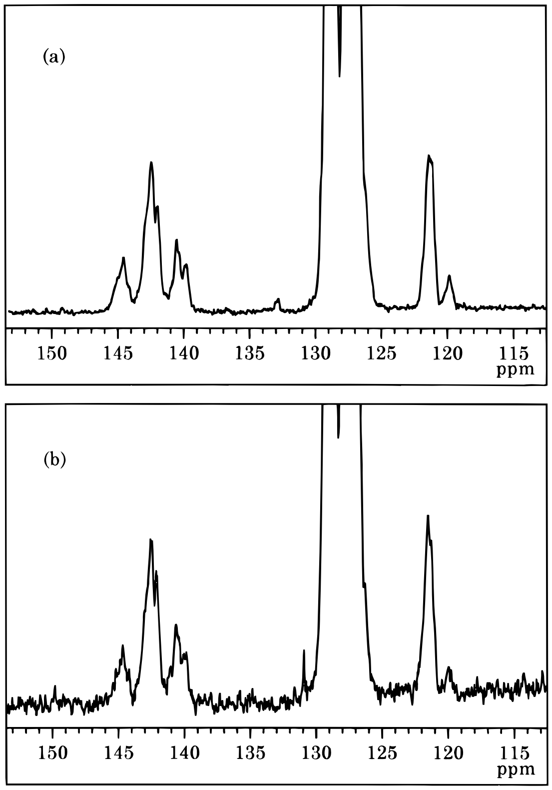

**Figure 2.** Portions of the $^{13}$C-NMR spectra of the PSANs of azeotropic composition obtained by (a) the TEMPO-mediated method (125 °C) and (b) the conventional radical polymerization (40 °C).

The success of these “living” radical copolymerizations has urged us to synthesize block copolymers[18] comprising random copolymer sequence(s) with narrow polydispersities. Various combinations of the above-mentioned monomers are possible, which would make a new group of block copolymers that have not existed before. In what follows, we describe briefly the synthesis and some of the properties of the diblock copolymers comprising a PS and a PSAN sequence.

The block copolymers were synthesized as follows: freshly distilled styrene, BPO (0.015 mol L$^{-1}$), and TEMPO (0.018 mol L$^{-1}$) were charged in a glass tube, degassed, and sealed off under vacuum. The mixture was preheated at 95 °C for 3.5 h to allow BPO to decompose completely. At this temperature, no polymerization proceeded.[1] Then the system was heated at 125 °C for 5.5 h to yield a PS with a number-average molecular weight $M_n$ of 2.2 × 10$^4$ and a polydispersity

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**Table 1. TEMPO-Mediated Copolymerizations of Styrene with Various Monomers at 125 °C**[a]

| comonomer | [BPO]/$10^{-2}$ mol $L^{-1}$ | [TEMPO]/$10^{-2}$ mol $L^{-1}$ | $f_1$ | $t$/h | $C_w$/% | $F_1$ | $M_n/10^4$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|
| AN | 7.0 | 7.0 | 0.63 | 10 | 69 | 0.64 | 1.6 | 1.23 |
| MA | 3.0 | 3.7 | 0.77 | 16 | 61 | 0.82 | 1.3 | 1.24 |
| EA | 3.0 | 3.7 | 0.77 | 15 | 49 | 0.83 | 2.3 | 1.18 |
| VCz | 6.3 | 6.3 | 0.79 | 15 | 60 | 0.91 | 3.8 | 1.27 |

[a] Preheated at 95 °C for 3.5 h; $f_1$ = styrene mole composition in the feed, $t$ = polymerization time, $C_w$ = weight conversion, $F_1$ = styrene mole composition of the polymer (see text for more details).

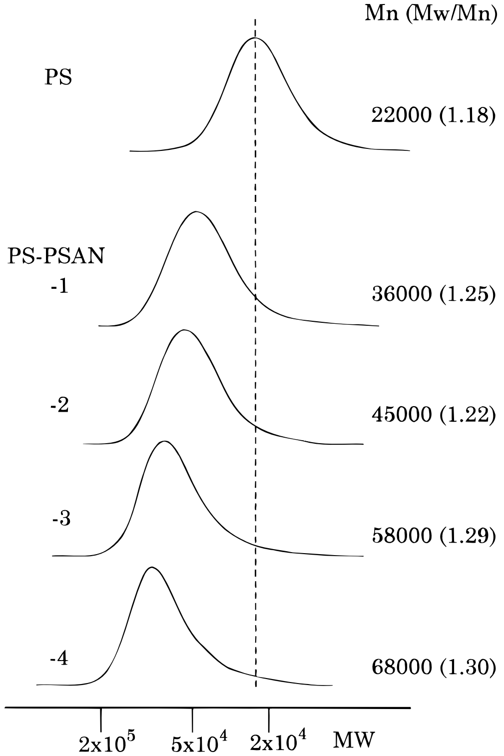

**Figure 3.** GPC curves for the precursor PS and the PS−PSAN diblock copolymers obtained at polymerization times of 1 h (PS−PSAN-1), 2 h (PS−PSAN-2), 5 h (PS−PSAN-3), and 10 h (PS−PSAN-4).

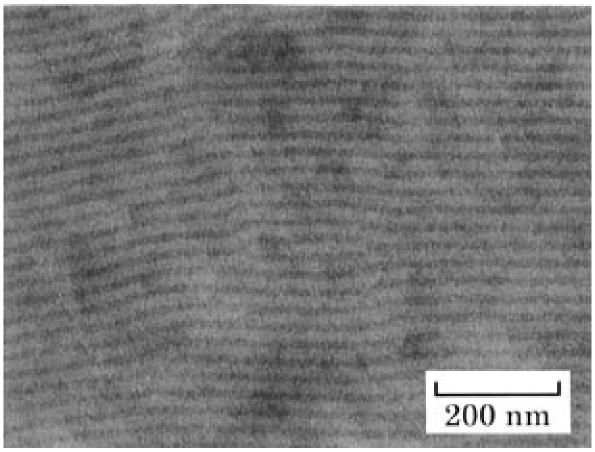

**Figure 4.** Transmission electron micrograph of PS−PSAN-2.

index $M_w/M_n$ of 1.18 (conversion 31%). This PS, purified by reprecipitation with a chloroform/methanol system, should have a TEMPO molecule at the chain end with essentially no free TEMPO. This was confirmed by a chain-extension test. Namely, the PS, when heated at 125 °C in pure styrene, was observed to propagate with no induction period, increasing its molecular weight proportionally to conversion and keeping its polydispersity narrow. No nonpropagating species was detectable by gel permeation chromatography (GPC). This was also the case with the block copolymerization, in which 22 parts by weight of the same PS was dissolved in 78 parts of an S/AN azeotropic mixture (mole fraction of S in the feed $f_1 = 0.63$), degassed, sealed off under vacuum, and then heated at 125 °C. Figure 3 shows the GPC chromatograms of the polymers recovered after the heat treatment of varying lengths. Clearly, the chain grows with time, and no appreciable amount of polymer, if any, remains at the elution position of the precursor PS, indicating a high efficiency of block copolymerization. The polydispersity index of the copolymer estimated by PS-calibrated GPC was below 1.30 in all cases. The copolymer mole composition $F_1$ determined by nitrogen elemental analysis was close to that expected for the PS−PSAN block copolymer with a PSAN sequence having the azeotropic composition of $F_1 = 0.63$ and the molecular weight calculated from the conversion. The independent experiment confirms that the feed monomer composition $f_1$ of 0.63 in fact gives a PSAN with $F_1$ close to 0.63 (Table 1). The $^{13}$C-NMR spectra of the block copolymers were essentially the same as that of the pure PSAN given in Figure 2 except for the relative magnitudes of the PS- and PSAN-related peaks.

Figure 4 shows an electron micrograph of PS−PSAN-2, which has a nearly symmetrical (equi-weight) block architecture. A film of the polymer was annealed at 170 °C for a sufficiently long time, stained by $RuO_4$ vapor, cut normal to the film surface into a ultrathin specimen, and observed with a JEOL transmission electron microscope JEM-2010. The micrograph shows regular, alternating dark and light regions with a repeat spacing of about 30 nm. This spacing is almost the same as the domain spacing of the lamellar microphase-separated structure of the PS−poly(2-vinylpyridine) symmetrical diblock copolymer having the same $M_n$ as the PS−PSAN sample.[19] Although the assignment of the dark and light regions remains unanswered at this time, the observed stripes may be ascribed to the microphase separation of the PS and PSAN sequences into a lamellar structure. This suggests that a well-defined block copolymer with the expected architecture has been obtained.

We also note that PS−PSAN-3 and -4 dissolved in 5-undecanone give a transparent colorless solution at high temperatures and a somewhat milky but homogeneous solution at and below the room temperature. This solvent dissolves PS but not the PSAN of this composition, and therefore the mentioned observation indicates the formation of multimolecular micelles by these polymers. This may be another piece of (indirect) evidence showing that the polymers comprise chemically linked PS and PSAN sequences, since the micellization in a selective solvent is characteristic of block copolymers,[20,21] but not of pure random copolymers nor of polymer mixtures.

Work is in progress to examine the microdomain-forming and micellization properties of PS−PSAN block copolymers in more detail.[22] Such block copolymers as well as other block copolymers comprising random copolymer sequence(s) are particularly interesting new materials, because a vast number of different molecular structures, and hence properties, may be obtained by changing the combination of monomers, block architecture, and the composition of each block. For example, the segregation power between the different blocks, and hence the microphase separation behavior, can easily be manipulated by adjusting the composition(s) within the random copolymer sequence(s). Such a study with PS−PSAN and other block copolymers is also in progress in our laboratory.[22]

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