Synthesis of block copolymers of *p*-methoxystyrene and vinyl ethers by the hydrogen iodide/zinc iodide initiating system

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Summary

Amphiphilic or polar–nonpolar AB block copolymers of *p*-methoxystyrene (pMOS) and vinyl ethers (VE; methyl or isobutyl) were synthesized by the sequential living cationic polymerization initiated with the hydrogen iodide/zinc iodide (HI/ZnI$_2$) system in toluene at −15 and +25 °C. pMOS–VE block copolymers of narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.05–1.25; $\bar{M}_n$ = 6000–16000) were obtained in nearly quantitative blocking efficiency, when methyl or isobutyl VE was polymerized first by HI/ZnI$_2$, followed by addition of pMOS to the resulting living polymer solutions; an additional amount of ZnI$_2$ was required to accelerate the second-phase living polymerization of the less reactive styrenic monomer. Similar block polymerizations in an opposite monomer-addition sequence (from pMOS to VE), in contrast, resulted in mixtures of the desired block polymer and homopolymer of pMOS.

Introduction

The synthesis of block polymers of vinyl monomers by sequential cationic polymerization often suffers from low blocking efficiency and broadening in polymer molecular weight distribution (MWD), primarily due to chain transfer reactions inherent in the carbocationic processes (1–5). Although the recent development of living cationic polymerization (6,7) has indeed contributed toward overcoming this particular problem, the reported examples of better controlled cationic block copolymer synthesis have been confined to combinations of structurally similar monomers, such as within vinyl ethers (8–12) or unsaturated hydrocarbons (13).

Block copolymers of vinyl monomers with different structures would be difficult to prepare by sequential cationic polymerization, as suggested by their nonideal "random" copolymerizations where cross-transfer predominates over cross-propagation for most of such comonomer pairs (14,15). An illustrative example of this difficulty can be found in the block copolymerization of *p*-methoxystyrene (pMOS) and alkyl vinyl ethers by iodine (4) or by the hydrogen iodide/iodine (HI/I$_2$) (8) initiating system. Even with the latter, which permits well-defined living cationic polymerization of vinyl ethers (6,8), the resulting products have MWDs broader than those of their parent homopolymers. Another disadvantage for the HI/I$_2$-mediated block copolymerization involves the rather low operational temperatures (below −5 °C) (8–12).

Recently, we have found that the hydrogen iodide/zinc iodide (HI/ZnI$_2$) initiating system, where the iodine of the HI/I$_2$ system is replaced by zinc iodide, induces living cationic polymerizations of not only isobutyl vinyl ether (16,17) but pMOS (18,19) and *p-tert*-butoxystyrene (20) even at room

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temperature.   These findings of improved living cationic systems   prompted
us to investigate block copolymerizations of pMOS and alkyl vinyl ethers by
HI/ZnI$_2$ (Scheme I). As the latter components, we herein employed isobutyl
vinyl ether (IBVE) and methyl vinyl ether (MVE), which afford hydrophobic
and hydrophilic segments, respectively.
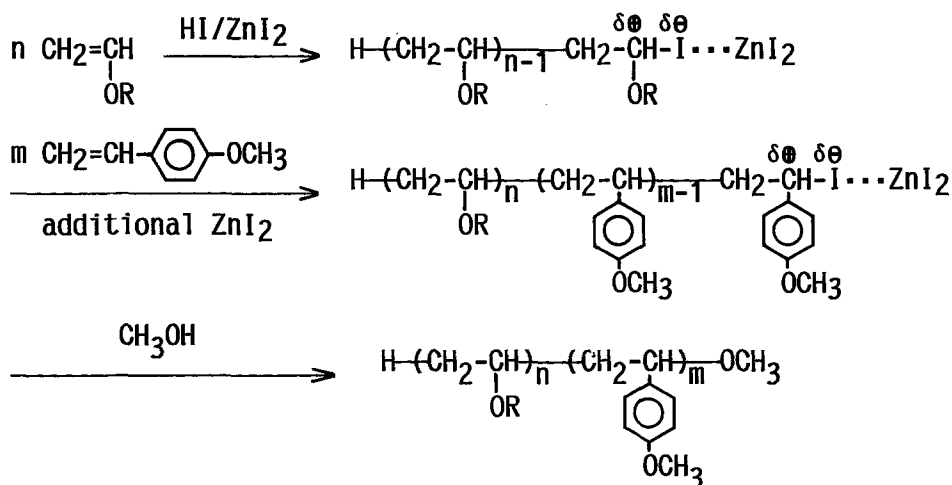
Scheme I [R = CH$_2$CH(CH$_3$)$_2$, CH$_3$]

Results and Discussion

Block Copolymerization from pMOS to IBVE

With use of the HI/ZnI$_2$ initiating system, block copolymerization was
first attempted by sequentially polymerizing first pMOS and then IBVE in
toluene solvent at −15 °C. As already reported (18,19), the first-stage
polymerization of pMOS led to a living polymer of a very narrow MWD (Fig-
ure 1, A), whose number average molecular weight ($\overline{M}_n$) was in good agreement
with the calculated value assuming the formation of one living chain per
molecule of hydrogen iodide. On addition of IBVE to the living poly(pMOS)
solution at pMOS conversion near 100%, a rapid polymerization of the added
IBVE immediately ensued, being completed in a few minutes.

The product, however, exhibited a bimodal MWD where one peak had a
molecular weight nearly the same as that of the living pMOS prepolymer,
whereas the other did a higher molecular weight (Figure 1, B) [in view of
the refractive index of the pMOS repeat unit considerably larger than of
the IBVE's, this MWD curve (in solid line) does not show the actual rela-
tive amounts of the two fractions]. Despite the molecular weight differ-
ence, both fractions showed intense ultraviolet absorptions (254 nm; in
broken line) due to the pMOS repeat units over the whole molecular weight
range. Thus, the sequential polymerization of IBVE from living poly(pMOS)
resulted in a mixture of a pMOS−IBVE block copolymer (higher M.W. peak) and
a homopolymer of pMOS (lower M.W. peak); it cannot be excluded entirely,
however, that the latter fraction consists of block copolymers with short
poly(IBVE) sequences.

Under the conditions shown in Figure 1, the livingness of the HI/ZnI$_2$−
mediated polymerization of pMOS is well established (18,19); particularly
relevant herein is the fact that repeated additions of pMOS feeds to com-

pletely polymerized reaction mixtures do not cause any loss of the living ends but lead to undisturbed polymer growth (i.e., increases in polymer molecular weight directly proportional to monomer conversion). Consequently, the pararell formation of homo-poly(pMOS) on the addition of IBVE is not due to a partial deactivation of the living prepolymer of the styrene derivative during the first-stage polymerization, but most probably due to the very rapid consumption of the added IBVE, during which period a part of the preformed living poly(pMOS) ends should have remained unreacted. This unfavorable situation stems from the difference in polymerization reactivity between pMOS and IBVE: In the first-phase living polymerization, less reactive pMOS requires a high ZnI_2 concentration (5.0 mM for $[HI]_0 = 10$ mM) (18) that is too high for IBVE to be polymerized at a controlled rate (16,17).
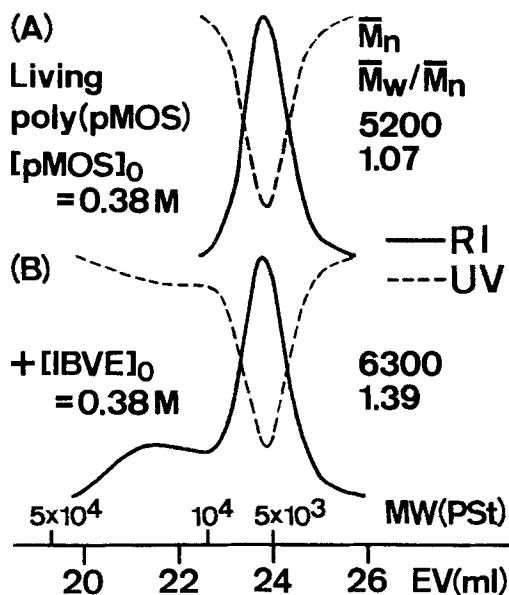

Figure 1. MWD curves of starting living poly(pMOS) (A) and the polymer (B) obtained after the addition of IBVE to sample A in toluene at –15 °C: $[pMOS]_0 = [IBVE]_0 = 0.38$ M; $[HI]_0 = 10$ mM; $[ZnI_2]_0 = 5.0$ mM. Conversions are 100% for both monomers.

Block Copolymerization from IBVE to pMOS

Considering such a reactivity difference, we then examined the reverse order of monomer-addition sequence, from IBVE to pMOS. Thus, the living polymerization of IBVE by HI/ZnI_2 was first carried out in toluene at –15 °C at a low ZnI_2 concentration (0.20 mM; $[HI]_0 = 10$ mM) that is most suited for the vinyl ether (16,17). The polymerization of IBVE was so rapid as to reach quantitative monomer conversion in 10 min to give narrowly distributed living polymers with controlled molecular weights (one living chain per molecule of hydrogen iodide); see Figure 2, A. At this low level of the zinc salt, as expected, subsequent addition of pMOS did not lead to a further polymerization from the living(IBVE).

However, when an additional dose of ZnI_2 (5.0 mM) was added to the quiescent reaction mixtures, then smooth polymerizations of the added pMOS followed and afforded apparently clean IBVE-pMOS block copolymers (Figure 2, B and C). In contrast to the bimodal distribution in Figure 1, B, the MWDs of both products now consist of a very narrow single peak, whose ultraviolet and refractive-index detector traces almost completely overlap with each other. The products are apparently free of homopolymers of IBVE, as evidenced by the absence of a tailing in the region where the starting living poly(IBVE) eluted (peak elution count ca. 24 mL).

As Figure 2, D and E show, a similarly successful block copolymeriza-

tion was achieved at +25 °C, for which the initial ZnI_2 concentration was further lowered to 0.10 mM to regulate the high reaction rate at this higher temperature near ambient. Even under these conditions, the high reactivity of IBVE permitted a rapid polymerization that was completed in a few minutes. Subsequent sequential addition of pMOS and ZnI_2 (5.0 mM) then led to block copolymers with a single-peaked, narrow MWD (Figure 2, E) which, however, was slightly broader than those for −15 °C. Further structural characterization of these IBVE-pMOS block copolymers is discussed in the later section.
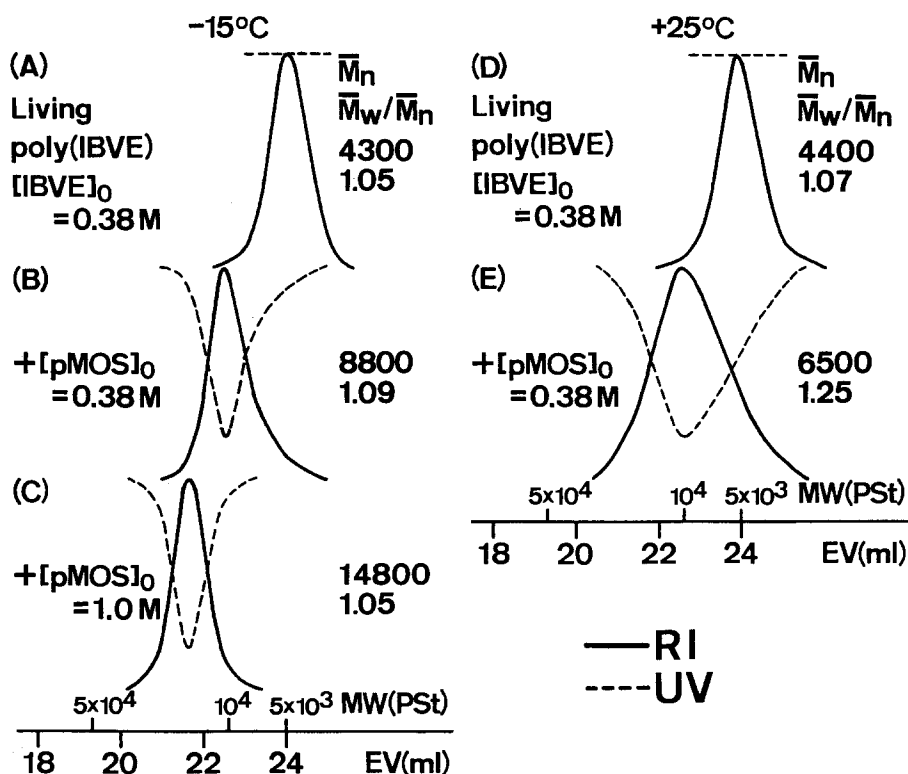

Figure 2. MWD curves of living poly(IBVE) (A and D) and the polymers (B, C, and E) obtained after the addition of pMOS to samples A and D in toluene. (A–C): −15 °C; $[IBVE]_0$ = 0.38 M; $[pMOS]_0$ = 0.38 M (B) or 1.0 M (C); $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 0.20 mM (+5.0 mM for B and C). (D and E): +25 °C; $[IBVE]_0$ = 0.38 M; $[pMOS]_0$ = 0.38 M; $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 0.10 mM (+5.0 mM for E). Conversions are 100% for both monomers.

Block Copolymerization of MVE and pMOS

Block copolymers of pMOS with MVE are of interest as polymeric amphiphiles because the latter monomer affords a water-soluble/hydrophilic segment. As with the IBVE-pMOS counterpart discussed above, the HI/ZnI_2-initiated block copolymerization with MVE turned out to be affected by the

order of monomer addition, and MVE should be polymerized first to achieve near quantitative blocking efficiency.

In an attempt to polymerize MVE from living poly(pMOS) prepared with HI/ZnI$_2$ in toluene at -15 $^\circ$C (Figure 3, A and C; $[ZnI_2]_0 = 5.0$ or 2.0 mM for $[HI]_0 = 10$ mM), the copolymerization products had bimodal MWDs (Figure 3, B and D) that are similar to the corresponding distribution with pMOS and IBVE (Figure 1, B). Even at the lower ZnI$_2$ concentration (Figure 3, C and D), the added MVE was polymerized much faster than pMOS, and no virtual improvement was found in the MWD of the product.
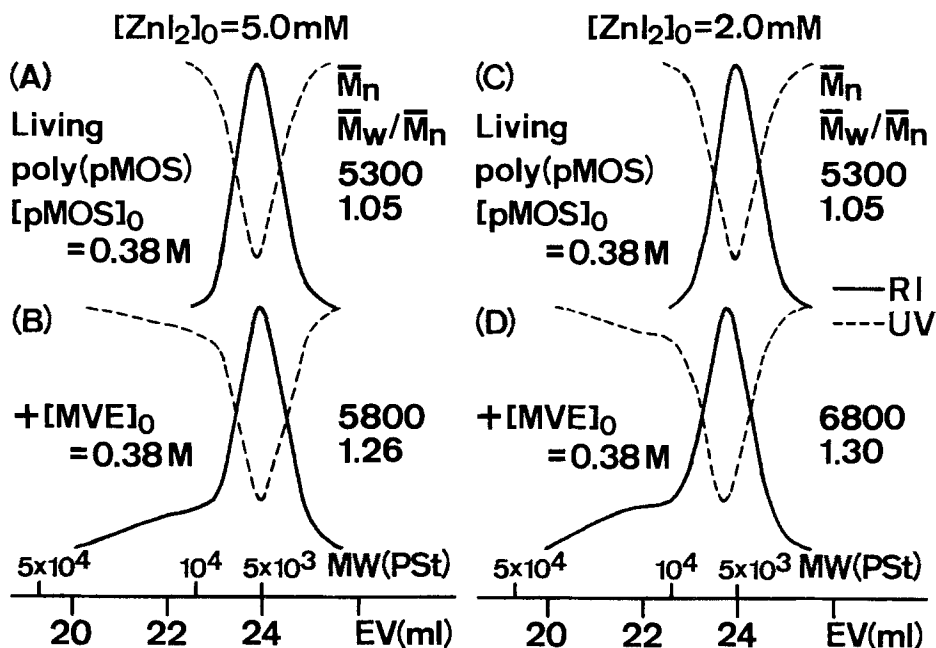

Figure 3. MWD curves of starting living poly(pMOS) (A and C) and the polymers (B and D) obtained after the addition of MVE to samples A and C in toluene at -15 $^\circ$C: $[pMOS]_0 = [MVE]_0 = 0.38$ M; $[HI]_0 = 10$ mM; $[ZnI_2]_0 = 5.0$ mM (A and B) or 2.0 mM (C and D). Conversions are 100% for both monomers.

A second series of pMOS–MVE block polymerization was then carried out in toluene at -15 $^\circ$C, in which pMOS was allowed to polymerize from preformed living poly(MVE) (Figure 4). The initial ZnI$_2$ concentration was as low as 0.20 mM ($[HI]_0 = 10$ mM), and after mixing a pMOS feed with a living poly-(MVE) solution (Figure 4, A), an additional amount of the zinc salt (5.0 mM) was added to accelerate pMOS polymerization. As shown in Figure 4, B and C, the products exhibited single-peaked, narrow MWDs without traces of unreacted MVE prepolymers. Although the MWD for the lower pMOS content was somewhat broader (Figure 4, B), both samples of the MVE–pMOS block copolymers with HI/ZnI$_2$ had clearly narrower distributions than the counterparts prepared with the HI/I$_2$ initiating system ($\bar{M}_w/\bar{M}_n = 1.08$–1.17 vs. 1.26) (8).
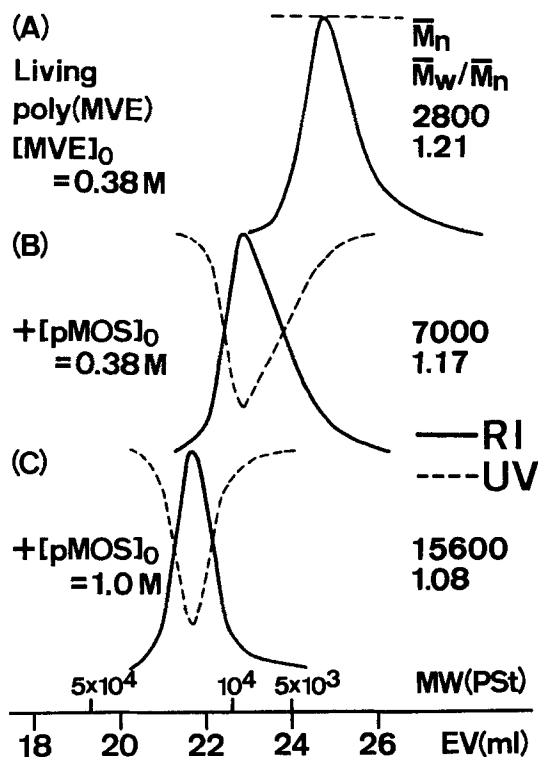
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Figure 4. MWD curves of living poly(MVE) (A) and the polymers (B and C) obtained after the addition of pMOS to sample A in toluene at -15 °C: $[MVE]_0$ = 0.38 M; $[pMOS]_0$ = 0.38 M (B) or 1.0 M (C); $[HI]_0$ = 10 mM; $[ZnI_2]_0$ = 0.20 mM (+5.0 mM for B and C). Conversions are 100% for both monomers.

Characterization of Block Copolymers

The structures and segment compositions of the block copolymers were determined by ^{1}H NMR spectroscopy. Figure 5 presents typical NMR spectra of pMOS-IBVE (sample B, Figure 2) and pMOS-MVE (sample B, Figure 4) block copolymers. Both spectra exhibit the aromatic (6-7 ppm) and methoxy (3.8 ppm) protons of the pMOS repeat units, along with the IBVE or MVE sequence (e.g., peaks b, c, and e, Figure 5, A; and peaks b and c, Figure 5, B); no other signals indicative of side-reactions or by-products are seen.

The compositions of block copolymers (IBVE/pMOS and MVE/pMOS ratios) were determined from the integrated signal intensity ratio of the aromatic protons (6-7 ppm; pMOS units) to the alkoxy-type protons (2.6-4.2 ppm; pMOS + vinyl ether units); the latter include the following italicized protons: [∿CH₂-CH(C₆H₄OC*H₃*)∿ + ∿CH₂-C*H*(OC*H₃*)∿ or ∿CH₂-C*H*(OC*H₂*CH(CH₃)₂)∿]. Table I shows the results. The compositions of the block copolymers (shown in DP, the degree of polymerization of each segment) were all in good agreement with the feed molar ratios of IBVE or MVE to pMOS. The spectral analysis thus confirmed the formation of the desired AB block copolymers of pMOS and the vinyl ethers (with up to 100 pMOS units per segment) in nearly perfect blocking efficiency.
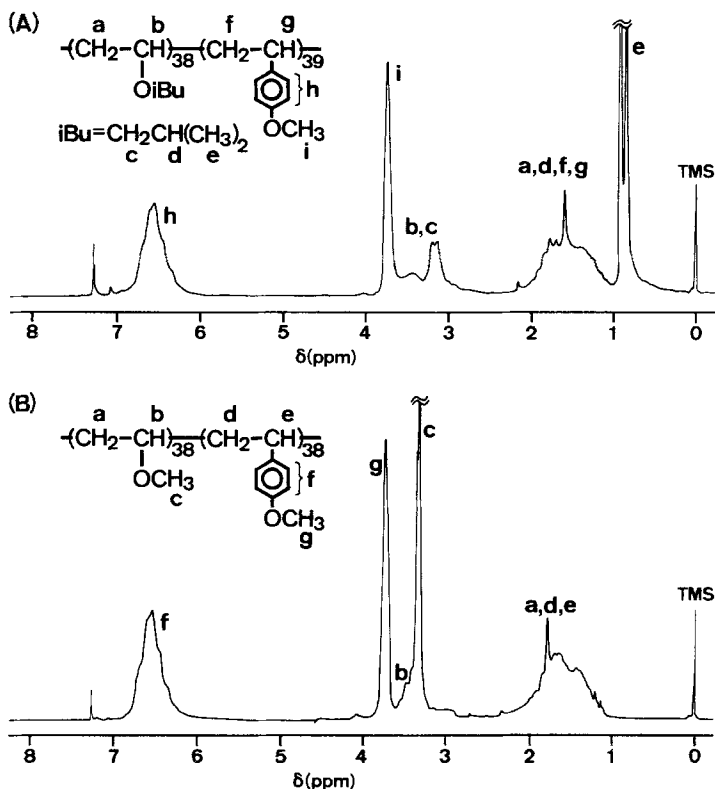
Figure 5. ^{1}H NMR spectra: (A) poly(IBVE-b-pMOS), IBVE/pMOS = 38/39 (segment DP), sample B in Figure 2, see line 2 of Table I; (B) poly(MVE-b-pMOS), MVE/pMOS = 38/38 (segment DP), sample B in Figure 4, see line 4 of Table I.

Table I. Block Copolymers of *p*-Methoxystyrene and Isobutyl or Methyl Vinyl Ether via Sequential Living Cationic Polymerization by HI/ZnI$_2$[a]

Block Copolymer	Vinyl Ether/pMOS[c] calcd[d]	obsd[e]	$\bar{M}_n$[f]	$\bar{M}_w/\bar{M}_n$[f]
poly(IBVE-b-pMOS)	38/38	38/39	8800	1.09
poly(IBVE-b-pMOS)[b]	38/38	38/39	6500	1.25
poly(IBVE-b-pMOS)	38/100	38/99	14800	1.05
poly(MVE-b-pMOS)	38/38	38/38	7000	1.17
poly(MVE-b-pMOS)	38/100	38/102	15600	1.08

a) In toluene at –15 °C; conversion = 100 %.   b) In toluene at +25 °C.
c) Shown in the degree of polymerization (DP) for each segment.
d) Calculated from the initial concentrations of the monomers and hydrogen iodide: segment DP (calcd) = [monomer]$_0$/[HI]$_0$.
e) By ^{1}H NMR spectroscopy.
f) By size-exclusion chromatography; polystyrene calibration.

Experimental

The monomers [pMOS (4), IBVE (6), and MVE (8)], hydrogen iodide (anhydrous) (9), ZnI_2 (16), and polymerization solvents (toluene, *n*-hexane, and diethyl ether) (6,16) were purified and dried as previously reported.

The block polymerizations were carried out under dry nitrogen by sequentially adding prechilled hydrogen iodide (in *n*-hexane; 0.50 mL) and ZnI_2 (in diethyl ether; 0.50 mL) solutions to a solution of the first monomer (in toluene; 4.0 mL), and then the second monomer and ZnI_2 (see text) were added immediately before the end of the first-phase polymerization. After the complete consumption of the second monomer, the polymerization was terminated with prechilled ammoniacal methanol (2.0 mL), and the resultant polymers were recovered as described (18,19). The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ of the polymers were measured by size-exclusion chromatography (polystyrene calibration) (17). ^1H NMR spectra (at 90 MHz; Jeol FX-90Q) were recorded in $CDCl_3$ at 30 °C.

Acknowledgment

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