Notes

Synthesis of Polyisobutylene-Based Macroinitiators and Block Copolymers via Multimode Polymerization[1]

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Introduction

Living polymerization[2−4] is one of the leading methods to design block copolymers via the sequential monomer addition (SMA) technique. Because of limitations on synthesizing different copolymers by using a single type of propagating species, multimode polymerization proves to be promising.[5] Multimode polymerization involving macroinitiators, classified on the basis of interconversion between various propagating mechanisms has been described in a recent book.[6] Most block copolymers containing a polyisobutylene (PIB) segment are made by either the SMA technique or cationic to anionic transformation (CAT).[7] While cationic to radical transformation (CRT)[6,7] is a promising method for the design of various other copolymers, the synthesis of PIB-based block copolymers by CRT is unknown.

The essence of this research is to design block copolymers by CRT. This note concerns the first synthesis of a PIB with a central azo group (PIB−N=N−PIB) and its application as a macroinitiator for the synthesis of block copolymers by CRT (multimode polymerization). The synthesis strategy involved a two-step process: First, isobutylene (IB) was polymerized cationically using an initiator system consisting of a difunctional organic tertiary ether {2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMD)} and $TiCl_4$ to generate the PIB macroinitiator (PIBMI). In the second step, the macroinitiator was used for the radical polymerization of styrene (STY) or methyl methacrylate (MMA). Figure 1 describes the reaction pathways.

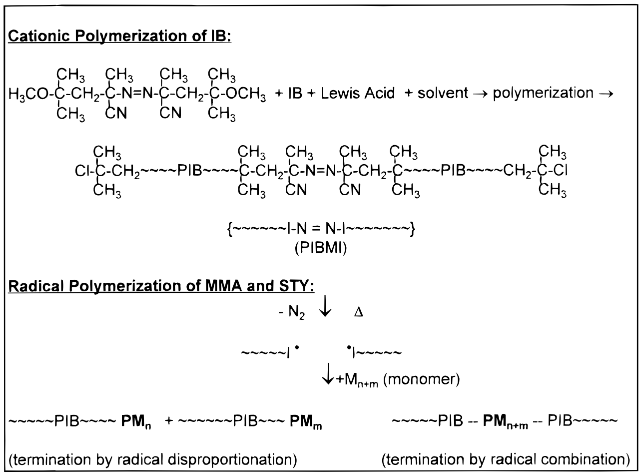

Figure 1. Reaction scheme for macroinitiator and block copolymer synthesis.

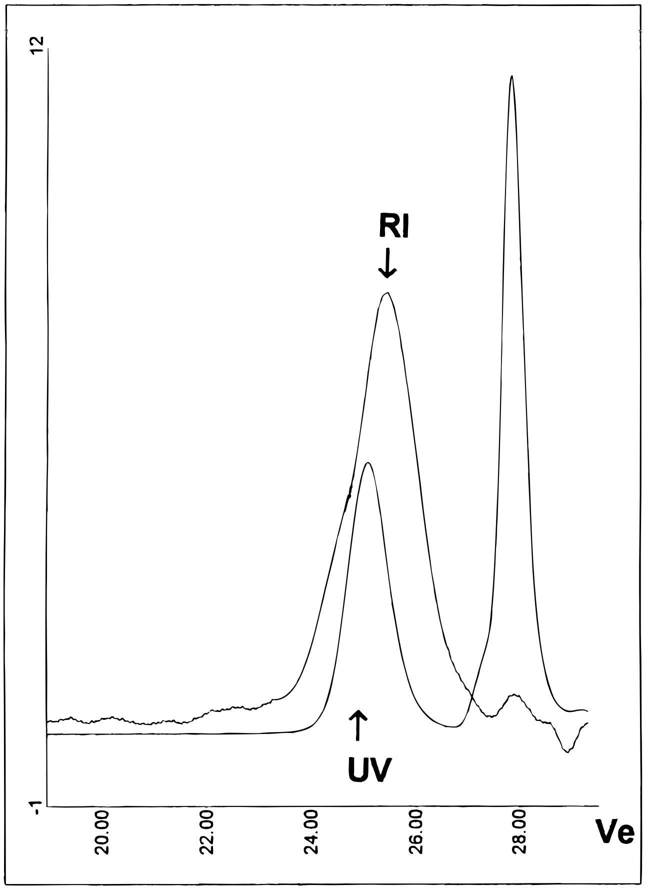

Figure 2. RI and UV traces of PIB synthesized by PDM.

Results and Discussion

Organic tertiary ethers[3,8,9] are well-known to initiate the living polymerization of IB in conjunction with Lewis acids. The use of the 2,6-dimethoxy-2,4,4,6-tetramethylheptane (TMHDiOMe)/Lewis acid initiating system for the polymerization of IB has earlier been reported.[10] It is now being postulated that AMD, which is analogous to TMHDiOMe, would initiate the polymerization of IB in conjunction with Lewis acids. The obvious benefit of introducing the azo group into the (PIB) chain is that the initiator fragment becomes part of the polymer chain and the polymer arms emanate from the initiating sites. With this thought in mind several scouting experiments were carried out to produce PIB with a central azo group. Synthesis of low molecular weight {M_n 3000−7000; M_w/M_n = ~1.6, initiator efficiency (I_{eff}) = ~90%} PIB using a monofunctional azoinitiator (2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile) (PDM) was also carried out. Samples were characterized by GPC coupled with RI and UV detectors. The presence of UV absorption

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Table 1. Preparation of PIB Containing a Central Azo Group by Polymerization of IB Using the AMD Initiator/$TiCl_4$ Coinitiator System[a]

expt no.	[I], mol × 10^3	[$TiCl_4$], mol × 10^2	[IB], mol × 10	amt of CH_3Cl, mL	amt of hexane, mL	amt of CH_2Cl_2, mL	M_n	M_w/M_n	I_{eff}, %
1		2.28	3.9	175	125		32 800	2.8	
2	1.3	2.28	11.0	175	125		49 600	1.4	86
3	1.3	2.28	3.9	175	125		19 850	1.5	82
4		2.28	3.7			300	26 100	2.0	
5	1.3	2.28	3.7			300	19 350	1.3	82

[a] Temperature = −65 °C; time ~30 min; conversion ≈ 100% (experiment 1 and 4 ~70%, controls); I = AMD.

Table 2. Polymerization of MMA and STY Initiated with PIBMI[a]

expt no.	amt of PIBMI, g	PIBMI [−N=N−], mol × 10^3	monomer	amt of monomer, mol × 10^3	conv, %	M_n[b] (block copolymer)
CRT-1	5.0	7.0	MMA	46.7	22.8	36 700
CRT-2	5.0	7.0	STY	43.6	17.6	28 750

[a] Solvent = toluene (50 mL), temperature = 70 °C, time = 7 h; PIB macroinitiator (PIBMI), M_n = 19 850 (sample from experiment 3, Table 1). [b] By GPC using a PIB standard.

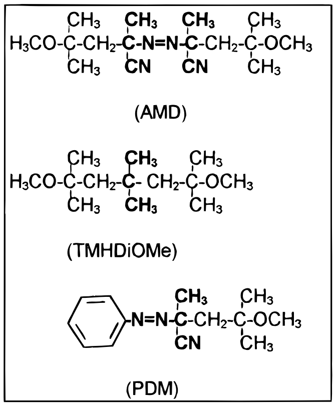

Figure 3. Empirical formulas of selected initiators.

corresponding to the RI peaks (Figure 2) indicates the presence of an aromatic fragment, which in turn indicates initiation by PDM. The structures of the initiators are presented in Figure 3. The general polymerization mechanism of IB has been described elsewhere.[3]

The polymerization of IB by AMD to produce PIBMI was carried out using the $TiCl_4$ coinitiator. Table 1 summarizes the results of the orienting experiment and indicates that AMD initiates the polymerization of IB. The control runs, carried out in the absence of AMD, produced broad polydispersities and incomplete IB conversions. Experiments with the AMD/$TiCl_4$ combination showed I_{eff} = 80−90% (at ~100% conversion) with a narrow molecular weight distribution (1.3−1.5). The initiating efficiencies of AMD/$TiCl_4$ in (CH_3Cl + hexane) and CH_2Cl_2 are similar (expiment 3 and 5). With the AMD/BCl_3 system, the I_{eff} and conversions were very low (in the range 5−20%; data not shown). Similar results have also been obtained with the analogous TMHDiOMe/BCl_3 combination.[10] The broad polydispersity is indicative of slow initiation. The key proof for the synthesis of PIBMI is the ability of this material to initiate the polymerization of vinyl monomers.

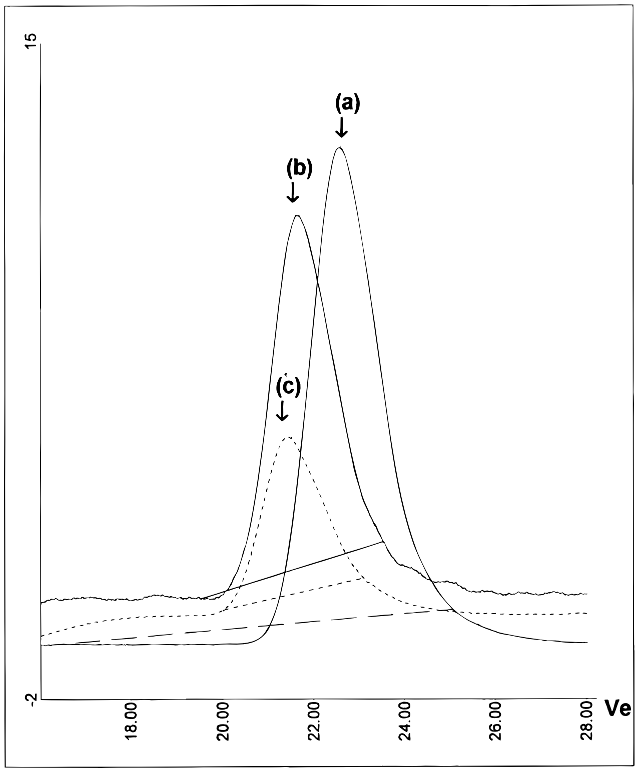

Figure 4. RI traces of (a) PIBMI and block copolymers of (b) IB with STY and (c) IB with MMA.

PIBMI was used to initiate the free radical polymerization of MMA and STY (Figure 1). Table 2 represents the result of two experiments, one with each monomer. Control experiments, i.e., polymerization of STY and MMA in the absence of PIBMI, did not produce homopolymer. However, in the presence of PIBMI, about 23% and 18% conversion was obtained with MMA and STY, respectively, indicating initiation by PIBMI. Normalized SEC traces of PIBMI and the block copolymers are in Figure 4. The chromatograms indicate that the peaks due to the block copolymers are shifted toward lower elution volumes, indicating a higher molecular weight than the starting PIBMI. The compositions of the copolymers were analyzed by ^1H NMR spectroscopy (Figure 5) and were found to contain 4% and 35 mol % PSTY and PMMA, respectively.

Experimental Section

Materials and Measurements. Various chemicals including BCl_3 (1 M solution in hexane) were obtained from Aldrich Chemical Co. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) was a gift from Wako Chemicals USA, Inc. and used as received. Depending upon the materials, they are used as received or purified according to standard procedures. Gaseous methyl chloride and isobutylene were purified according to standard procedures.[11]

Molecular weights of polymers were determined by a gel permeation chromatograph (GPC) equipped with a differential

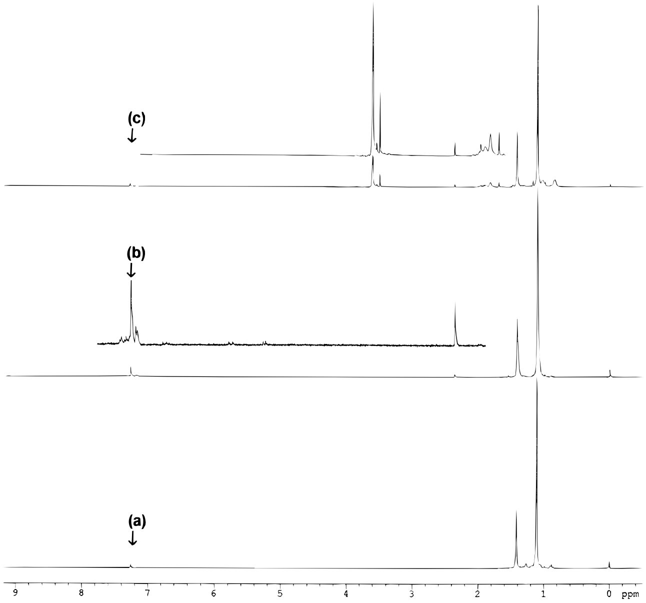

Figure 5. ^{1}HNMR spectra of (a) PIBMI and block copolymers of (b) IB with STY and (c) IB with MMA.

refractometer, ultraviolet detector, and three μ-Styragel mixed bed columns. A PIB broad standard calibration was employed to determine molecular weights. Tetrahydrofuran was the eluent at a flow rate of 1 mL/min. A Varian VXR-300 NMR spectrometer was used. Samples (solutions with deuterated chloroform) were characterized at a ^{1}H resonance frequency of 299.9 MHz.

Synthesis of PIB Macroinitiator (Cationic Polymerization). Cationic polymerization of IB was carried out in a 500 mL resin kettle fitted with a stirrer, gas inlet outlet ports, a thermometer, etc. All the manipulations were carried out under a dry nitrogen atmosphere. Initiator and solvent (CH_3Cl or CH_2Cl_2) were placed in the reactor, and the solution was stirred at −65 °C maintained by a bath cooled with dry ice and heptane. The required amount of condensed IB was introduced by cannulation under nitrogen pressure. Polymerization was initiated by the addition of $TiCl_4$ (or BCl_3) under stirring. The onset of the reaction was marked by the appearance of haziness, color, and later precipitation. After 30−60 min the polymerization was terminated by the introduction of 10−30 mL precooled methanol, the temperature was allowed to rise to ambient, the solvent was evaporated, and the product was dissolved in hexane and precipitated into methanol. The polymer was redissolved in hexane. The mixture was repeatedly washed with water. The hexane solution was dried overnight (about 16 h) over anhydrous sodium sulfate. Finally, the product was filtered, the solvent was evaporated (rotavap) under reduced pressure at ambient temperature, and the polymer was further dried under reduced pressure for 48 h. The procedure for IB polymerization has been described elsewhere.[11]

Synthesis of Block Copolymers (Radical Polymerization). Radical polymerizations of STY and MMA using PIB-based macroazoinitiators were carried out in 250 mL three-necked round-bottom flasks fitted with a condenser, thermometer/thermocouple, and magnetic stirrer. The required amount of PIB was weighed into the flask, an appropriate amount of toluene was introduced, and the solution was stirred by a magnetic stirrer. The flask was kept under nitrogen, and the solution was degassed by bubbling nitrogen. Then the required amount of inhibitor free monomer was added and the flask was heated to 70 °C. After the desired reaction time the heating was discontinued, the solvent was evaporated, and the polymer was dried under high vacuum for about 48 h at 70 °C. To obtain pure block copolymers, hexane solutions of the crude products were precipitated in acetone.[12] The precipitated polymer was dried under high vacuum for about 48 h at 70 °C.

Conclusion

There are generally two types of transformation processes, i.e., direct and indirect transformations.[13] This study represents an example of the indirect transformation involving the combination of two polymerization modes. Using this multimode polymerization, i.e., combining various polymerization mechanisms, novel polymeric materials may be synthesized from new and classical monomers.

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References and Notes

(1) This work was presented in part at the following meetings. (a) The 1st International Conference on Advanced Polymers via Macromolecular Engineering, APME'95, June 24−29, 1995, Poughkeepsie, New York. (b) The 5th SPSJ International Polymer Conference, Osaka, Japan, Dec 1994; paper no. 30A26, preprint p 35.
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