Thermoplastic elastomers by sequential monomer addition

VI. Poly(p-methylstyrene-b-isobutylene-b-p-methylstyrene)*

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I. Abstract

The living carbocationic polymerization (LC\textsuperscript{Pzn}) of p-methylstyrene (pMeSt) was achieved by the use of the 2-chloro-2,4,4-trimethylpentane (TMPCl)/TiCl\textsubscript{4} initiating system in the presence of triethylamine (Et\textsubscript{3}N) electron donor in CH\textsubscript{3}Cl/nC\textsubscript{6}H\textsubscript{14} mixed solvent at -80°C. Next, the synthesis, characterization, and some physical-mechanical characteristics of a series of poly(p-methylstyrene-b-isobutylene-b-p-methylstyrene) (PpMeSt-PIB-PpMeSt) triblocks is described. The latter synthesis involved two steps in one reactor: 1) The generation of diliving polyisobutylene dications (PIB) by the dicumyl chloride (DiCumCl)/TiCl\textsubscript{4} system under similar conditions followed by 2) the addition of pMeSt and growth of living PpMeSt cations. The PpMeSt-PIB-PpMeSt triblocks are soft thermoplastic elastomers (TPEs).

I. Introduction

In the course of our fundamental investigation on LC\textsuperscript{Pzn}, we have explored the synthesis by sequential monomer addition of a variety of glassy-rubbery-glassy triblock copolymers exhibiting TPE character (1-4). This paper concerns a demonstration of LC\textsuperscript{Pzn} of pMeSt, and the subsequent synthesis of PpMeSt-PIB-PpMeSt triblocks. The latter were prepared in two steps in one reactor: The first step was the bidirectional LC\textsuperscript{Pzn} of isobutylene (IB) to PIB up to $M_n \approx 50,000\text{g/mole}$, followed by the addition of pMeSt and growth of the PpMeSt blocks until $M_n \approx 15,000\text{g/mole}$.

III. Experimental

The synthesis of 2-chloro-2,4,4-trimethylpentane (TMPCl) and 1,4-bis(2-chloro-2-propyl)benzene (or p-dicumyl chloride, DiCumCl) have been described (5,6). pMeSt was washed with 10% aqueous NaOH, with distilled water until neutral, dried over CaCl\textsubscript{2} and distilled over CaH\textsubscript{2} in vacuo. Et\textsubscript{3}N was distilled over KOH. The source and purification of IB, TiCl\textsubscript{4}, CH\textsubscript{3}Cl and nC\textsubscript{6}H\textsubscript{14} have been described (7,8). Methanol and toluene (Fisher Scientific Co.) and CDCl\textsubscript{3} (Aldrich) were used as received. Polymerizations were carried out in a drybox under dry nitrogen.

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The synthesis of diliving PIB by the DiCumCl/TiCl₄ initiating system in the presence of electron donors (EDs) has been described (8,9). In the blocking step, prechilled dilute pMeSt solution in the absence or presence of Et₃N was added to charges stirred at -80°C. After one hour the charges were poured into a large excess of methanol. The precipitated products were dissolved in toluene, washed with aqueous HCl, with distilled water, with aqueous NaHCO₃, with distilled water until neutral, dried over MgSO₄, precipitated slowly into methanol and dried under vacuum at 60°C.

Molecular weights and MWDs were obtained by a Waters high pressure GPC assembly (Model 6000A pump, Microstyragel columns of 10⁵, 10⁴, 10³, 500 and 100Å, UV and RI detectors). Elution counts were calibrated by well-fractionated, narrow MWD PIB and PSt standards. Block copolymer molecular weights were also determined by ¹H-NMR spectroscopy. ¹H-NMR spectra were taken on a Varian Gemini 200 MHz spectrometer using CDCl₃ solvent.

For mechanical property analysis of TPEs, microdumbells were stamped from homogeneous bubble-free optically clear films cast from toluene solution. Stress-strain measurements were carried out on microdumbells at room temperature by an Instron Tensile Tester Strain rate: 3.94 min⁻¹. Shore A hardness was measured by a Shore Durometer, according to ASTM D2240. The averages of 6 samples are recorded.

IV. Results and Discussion

IV.1. LC Pzn of pMeSt

Preparatory to the synthesis of PpMeSt-PIB-PpMeSt, conditions for the LC Pzn of pMeSt have been developed. This phase of our research was guided by information accumulated earlier during research with pMeSt (10,11) and similar systems (1-4). After some orienting experimentation we found that the LC Pzn of pMeSt can be achieved by the TMPCl/TiCl₄ initiating system in the presence of Et₃N. Figure 1-1 shows the Mₙ versus Wₚ (g of polymer obtained) and Mₙ versus Iₑₑᵢ (initiator efficiency, (g polymer/Mₙ)/TMPCl)) plots. Evidently the experimental Mₙ’s are higher than theoretical, i.e., expected by assuming Iₑₑᵢ = 100% (see dotted lines in Figure 1-1). Higher than theoretical Mₙ’s are obtained because the rate of initiation (Rᵢ) is relatively lower than that of propagation (Rₚ); in other words TMPCl/TiCl₄ induces relatively slow initiation and pMeSt is rapidly consumed by a fraction of initiating entities leading to Iₑₑᵢ <100%.

By plotting the data in Figure 1-1 according to -ln(1-Iₑₑᵢ)-Iₑₑᵢ versus [M₀] (monomer concentration), i.e., by the diagnostic plot of a slowly initiating LC Pzn (12), a straight line without intercept is obtained (see Figure 1-2). According to this evidence the polymerization of pMeSt under the above conditions is living with the rate of initiation lower than that of propagation. This treatment has been used previously to gain insight into the mechanism of LC Pzn of p-tert-butylstyrene (p₉BuSt) (4) and indene (In) (3).