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Synthesis of long-chain branched isotactic-rich polystyrene *via* cationic polymerization

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ABSTRACT

Cationic polymerization of styrene was conducted with 1-chloro-1-phenylethane (SCl)/$AlCl_3$/phenyl methyl ether (PME) initiating system in hexane/CH_2Cl_2 (60/40, v/v) at −80 °C. The kinetics for cationic polymerization of styrene was investigated by in-situ ATR-FTIR spectroscopy. The isotactic-rich polystyrene (*i*PS) with m dyad of 81%, mm triad of 63% and mmmm pentad of 50% could be synthesized. Small amounts of crystalline regions in *i*PS formed after flow-induced crystallization and the crystallinity increased with increasing the molecular weight of *i*PS. Furthermore, the long-chain branched isotactic-rich polystyrene (*bi*PS) with around 12 times higher molecular weight than that of corresponding *i*PS could be synthesized *via* cationic polymerization of styrene by introducing a small amount of isoprene (Ip) as a comonomer and branching sites as well. The possible mechanism for long-chain branching formation *via* intermolecular alkylation reaction by using Ip structural units along polymer chain as branching sites was proposed. The nucleation rate of *bi*PS could be greatly enhanced with increasing the content of branching sites, leading to an obvious increase in crystallinity. The multi-melting temperatures from 140 °C to 237 °C were observed in DSC curves of these PS products. The tensile strength of commercial atactic polystyrene could be improved remarkably from 41.4 MPa to 55.7 MPa by adding 16.7% of *bi*PS.

1. Introduction

Polymer crystallization directly affects the properties of polymeric materials, and the stereoregularity is a crucial factor that seriously affects polymer crystallinity. The stereoregular polystyrenes are mainly produced *via* coordination polymerization [1]. Polystyrene with high stereoregularity can crystallize through many ways, such as gel route [2], flow-induced crystallization [3]. The quality and quantity of crystalline zones depend on interchain friction [4], chain branching [5], chain length and its distribution [6].

The controlled/living cationic polymerization of styrene has been achieved by using coinitiators such as BCl_3, $SnCl_4$, $TiCl_3(OiPr)$, $EtAlCl_2$, $TiCl_4$, $B(C_6F_5)$, $AlCl_3$ and $FeCl_3$ [7]. However, it is still difficult to achieve high stereoregulation because of difficulty in controlling stereochemistry of carbocation. Very recently, polystyrenes with some stereoregularity of mixed triad sequences of predominance syndiotactic sequences ([rr] < 43%) or uncontrolled low isotacticity were prepared by cationic polymerization of styrene in ionic liquid [8]. However, molecular weights were very low ($M_w < 3000$ g mol^{-1}) and crystallizability of PS products was not mentioned due to the relatively low regularity and low molecular weight of PS products [8].

In this present work, the initiating system 1-chloro-1-phenylethane (SCl)/$AlCl_3$/phenyl methyl ether (PME) has been developed for cationic polymerization of styrene in mixed solvent of hexane/CH_2Cl_2 (60/40, v/v) at −80 °C to produce linear or long-chain branched polystyrene with isotactic-rich sequences ([m] > 80%). Effect of molecular weight, long-chain branching topology and branching degree on crystallization of PS was investigated. The possible mechanism for branching formation during cationic polymerization was proposed. The long-chain branched polystyrenes with isotactic-rich sequences ([m] > 80%) would have unique thermal and mechanical properties due to the rapid formation of crystallization at relatively low processing temperature.

2. Experimental section

2.1. Materials

Styrene (St, Beijng Yanshan Petrochemical Co.) was dried overnight over calcium chloride and distilled twice over calcium

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hydride (CaH_2) under reduced pressure before use. Isoprene (Ip, Beijng Yanshan Petrochemical Co.) was distilled twice from CaH_2 before use. 1-chloro-1-phenylethane (SCl) was synthesized by hydrochlorination of St in CH_2Cl_2 (1:3 v/v) at 0 °C [9]. Hexane and CH_2Cl_2 (Beijing Houhui Experimental Instrument Technology Co.) tetrahydrofuran (THF, Beijing Jingyi Chemical Co.), phenyl amine (PA, purity>99%, Beijing Chemical Plant) and phenyl methyl ether (PME, purity>99%, Tianjing Guangfu Chemical Co.) were distilled from CaH_2 before use, respectively. $AlCl_3$ (purity > 99%, ACROS Co.) and ethanol (AR, Beijing Jingyi Chemical Co.) were used without further purification.

2.2. Procedures

All the procedures were carried out under dry nitrogen in baked glassware equipped with three-way stopcocks. Specific reaction conditions are listed in the Figure and Table captions. A representative procedure is described as follows: The styrene solution in mixed hexane and CH_2Cl_2 was prepared in a chilled 1000 mL round-bottom flask at - 80 °C. The monomer solution was air-tightly transferred to 20 mm × 200 mm test tubes (polymerization reactors) *via* a 20 mL volumetric pipette and cooled at −80 °C for more than 30 min. The solutions of SCl, PME and $AlCl_3$ in CH_2Cl_2 were added into monomer solutions to initiate the polymerization. After predetermined time, the polymerization was terminated by injection of 4 mL of prechilled ethanol containing 1% NaOH. After evaporation of the volatiles, the polymer was purified two times by reprecipitation from CH_2Cl_2/ethanol and finally washed with ethanol and water. The polymer products were dried thoroughly in a vacuum oven at 40 °C. The monomer conversion was determined gravimetrically. Some of the crude polymers were further separated into an insoluble fraction and a soluble fraction by butanone (MEK) extraction. The content of MEK-insoluble fraction (F_B) in polymer product was calculated according to the following equation:

$$F_B = \frac{\text{mass of PS fraction insoluble in MEK}}{\text{mass of PS product}} \times 100\% \qquad (1)$$

2.3. Measurements

The H_2O concentrations in the polymerization systems were monitored electrochemically with an SF-6 water determination apparatus in conjunction with a Karl-Fischer reagent (Shandong Zibozifen Instrument Co.) for coulometric titration according to the method described previously [10]. The polymerization kinetic data were obtained from in-situ FTIR spectra recorded by a Nicolet 6700 spectrophotometer with a diamond tipped ATR immersion probe (Axiom DMD-270X-LT). FTIR data collection and processing were performed with Nicolet's OMNIC Series software. The number-average molecular weight (M_n), weight-average molecular weights (M_w) and molecular weight distribution (MWD, M_w/M_n) of polystyrenes (soluble in MEK and THF) were measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF) on four polystyrene gel columns that were connected to a Waters-1515 isocratic HPLC pump and a Waters-2414 refractive index detector thermostated at 30 °C. The columns were calibrated against 25 standard polystyrene samples (M_n = 168–8,500,000 g mol^{-1}; $M_w/M_n \le 1.1$). THF was eluted at a flow rate of 1.0 mL min^{-1}. Additionally, the absolute weight-average molecular weight (M_w), hydrodynamic radius (R_h), intrinsic viscosity ($[\eta]$) and branched ratio (g_m) of branched polystyrene were determined by chromatographic system (Wyatt Technology) equipped with Refractive Index (RI, Optilab rEX), four-bridge capillary viscometer (Wyatt ViscoStar) and Multi-Angle Laser Light Scattering (MALLS, DAWN HELEOS II, laser wavelength was 658 nm) triple detectors at 35 °C. Three PLgel columns (Mz GPC, 300 × 8 mm, 10 μ) of 10^3 Å, 10^4 Å, and 10^5 Å were equipped in series. Filtrated THF was used as an eluent at a flow rate of 1.0 mL/min. Narrow PS standard with M_w of 300,000 g/mol were used for normalization of LS signals. Sample solution of 100 μL in a range of 2 mg/mL was injected, and d*n*/d*c* value of 0.1845 mL/g was used for PS standards.

The films of polymers for polarized optical microscope (POM) characterization were prepared on glass slide under a constant pressure of 10 kg cm^{-2} about 30 s from melting state to solid state at room temperature, and micrographs were obtained by using Leitz SM-LUX-POL POM. The thermal property was characterized by the Q200 MDSC (TA Instruments co.) at a scanning rate of 5 °C min^{-1} by modulated-heat procedure under nitrogen. ^{13}C NMR spectra were recorded on a Bruker AV600 MHz spectrometer in o-dichlorobenzene at room temperature (25 °C). On the basis of ^1H NMR characterization of double bond assignment ($\delta = 4.75$ ppm) in Ip units and phenyl group assignments ($\delta = 6.5$ ppm and 7.2 ppm) in styrene units, the content of isoprene (F_{Ip}) structural units in copolymer of styrene and a small amount of isoprene was calculated according to the following equation:

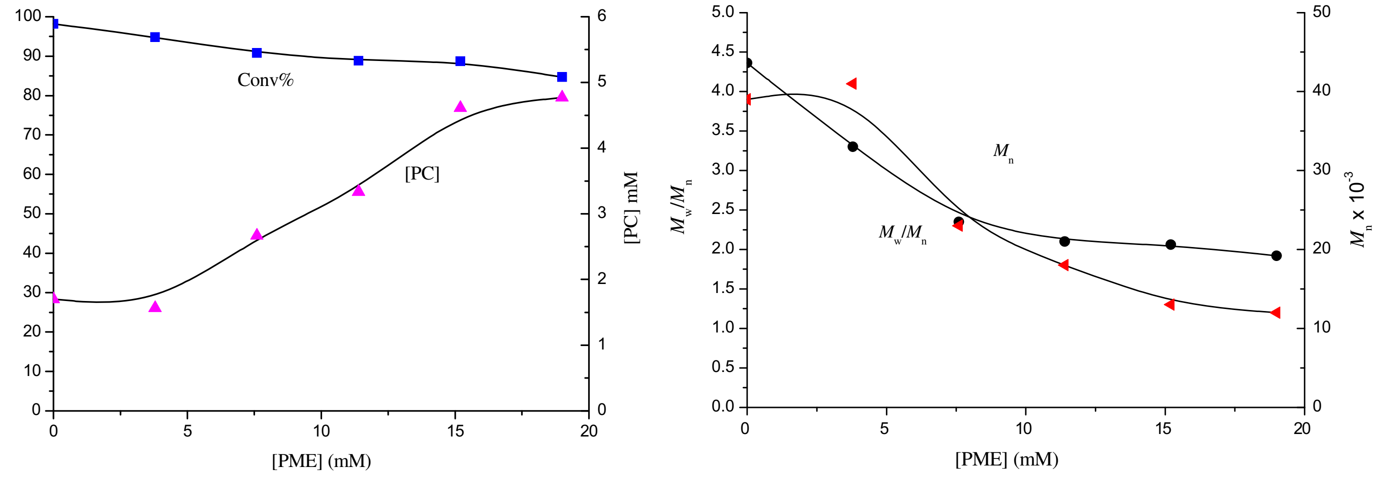

Fig. 1. Effect of [PME] on monomer conversion, M_n, M_w/M_n and concentration of polymer chains in cationic polymerization of styrene with SCl/$AlCl_3$/PME initiating system: [SCl] = 3.8 mM; [$AlCl_3$] = 3.8 mM; $V_{Hexane}/V_{CH_2Cl_2} = 6/4$; $T_p = -80$ °C; t_p = 30 min; [St] = 0.65 M. [CP] = [St] × Conversion × 104/M_n.