Conversion Studies in a Novel Reaction Injection Molding Process for Syndiotactic Polystyrene

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ABSTRACT: Syndiotactic polystyrene (sPS) has successfully been produced using a novel reaction injection molding (RIM) process and a metallocene catalyst. Previous studies have shown that many of the requirements for a RIM process are achievable. However, problems due to incomplete conversion of monomer have hindered the commercial development of this process. In attempts to overcome this conversion limitation and gain insight into its nature, the effects of the extent of mixing, reaction time, and mold wall temperature were investigated on the monomer conversion and polymer properties. The properties of interest included the sPS fraction, molecular weight, melting point, and stereoregularity of the polymer produced. It was found that this RIM process was not mixing limited. Longer reaction times resulted in an increase in conversion, with no significant change in the polymer properties. Mold wall temperature had the greatest effect on both the conversion and polymer properties. Lower mold wall temperatures resulted in an increase in the conversion. At both of the temperature extremes studied, the polymer properties deteriorated. Infrared spectroscopic analyses of the as-polymerized samples indicated that sPS helical conformations were present. This suggested that the styrene monomer may be entrapped within the helical crystalline structures of sPS, preventing complete monomer conversion during this sPS RIM process. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2679–2693, 1998

Key words: reaction injection molding; syndiotactic polystyrene; conversion; polymorphism; solvent-induced crystallization

INTRODUCTION

Since the discovery of syndiotactic polystyrene (sPS) by Ishihara and colleagues,[1] there has been great interest in developing new processes for the commercialization of this polymer. The development of a novel reaction injection molding (RIM) process for sPS introduces the possibility of producing complex plastic parts with engineering thermoplastic properties. The rapid production of high-value, high-quality parts at the price of a commodity monomer, styrene, could expand sPS's use in a broad range of applications.

sPS has many attractive properties, such as a high melting point of 270°C and a rapid crystallization rate that is practical for industry.[2] Having such a rapid crystallization rate allows sPS to be used in a number of forming operations, including injection molding, extrusion, and thermoforming. When molded, a higher degree of dimensional accuracy and stability can be achieved because sPS exhibits lower moisture uptake and shrinkage when compared with other thermoplastics.[2] Although sPS retains the T_g of atactic polystyrene (aPS) ~ 100°C, it has high heat resistance due to its crystalline nature. This fea-

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ture, coupled with its hydrocarbon backbone, results in excellent resistance toward moisture and various chemicals. For sPS to be used as an engineering thermoplastic, it must be reinforced with fiberglass, mineral fillers, and/or rubber elastomers. Fiberglass-reinforced sPS demonstrates good dynamic and thermomechanical properties exhibiting a high load heat distortion temperature of 250°C.[2] All of the previously described properties—combined with its exceptional electrical performance, low specific gravity, and toughness—make it potentially competitive with other high heat crystalline engineering thermoplastics. As a result, a number of applications are expected in the areas, such as electrical, automotive, films, and fibers.

RIM is a polymer process for the rapid production of complex plastic parts. The process involves the impingement of two reactive liquid components just before they are injected into a mold, the shape of the finished part. During mixing and filling the mold, the reaction mixture usually polymerizes rapidly. Once the polymerization is complete, the polymer is cooled and the part can often be demolded in < 1 min.[3a] Once the polymerization is near completion or solid enough to withstand the stresses of demolding, the part is ejected. This demolding usually occurs between 0.5–4 min, depending on the system.[3a] One of the main advantages of RIM is that it is not a very energy intensive process. The key to RIM processing is the activation of the reaction by impingement mixing of low viscosity liquids. This use of low viscosity liquids avoids the high temperatures and pressures required by conventional thermoplastic injection molding. This leads to less expensive tooling and operation, especially when producing large parts.

Very few polymerization chemistries are suitable for a RIM process and as a result typical RIM systems have been developed only for polyurethanes. The polymerization chemistry for this type of polymer is suitable for RIM, because the kinetics of the reaction are quite rapid and the polymer can be produced to high conversion within minutes. The reaction between a diisocyanate and dialcohol occurs by a "stepwise" polymerization mechanism and proceeds cleanly because no small molecule is eliminated. Quite differently, sPS is synthesized *via* a coordination polymerization mechanism. With the use of a homogeneous metallocene catalyst system, styrene can be polymerized to the syndiotactic form. Typical systems have been based on titanium centers substituted with bulky ligands such as Cp (cyclopentadienyl) and Cp* (pentamethylcyclopentadienyl) coactivated by methylaluminoxane or a trisubstituted boron derivative. The more active and temperature stable catalysts are the Cp* systems.[4–8] Since the initial discovery, other highly active systems have been discovered as the catalyst chemistry is being studied to elucidate the mechanism and active species. It has been agreed that the syndiospecific polymerization occurs by a 2,1 head-to-tail insertion similar to a Ziegler–Natta mechanism.[5] A schematic of the proposed mechanism for a $Cp^*TiMe_3/B(C_6F_5)_3$ system is shown in Figure 1. The syndiotactic configuration arises from the bulk steric hinderance of the ligand, and the phenyl–phenyl repul-

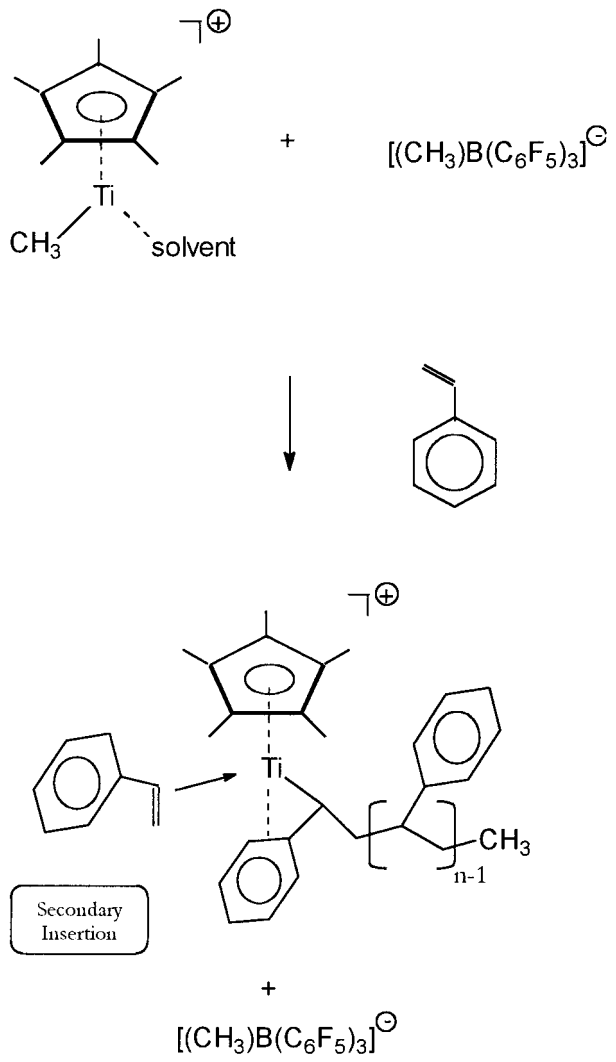

Figure 1 Metal-coordinated insertion mechanism of styrene.

sive interaction between the last inserted unit of the growing chain and the incoming monomer.

What is also very important for the aforementioned polymerization is that solid polymer plugs were formed in times of < 1 min. Thus, we have been able, in an early study, to produce highly syndiotactic polystyrene using a novel RIM process.[9] With the use of a methylaluminoxane-free $Cp^*TiMe_3/B(C_6F_5)_3$ metallocene catalyst, styrene monomer was polymerized in bulk using a minibenchscale RIM apparatus. Some of the major requirements for a nonurethane chemistry system have been outlined by Macosko.[3b] It was demonstrated that most of the requirements were achievable, such as the rapid reaction kinetics, use of low viscosity liquids for good impingement mixing, and sufficient green strength upon demolding. However, it was found at the time of demolding that only 70–80% conversion of monomer resulted, which is considerably less than what is considered necessary for a feasible process. The removal and flashing of this excess residual monomer would cause part deformation problems and brings about health/environmental concerns.

High conversions in a coordination RIM polymerization have been shown to be possible with the development of a polydicyclopentadiene developed by Hercules, Inc.[3c] With the use of a tungsten chloride catalyst and diethyaluminum chloride cocatalyst, dicyclopentadiene is polymerized to a crosslinked, noncrystalline polymer within minutes to complete conversion. Given the similarities to a dicyclopentadiene RIM formulation, the adaptation of a metallocene RIM process seems feasible. To overcome this conversion limitation, many attempts have been made by Baker and colleagues to increase the conversion by conventional and unconventional means.[9,10] Methods such as increasing the catalyst concentration by 10-fold, disrupting the crystallinity by copolymerizations with 3(4)-methylstyrene, and imparting energy to the reaction with the use of ultrasonic and neutron bombardment have all failed to increase the conversion significantly or have resulted in undesirable side effects.

Up to this point, an obvious limitation exists in achieving high conversions in this sPS RIM process. Some of the concerns that were being speculated for the nature of the conversion limitation were linked to the activity of the catalyst species, diffusion-controlled nature of this bulk polymerization, and the crystalline nature of sPS. Most of the sPS polymerizations reported in the literature have been solution polymerizations. A high concentration of toluene allows for better temperature control and helps to increase the fluidity of the reaction mixture to prevent the very high viscosities at higher conversions. For Cp* systems, it has been found that an optimum activity occurs around a temperature of 70°C.[4,11] Rising above this temperature causes appreciable catalyst deactivation and a lower temperature reduces the concentration of active species.

Polymerizing under bulk conditions can lead to uncontrollable reaction conditions with heat transfer and diffusion limitations. From a reaction engineering point of view, the bulk polymerization of styrene typically gives rise to diffusion controlled systems. Most notable are the bulk systems, such as styrene and methyl methacrylate, that exhibit the autoacceleration or Norrish–Tromsdorff phenomenon and the glass effect.[12,13] This autoacceleration effect is usually observed as a sudden increase in the reaction rate due to the reduction in termination sites. For this sPS polymerization, unlike free radical systems, no reduction in termination can occur, because coordination polymerizations have no definitive termination reactions. However, the glass effect may be of importance. Once a reaction temperature drops below the system T_g (mixture of monomer/polymer), the mobility of the polymer molecules becomes constrained and the ability for the active sites to meet monomer is reduced.

Since the discovery of sPS, there have been many studies into the nature and formation of its crystalline structure. Originally, Ishihara and colleagues[1] reported a zigzag planar structure based on X-ray diffraction data. Today, sPS has been shown to have very complex polymorphic structures dependent on the crystallization conditions. Using the nomenclature proposed by Guerra and colleagues,[4] four different crystalline forms exist. An α and β form contain planar zigzag chains (TTTT) with fiber identity periods of 5.0–5.1 Å, whereas two others, the δ and γ form contain (2/1)2s helical chains (TTGG) with fiber identity periods of 7.5–7.7 Å. Of interest to this study are the helical conformations, because they are formed through a solvent-induced crystallization process.[14–18] In particular, the δ form has been shown to form stable polymer–solvent molecular compounds. These solvent molecules are hypothesized to be housed in cavities formed by the phenyl groups between the helices. This results in helix stabilization and prevents the chains from folding, which in turn causes the

formation of a gel. Chatani and colleagues[15] and Guenet and colleagues[16,17] have demonstrated the formation of these sPS compounds for toluene and benzene. Although there is some debate on the stoichiometry and location of the trapped solvent within the helical polymer chains, it is agreed that there is sufficient space for its entrapment. Chatani and colleagues reported that up to 4 : 1 monomer/solvent is possible, based on the difficulty of removing up to 14% toluene solvent from sPS samples. Guenet has recently shown that there are loosely bound and tightly bound molecules, with the tightly bound having a stoichiometry of 1 : 1 for benzene and chloroform. Similarly, toluene has also been shown to form complexes in a 0.8 : 1 ratio of toluene units per monomer repeat unit. It is interesting to note that potential applications of sPS being used as inclusion compounds (clathrates) have been investigated.[19] Typically these clathrates mainly involve zeolites; but, helical structural polymers like sPS, that can include guest molecules, are being considered for applications for chemical separation, purification of liquids, and catalysis.

In an attempt to increase the conversion, the following study was conducted to investigate the effect of the extent of mixing, reaction time, and the mold wall temperature on the monomer conversion and final polymer properties.[20] An insight to the conversion limitation was gained, and the results will be discussed in terms of either being limited by the bulk diffusion, temperature-sensitive catalyst, or the crystalline nature of the polymer.

EXPERIMENTAL

All of the syndiospecific styrene polymerizations were conducted in a nonsolvent bulk condition using a specially constructed mini-RIM apparatus. Due to the air and moisture-sensitive nature of the metallocene compounds, all reactions were performed under inert and dry conditions.

Materials

Styrene monomer (99%; molecular weight = 104; Aldrich Chemical Co., Milwaukee, WI), inhibited with 10–15 ppm 4-*tert*-butylcatechol, was dried over calcium hydride (95%; Aldrich) and distilled under reduced pressure to remove the inhibitor and moisture. The styrene was kept dry over activated 4A molecular sieves (BDH Chemicals Ltd., Poole, Dorset, UK) under a blanket of nitrogen. To prevent any thermal polymerization, the monomer was refrigerated and stored in the dark.

Polymerizations were conducted under nitrogen (Liquid Carbonic, prepurified) that was further dried by passing through a column of dry 4A molecular sieves.

The materials for the catalyst syntheses were purchased from Aldrich and were used without further purification. η^5-Pentamethylcyclopentadienyltitaniumtrimethyl (Cp^*TiMe_3) catalyst and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) cocatalyst were synthesized in-house from literature preparations,[21,22] under purified nitrogen using standard Schlenk line techniques—a Vacuum Atmospheres glovebox and dried/deoxygenated solvents.

Methyl ethyl ketone (MEK) and methanol used in the purifications were reagent grade.

RIM Mixing Apparatus

The RIM apparatus consisted of a specially constructed glass mixhead and a polypropylene Kenics static mixer (Chemineer-Kenics) combination [Fig. 2(a)]. The impingement mixhead had injection port bore diameters of 1.4 mm and a 0.50 cm cavity diameter (8 mm, sp wall). To measure the effectiveness of the impingement mixing, an estimation of the Reynolds number (Re) was used. Macosko has outlined that a value of Re > 300 provides good impingement mixing for a RIM process based on polyurethane chemistry.[3b] A similar calculation for the system, based on 1 mL s^{-1} flowrates, the room temperature density, and viscosity of styrene and the injection port diameter resulted in a Re of $\approx 1{,}070$, which should provide sufficient mixing. To enhance the mixing from the impingement section, a 24-element 0.5 cm o.d. Kenics static mixer was also used. The Kenics mixer design consisted of a series of 180° twisted left-handed and right-handed elements aligned at 90° to complete the mixing by flow division, flow reversal, and radial mixing.

RIM Technique

A typical polymerization run was conducted as follows. All apparatus materials were dried in a vacuum oven at 60°C before use. The apparatus was assembled as diagrammed in Figure 2(b). The mixhead ports were sealed with rubber septa (8 mm o.d.; Aldrich) and fitted to the Kenics static mixer by PE tubing ($\frac{1}{4}$ inch i.d.; Fisherbrand).

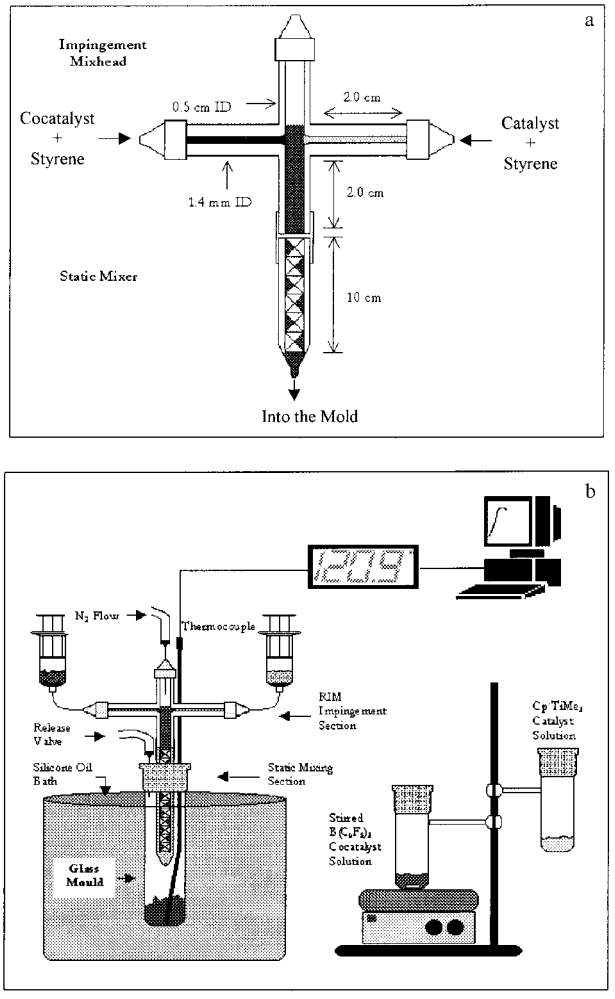

Figure 2 (a) RIM mixhead schematic. (b) RIM experimental setup.

Both the mixhead/static mixer and the thermocouple were fitted through a rubber septum (20.5 mm; Aldrich) and sealed inside a test tube mold (25 × 150 mm; Corning Glass Works, Corning, NY). After sealing the fittings with parafilm tape, the apparatus was evacuated and then backfilled with nitrogen. To provide a consistent mold wall temperature, the glass mold was submersed in a large silicone oil bath. PE/PP syringes (10 mL; Fortuna) were fitted with stainless-steel needles (PT2, 5-inch; Hamilton) and backfilled with nitrogen in a separate sealed test tube. Previously distilled styrene was removed from the refrigerator and allowed to warm to room temperature.

Both the catalyst and cocatalyst were weighed and retrieved in test tubes that were individually sealed in a Vacuum Atmospheres glovebox. In the following order, styrene was added to the Cp^*TiMe_3 to achieve a concentration of 0.241*M*. Styrene was added to the $B(C_6F_5)_3$ to achieve the same concentration along with a $\frac{1}{8}$-inch Teflon magnetic stir bar. The stir bar and stir plate were used to promote better mixing of the borane and styrene. Two milliliters of the Cp^*TiMe_3 solution was taken up, and then the needle tip was inserted into the right sealed port of the mixhead. Next, 2 mL of the $B(C_6F_5)_3$ solution was taken up and inserted into the left sealed port of the mixhead. The preparation time of the catalyst solutions was estimated to be between 45–60 s. Finally, both syringes were simultaneously depressed slowly and metered to keep the flow and impingement uniform. The material could be viewed while flowing through the mixhead, forming a black-colored complex and then passing through the Kenics mixer. In the bottom of the mold, the polymer plug solidified between 15–20 s, and it was estimated that the injection process occurred within 4 s. Due to the short solidification time, it was observed that up to 1 g of the reactant material became trapped in the mixhead, mostly in the static mixer. On average, the total time for preparation and complete injection into the mold was ~ 1 min. During the experiment, the reaction temperature was monitored by a $\frac{1}{16}$-inch type K thermocouple supplied by Omega engineering. Just before the injection of the reactant materials, a data acquisition program was initiated to record the temperature and time *via* an Omega Engineering DP-41 Temperature Meter.

Benchmark Study

To establish a well-defined benchmark condition and to test the reproducibility of the reaction procedure, four polymerizations were conducted as described with the standard catalyst recipe, room temperature reactants, and a 1-h reaction time. The results of these polymerizations were statistically tabulated as the benchmark to which all other polymerization conditions were compared.

Mixing Study

To determine whether or not the polymerizations were mixing-limited, four different mixing conditions were studied. The first was with no impingement or static mixing (liquids injected directly from the syringes into the test tube), the second with impingement mixing only, the third was the standard condition with impingement and static

mixing, and lastly, a larger chamber diameter mixhead and static mixer combination.

Reaction Time Study

To determine the effect of total reaction time, the RIM polymerizations were conducted with reaction time intervals of 2 min, 10 min, 1 h, 6 h, and 24 h.

Mold Wall Temperature Study

To determine the effect of mold temperature on the RIM polymerization, mold wall temperatures above and below room temperature were evaluated in a range from −26°C to 110°C. Room temperature polymerizations were conducted in a silicone oil bath as a heat transfer medium. Runs performed at elevated temperatures were thermostatically controlled using a Haake DC5 Temperature Controller. Runs performed at 0°C were cooled using a stirred ice-water bath. Runs performed at −20°C and −26°C were cooled using a tetrachloroethane/liquid nitrogen slush bath. Liquid nitrogen was added to a bath of tetrachloroethane and stirred to reach a temperature in the −20°C range. Both the mold and reactant styrene were also chilled before mixing of the catalyst solutions and injection into the RIM apparatus.

Analysis

To estimate the monomer conversion, the RIM polymerized plugs were powdered in a coffee grinder and then subsequently dried *in vacuo* at 80°C until a constant weight was achieved. To determine the fraction of sPS in the samples (MEK insoluble), the aPS fraction was extracted with MEK solvent for 48 h inside a Soxhlet extraction setup. The resulting MEK insoluble/soluble portions were characterized by both nuclear magnetic resonance (NMR) spectroscopy. ^{1}H NMR spectroscopy was performed on a Bruker ACF-200 spectrometer operating at 200 MHz, whereas the sPS ^{13}C NMR spectra were obtained on a Bruker CXP-200 running at 50 MHz. The polymers were dissolved in 1,1,2,2-tetrachloroethane-d_2 and run at 393K. The sPS polymer was identified by ^{1}H NMR with the characteristic triplet and multiplet in the 1–3 ppm range.[2] A measurement from ^{13}C NMR of the pentad distributions in the 145–146 ppm range was used as an indicator of the stereoregularity of the polymers.[2] High-temperature gel permeation chromatography (GPC) was conducted on a Waters 150-C GPC at 145°C. The polymer samples were dissolved in trichlorobenzene, and the GPC chromatograms were used to determine the weight average molecular weight and distribution. Melting points and crystallinity estimates were determined in a Mettler TA3000 differential scanning calorimetry (DSC). To erase the thermal history, the oven-dried ground samples were first ramped from 50–300°C at 20°C min^{-1}, followed by rapid cooling with liquid nitrogen. On the second scan at 10°C min^{-1}, the observed glass transition was noted by the change in slope in the 80–100°C region, whereas a large endothermic peak at ≈ 267°C signified the melting point. A small exothermic peak around the 150°C was also observed. This was interpreted to be the characteristic cold crystallization peak.

To estimate the degree of crystallinity of the sPS sample, the enthalpy of melting was measured by DSC. The undried polymer sample was scanned at 80°C min^{-1} in a range of 25–340°C.[23] The melting endotherm that occurred at ~ 270°C was integrated to estimate the enthalpy of melting of the crystallizable portion of the sample. This enthalpy was compared with the enthalpy of fusion of 100% crystalline sPS ($\Delta H°$ 53.2 J g^{-1})[24] to estimate the % crystallinity of the sample. Although DSC crystallinity estimates of sPS samples tend to be high due to the possibility of isothermal crystallization, this technique, developed by Kryzstowczyk and colleagues,[23] showed the results were comparable with FTIR and X-ray.

To determine the crystalline form produced during the sPS polymerization, Fourier transform (FT) infrared (FTIR) spectra analysis was conducted on an undried polymer sample. The spectra were obtained from a BOMEM MB Series IR instrument in FT mode with a resolution of 4 cm^{-1}. The sample was powdered and pressed between KBr disks before scanning between 400–4,000 cm^{-1}. To identify the sPS crystalline form, the sample was analyzed in the regions between 1,100–1,400 cm^{-1}, 800–1,000 cm^{-1}, and 400–650 cm^{-1}, and the spectra were compared with the literature spectra of Guerra and colleagues[14] depicting the differences between amorphous, δ-helical, β-zigzag, and α-zigzag structural forms.[25] A specific band at 1,222 cm^{-1} denotes a planar zigzag form (α or β). The β form can be identified by a presence of characteristic 860 cm^{-1} peak. Absence of the 1,222 cm^{-1} peaks suggests helical δ and γ forms and in the 400–650 cm^{-1} region, peaks at 500 and 570 cm^{-1} clearly depict a helical structure. The γ form spectrum looks very similar

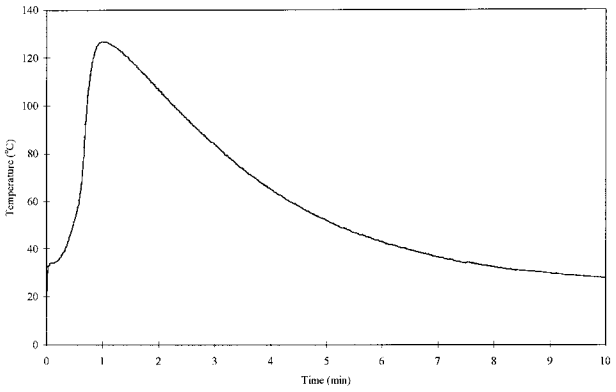

Figure 3 Typical sPS RIM reaction temperature profile.

to the δ form, except for a shift in intensities. A larger intensity for the 975 cm^{-1} peak when compared with the 965 cm^{-1} peak is indicative of the γ form.

RESULTS AND DISCUSSION

General Observations

During the initial stages of the reaction, observations of the rapid solidification and a rapid temperature rise were used as criteria for reproducibility. In dealing with the air-sensitive organometallic compounds, reproducibility was always a concern. The catalytic activity of these compounds can vary, depending on the amount of impurities inadvertently allowed into the system. These impurities can be linked to a number of sources, such as oxygen/moisture content in the atmosphere, adsorbed moisture on the glassware, and handling and transfer techniques of the catalyst materials and monomer.

A typical temperature profile of the reaction is shown in Figure 3. This rapid temperature rise, although similar to a Norrish–Tromsdorff gel effect, is probably not due to a reduction in the termination rate, as mentioned previously. Instead, this rapid temperature rise is attributed to the acceleration of the reaction rate as the temperature of the reaction mixture increases. After the peak temperature, the reaction temperature dropped rapidly back to the initial silicone oil bath temperature after 10 min. A time-weighted average for the reaction temperature over the first 2 min indicated that the temperature experienced was ~ 90°C for this profile.

Benchmark Study

To define the benchmark reproducibility and to minimize any systematic errors due to impurity buildup, the experimental run order was randomized and conducted over a period of 2 months. The four standard benchmark runs were conducted at room temperature with a 1-h reaction time, using the standard RIM mixing apparatus. The individual and averaged results are shown in Table I. After drying the ground polymer samples, it was found that the average residual monomer removed was 23.9 ± 1.3%, which corresponds to a 76.1 ± 1.3% conversion both at a 95% confidence level with 3 degrees of freedom. All other reported confidence intervals are also at the 95% level. After extraction in MEK, an average insoluble fraction was found to be 63.7 ± 2.6%. The MEK

Table I Benchmark sPS Polymerization Results

Run	Monomer Conversion[a] (%)	sPS Fraction (%)	sPS Weight Average Molecular Weight [PDI] (g mol^{-1})	aPS Weight Average Molecular Weight [PDI] (g mol^{-1}) $\times 10^{-3}$	Melting Point/ T_g (°C)	Tacticity (%)
BM #1	74.4	65.0	136 [4.0]	28 [3.7]	—	—
BM #2	76.4	62.8	167 [3.3]	16 [5.0]	267.5/85	+99
BM #3	78.2	59.5	104 [4.2]	8.3 [4.5]	—	—
BM #4	75.5	67.3	100 [3.4]	9.9 [4.6]	266/85	—
Average	76.1 ± 1.3	63.7 ± 2.6	127 [3.7]	16 [4.5]	267/85	+99

PDI = polydispersity index; BM = benchmark.
[a] Polymerization conditions: [Cp*$TiMe_3$], [$B(C_6F_5)_3$] = 0.241*M*, [styrene] = 8.3*M*, T_p = 25°C, t_p = 1 h.

insoluble fraction is considered to be the fraction of sPS as identified by ^{1}H NMR. This result was surprisingly low when compared with the toluene solution polymerizations reported in the literature that have syndiotactic fractions in the 90% range.[7,26,27] It has been reported by Wang and colleagues[7] that the borane cocatalyst alone can be a good carbocationic initiator of styrene polymerization to aPS. In a prepolymerization study, it was determined that up to 22% of low molecular aPS can be formed during the premixing stages.[20] This prepolymerization study was conducted by dissolving the borane itself in bulk styrene at a similar concentration to the study. After 1 min, followed by termination with methanol, it was found that both at 23°C and 100°C, 22% of the initial styrene monomer was converted to aPS. This amount would account for a large portion of the aPS formed during the RIM polymerization. The rest is probably due to spurious radical formation produced during the high temperature rise. Given the short length of time experienced at elevated reaction temperatures, the amount of thermal polymerization occurring was considered negligible. Adjusting the aPS fraction by taking into consideration the amount of atactic prepolymerization by the borane occurring results in aPS fractions in the 20% range. This value is still high and as described is probably due to radical propagation during the high-temperature rise.

High-temperature analysis indicated that the sPS polymer weight average molecular weight was in the 130,000 g mol^{-1} range with a polydispersity index of 3.7, whereas the aPS polymer was low molecular weight in the 8,000–30,000 g mol^{-1} range. These results suggest that more than one catalytic site is active, causing a broadening of the molecular weight. Another explanation may be a reflection of the fact that the polymer chains are being formed at the different temperatures during the reaction.

^{13}C NMR indicated that the stereoregularity of the pentad distributions were for all intensive purposes essentially 99+% syndiotactic. Correspondingly, the melting point of the sPS polymer formed was found to be ≈ 267°C from DSC analysis. Interestingly, the glass transition for the dried polymer sample was identified to be ~ 85°C, which is significantly lower than the T_g for high molecular weight aPS and pure sPS. The effect of molecular weight to decrease the T_g for low molecular weight aPS has been predicted to be 64°C.[28] Using the Fox[29] equation, the prediction of the T_g for a 64/36 sPS/aPS having component molecular weights of 127,000/16,000 g mol^{-1} would be 82°C. The cold crystallization peak was found to occur at 150°C. This is also lower than the reported 160°C maximum crystallization rate peak. This lowering of the cold crystallization peak has also been reported in the literature for aPS/sPS blends. This reduction in temperature has been explained by the interference of the atactic polymer in the sPS crystallization process, causing the formation of less perfect crystals by way of disordering the lamellae stacking in the interfibrillar regions.[30]

It has been demonstrated that the RIM benchmark polymerizations were statistically reproducible, both related to the conversion and properties of the polymer. This allows the other reaction conditions to be compared with these benchmarks to determine any significant effects.

Mixing Study

To evaluate the effect of mixing on the conversion, four different mixing conditions were studied. Two extreme cases were considered: the no impingement or static mixing condition (direct test tube addition of components) and the standard RIM mixhead/static mixer condition. To evaluate the effectiveness of the RIM impingement mixhead, runs were also performed without the Kenics static mixer and with a mixhead with a larger chamber diameter.

The effects of the four different mixing conditions on the monomer conversion levels are shown in Figure 4(a). As shown in the results, no significant effect of the mixing method on the conversion could be seen for the test tube mixing condition, impingement mixing only, and impingement/static mixing conditions. However, with the use of a larger chamber mixhead/static mixer, a slight effect was observed. The mixhead used had four times the bore diameter than that of the standard mixhead. This increase in conversion to 78% was probably due to the increased amount of interfacial contact that occurs initially within the mixhead. Although this increase in conversion is not great, it may imply that the rate of mixing is important and should be studied in the future.

Regardless, the results indicate that even test tube mixing is sufficient for this process, which is probably acceptable because mixing in a coordination polymerization is less critical than in a urethane condensation polymerization.[3d] Further separation of the polymer samples in MEK showed no change in the sPS fraction from the

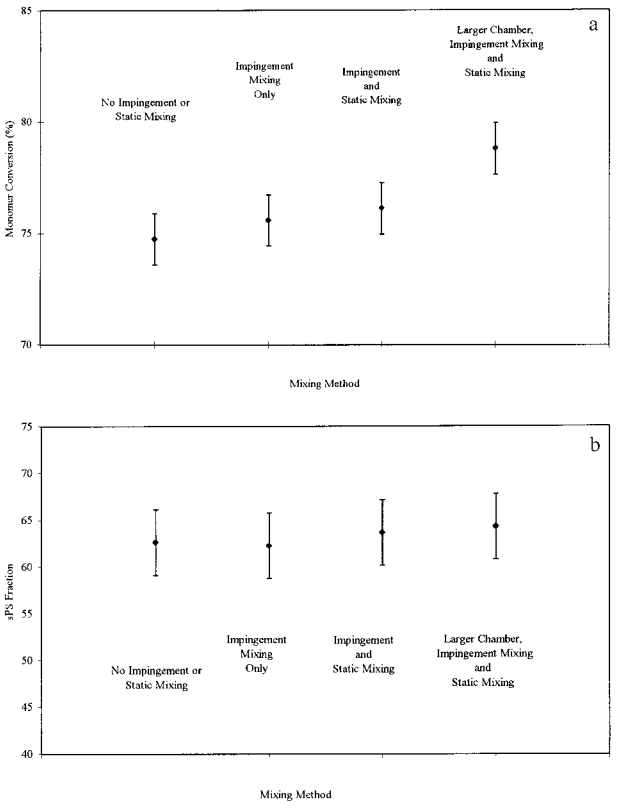

Figure 4 (a) Effect of mixing method on monomer conversion. (b) Effect of mixing method on sPS fraction.

benchmark conditions. The fractions are shown in Figure 4(b) and the lack of change suggests that the polymerization proceeds by the same mechanism for all of these runs. Therefore, it was assumed that the stereoregularity, thermal properties, and molecular weights would be similar to the benchmark runs.

Reaction Time Study

In an attempt to establish the time required to complete polymerization, reaction times were studied between 2 min and 24 h. For a RIM process, short demolding times are desired; therefore it was of great interest to estimate the conversion at 2 min. To investigate if longer polymerization times were required for higher conversions, polymerizations up to 24 h were also studied. The effect on the monomer conversion is shown in Figure 5(a). A longer polymerization does indeed result in a higher conversion of monomer. Conversions ~ 81% were achieved and are significantly higher than 1-h benchmark conversions of 76%. The results from the runs <1 h demonstrated that the reaction occurs very rapidly, and the majority of the polymerization was completed in under 2 min. Further analysis of the fraction of sPS produced with time also suggested that once the temperature and polymerization mechanism stabilizes, the sPS fraction plateaus [as shown in Fig. 5(b)].

GPC analysis of the weight average molecular weight of the sPS polymer indicated that, with longer polymerization times, a larger fraction of higher molecular weight material was formed as

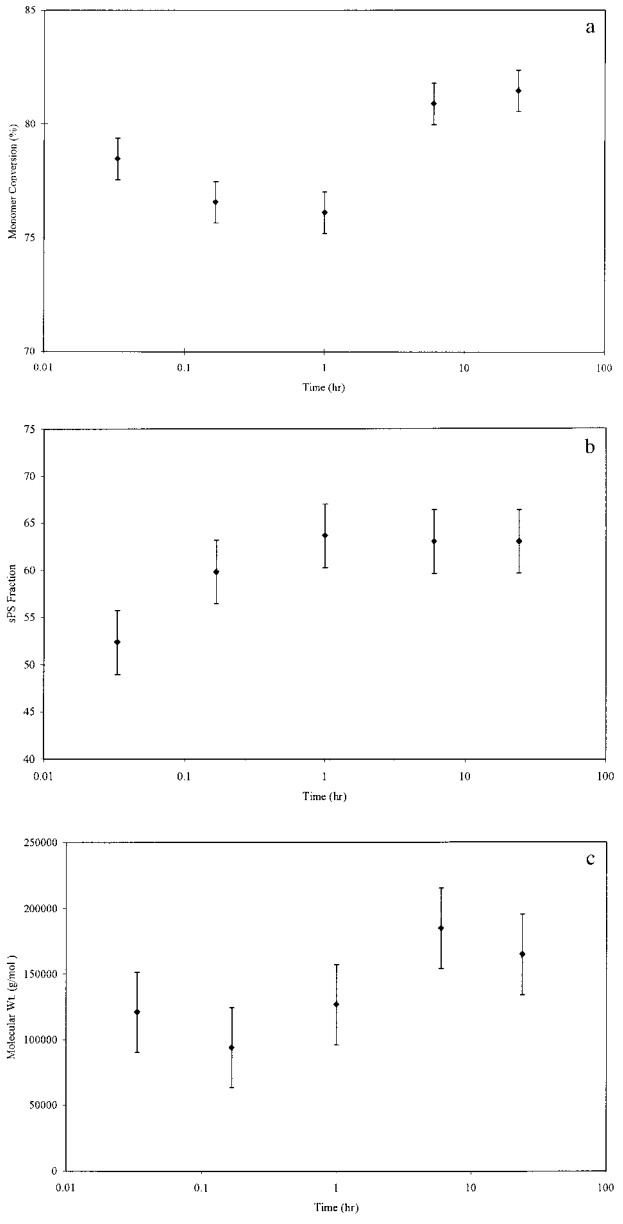

Figure 5 (a) Effect of reaction time on monomer conversion. (b) Effect of reaction time on sPS fraction. (c) Effect of reaction time on sPS weight average molecular weight.

shown in Figure 5(c). GPC analysis of the atactic polymer revealed its molecular weight to remain in the range of 10,000–30,000 g mol^{-1}.

These results are very encouraging, because it has been demonstrated that indeed the catalyst species remains active as opposed to being deactivated after experiencing a peak temperature of +120°C. This sustained catalyst activity allows for an increase in conversion and a slight increase in molecular weight.

Mold Wall Temperature Study

To determine the effect of mold wall temperature on the sPS RIM polymerization, reactions were conducted in a range between −26°C and 110°C. The motivation behind using higher temperature molds was to increase the polymer chain mobility above the system T_g to reduce any diffusion limitations of the monomer. Although increasing the temperature would increase the monomer mobility, it was also known that deactivation of the catalyst could occur more readily. In an attempt to reduce the peak temperature, lower mold temperatures were attempted in hopes of prolonging the catalyst activity. The resulting effect of varying the mold wall temperature was to either raise or lower the reaction temperature experienced by the system.

The effect of mold wall temperature on the monomer conversion is shown in Figure 6(a). At the highest mold wall temperature studied, it was found that the conversion decreased to a low of 70%. This can be attributed to the increased amount of catalyst deactivation occurring at this higher temperature. At a moderate temperature of 60°C, no change in the conversion was observed. However, the lower mold wall temperatures, between 0°C and −26°C, resulted in higher conversions of up to a maximum of 83%. At these temperatures, an increased amount of heat transfer occurred that resulted in lower reaction temperatures. Estimation of the time-weighted reaction temperature over the first 2 min resulted in an average of 71°C for the 0°C mold and 60°C for the −26°C mold. These temperatures are close to the 70°C optimum activity temperature for Cp* systems as reported by Campbell and colleagues[4] and Grassi and colleagues.[11] However, the 60°C and 110°C runs resulted in average estimated reaction temperatures of 110°C and 120°C, respectively. Further analysis of the sPS fraction produced indicated that, at both temperature extremes studied, a significant decrease in the amount of sPS was observed [Fig. 6(b)]. At 110°C, an increased amount of catalyst deactivation probably occurred, which lowered the conversion and also the amount of sPS produced. At 60°C, a slight decrease in the sPS fraction was observed, which is demonstrating that the polymerization activity was sustained during the 1 h at this temperature. At the 0°C temperature, no change in the sPS fraction was found; but, at subzero temperatures, there was found a decrease in the amount of sPS formed. This result is consistent with Wang and colleagues[7] finding that, at sub-

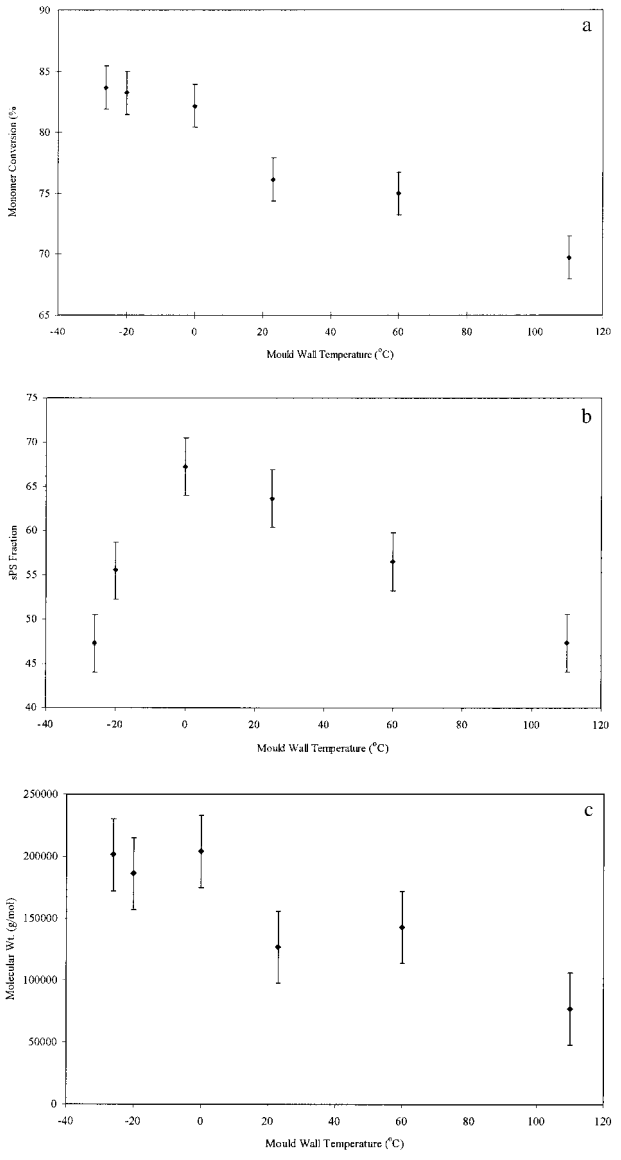

Figure 6 (a) Effect of mold wall temperature on monomer conversion. (b) Effect of mold wall temperature on sPS fraction. (c) Effect of mold wall temperature on sPS weight average molecular weight.

zero temperatures, a change in the catalytic mechanism from a Ziegler–Natta to a carbocationic mechanism takes place that increases the amount of atactic polymer formed. GPC analysis of the sPS fraction showed that at lower temperatures, higher molecular weight material was produced [Fig. 6(c)], whereas at 110°C a much lower molecular weight material was formed. These trends are readily explained by the amount of β-hydrogen elimination taking place at the higher temperatures. These results imply that Cp* catalysts are fairly resilient to β-hydrogen elimination, as shown by the lack of significant decrease until a very high temperature was used.[4–8] Melting point and stereoregularity analysis of the sPS polymer synthesized at the various temperatures showed no significant change from the benchmark conditions. These results demonstrate the robustness of the Cp^*TiMe_3 catalyst system to produce sterically pure sPS under a variety of conditions.

Whereas these results give some indication of the effect of reaction time and mold wall temperature on this reaction molding process, these results need to be reconfirmed in larger molds where heat transfer rates would be different.

Conversion Limitations of the Polymerization

In this and previous studies,[9,10] the maximum conversion achieved from comparable polymerizations ranged from 80 to 85%. Many different approaches and techniques have been used in an attempt to overcome this conversion limitation. These approaches have mostly aimed to reduce the diffusion and heat transfer limitations. The conventional method of increasing the reaction temperature to maintain the fluidity of the system while trying to avoid catalyst deactivation failed to increase the conversion. Certainly, at temperatures higher than the T_g of the system, no diffusion limitation from the glassy phase should occur. At these temperatures, questions of catalyst activity are still a concern; but, from the reaction time study, it was demonstrated that, even after passing through a +120°C peak temperature, the polymerization continued for several hours—thus resulting in an increase in the conversion to another limiting value. However, a temperature limitation was shown in the mold wall temperature study, because maintaining the mold at 110°C does result in a reduction in catalyst activity. Attempts to polymerize at a moderate temperature of 60°C showed that the catalyst species is still active and remains intact. At this temperature, the diffusion limitation, if any, should have been reduced; but, unfortunately, no increase in conversion was found. Ironically, the highest conversions were achieved at lower temperatures. At these low temperatures, the mobility of the system should be quite hindered, being well below the system T_g. Possible extension of the catalyst life or an increase in the catalyst activity may have occurred, resulting in higher conversions; but, the glass effect may have constrained the conversion. From the previous work of Liu and colleagues,[9] other studies—including increasing the catalyst concentration by 10-fold—resulted only in a slight increase in conversion. Increasing the catalyst concentration should have circumvented the diffusion limitation by providing a surplus of catalytic sites. In the initial development of this process, polymerizations were conducted with 50% toluene as a solvent for the borane cocatalyst.[9] The use of solvent in a RIM process is undesirable; but, even with its use, only 80% conversion of styrene was achieved. A diffusion limitation with a 50/50 styrene/toluene system should not exist. It was also observed sometimes that high conversions could be achieved even though polymerizations exhibited abnormally low peak temperatures. Although many other polymerization trials have been attempted, such as the use of different heat transfer mediums and mold shapes to control the temperature rise, none of them showed improvements in the conversion.[10] Based on all the current and previous findings, it is believed that the reaction conversion is neither completely diffusion limited nor temperature limited.

This leads one to seek an alternative explanation that may be related to the unique nature of the sPS polymer. It has been observed that the reaction mixture solidifies or gels within 15–30 s. No matter if the polymerization was conducted with bulk styrene or 50/50 styrene/toluene, it was observed that the viscosity increase is not gradual and occurs very suddenly. Although the rapid solidification may be the result of high molecular weight polymer, it might also be due to the rapid crystallization of the sPS polymer. Upon drying the samples, up to 1 month was required to reach a constant weight at 80°C. Intuitively, removal of solvents from amorphous polymers should not take this long. As reported in the literature, crystalline sPS is polymorphic.[14–18] Many crystalline forms can exist, depending on the conditions under which crystallization is conducted. It is possi-

ble, due to the crystalline nature of sPS, that the styrene monomer is being trapped. Referring to the helical δ-form, there is literature evidence that this form is produced *via* a solvent-induced crystallization (SINC) process and that stable solvent molecular compounds are formed. In the study of concentrated gels, these polymer–solvent complexes can house solvent molecules within the cavities formed by the adjacent phenyl groups. A stabilization occurs and the solvent prevents the chains from folding. The gels formed from this SINC process can form fibrillar and spherulitic morphologies, as is the case for toluene. This entrapment was explained for toluene by Daniel and colleagues,[17] in that the sPS chains take on helical form that minimizes the free energy of the polymer–solvent system. It was proposed that the solvent may not be trapped between the phenyl groups. Instead, the solvent molecules can exchange; and as long as an outgoing molecule is immediately replaced by an incoming molecule, it appears that the solvent is permanently housed between the phenyl groups. Representative structures of the possible entrapment of toluene and benzene solvent have been shown by Chatani and colleagues,[15] Guenet and colleagues,[16] and Daniel and colleagues.[17] Chatani and colleagues elucidated lattice parameters $a = 17.58$ Å, $b = 13.26$ Å, $c = 7.71$ Å, $\gamma = 121.2°$, and space group = $P2_1/a$. These structural parameters have been shown to be relatively unchanged in the cases for benzene and chloroform. Given that the solvent molecules are supposedly trapped along the b axis, if a sPS–styrene molecular complex were to have similar structure, there is sufficient space for a styrene molecule to be housed within a cavity. The only difference lies with the functionality of the substituent, an alkene as opposed to a methyl in the case of toluene. Therefore, it is highly possible that styrene can form a similar complex that may be binding the monomer in the helical conformation, thus preventing complete conversion.

To test this hypothesis of monomer entrapment by helical structures, FTIR analysis was conducted on the undried samples to determine which crystal structure had been formed during the polymerization. The FTIR spectrum in the regions of interest for an undried sample are shown in Figures 7(a–e). As shown in Figure 7(a) in the 400–650 cm^{-1} region, characteristic peaks of the helical conformations of sPS are detected at 500 and 570 cm^{-1}. In the 860–940 cm^{-1} region, shown in Figure 7(b), a hump/shoulder at 937 cm^{-1} is also present—thus reinforcing the presence of a helical structure. In the 1,150–1,400 cm^{-1} range shown in Figure 7(c), a small peak at 1,222 cm^{-1} indicates the presence of some planar zigzag conformation corresponding to the α or β crystalline form, although the series of small peaks between 1,320–1,375 cm^{-1} have more resemblance to the helical conformations of δ or γ crystalline form than the planar zigzag structures. From these peaks, the definite presence of a helical form and possibly some zigzag form is indicated. Further inspection of the 966 and 977 cm^{-1} peaks in Figure 7(d) show a lack of intensity difference between the two, which narrows the identification of the helical structure to the δ form. To identify the specific zigzag structure, one can examine the 820–860 cm^{-1} range closely [Figure 7(e)], which matches closely the amorphous form. The absence of a shoulder or peak at 855 cm^{-1} leaves the zigzag form identification inconclusive.

Similar analyses were conducted on the 110°, 0°, and −26°C samples, which were found to exhibit similar spectra. The only difference was with the −26°C sample, which had an absence of the 1,222 cm^{-1} peak—thus indicating no zigzag structure was formed. It should be noted that these samples contained significant fractions of amorphous aPS that may be masking some of the observed intensities. Regardless, there is evidence to support the formation of the δ form, suggesting that SINC may take place during the polymerization. This δ form has only been reported during the formation of sPS gels and is unreported for bulk polymerized material. Given that this δ crystal form is present, the next question would be whether or not there was sufficient crystallinity to trap the residual monomer. Crystallinity estimations from DSC analysis based on the enthalpy of sample melting, compared with that of a 100% crystalline sPS, are shown in Table II. The scans were performed at a rate of 80°C min^{-1} to avoid the α,β zigzag transitions and any cold crystallization. This technique was reported by Krzystowczyk and colleagues[23] and confirmed to be comparable with estimates of crystallinity by X-ray and FTIR. Crystallinity estimations by X-ray were also performed; but, due to the presence of a high fraction of aPS, it was difficult to deconvolute the resulting amorphous-like diffraction patterns. FTIR was also considered, but there was difficulty in preparing samples with uniform thickness without altering the original crystallinity. For the DSC runs used to estimate the crystallinity,

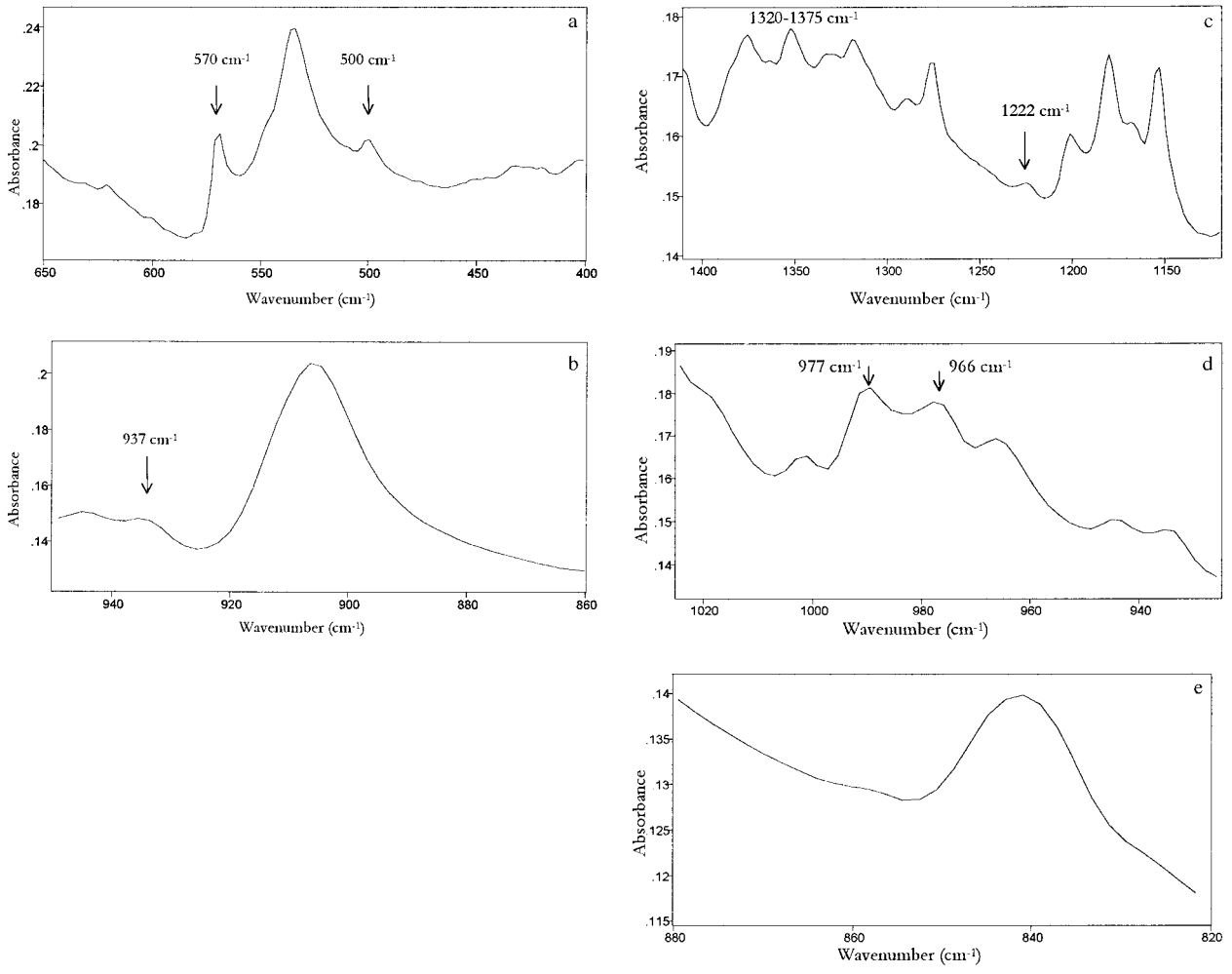

Figure 7 (a) FTIR—identification of the sPS helical forms in the 400–650 cm^{-1} region. (b) FTIR—identification of the sPS helical forms in the 860–940 cm^{-1} region. (c) FTIR—suggested presence of zigzag forms in the 1,150–1,400 cm^{-1} region. (d) FTIR—distinguishing the δ form from the γ form in the 940–1020 cm^{-1} region. (e) FTIR—identification of the amorphous form in the 820–860 cm^{-1} region.

a broad styrene evaporation peak was observed, but no cold crystallization peak. A calculation based on the polymer yield, the conversion, sPS fraction, and the estimated crystallinity can indicate the amount of crystalline sPS polymer. If styrene monomer is trapped by the sPS helical polymer in a 0.8 toluene units per monomer unit, as determined by Daniel and colleagues, calculations predicting the monomer conversion are comparable.[17] These predictions are shown in Table II and predicted conversions ~ 73% have been calculated. The values calculated are close to the experimental values, which makes the hypothesis of the entrapment of styrene monomer within sPS's helical chains highly plausible. Further investigations are underway to isolate whether or not this is in fact the case.

After all of the investigations into improving the monomer conversion of the RIM sPS polymerization, a reasonable explanation to the conversion limitation has been found. All of the attempts of adjusting the reaction conditions to improve the monomer mobility or maintaining the catalyst activity failed to increase the conversion significantly. This suggests that the polymerization is neither diffusion-limited nor temperature-limited. Instead, it is believed that SINC is occurring by trapping the monomer within sPS's helical chains. It is this housing of monomer within cavities formed by the phenyl groups that may be causing the polymerization to cease prematurely before complete conversion can be reached.

Table II Predicted Conversion Estimates for Monomer Entrapment within sPS Helical Chains

	Experimental Values						Predicted Values		
Sample Description	Conversion (%) A	Wet Polymer Yield (g) B	aPS/sPS Polymer (g) C	sPS Fraction (%) D	sPS Polymer (g) E	Crystallinity (%) F	Calculated Trapped Monomer (g) G	Wet Polymer Yield (g) H	Predicted Conversion (%) I
BM #3	78.2	2.78	2.17	59.5	1.29	79.1	0.82	2.99	72.6
BM #4	75.5	2.79	2.11	67.3	1.42	67.8	0.77	2.88	73.3
0°C	80.9	2.67	2.16	67.3	1.45	70.3	0.82	2.98	72.5

BM = benchmark.

Columns A, B, D, and F are from measured values; column C equals A × B and is the amount of dried polymer; column E equals C × D and is the amount of crystallizable sPS polymer; column G equals (E × F)/100 × 0.8—this is the amount of monomer trapped within the sPS crystalline chains, calculated by the crystallizable amount of sPS times the hypothetical monomer/sPS mer unit entrapment ratio of 0.8 : 1 as proposed by Daniel and colleagues[17] for toluene/sPS; column H equals C + G and is the dried polymer plus the predicted amount of entrapped monomer; column I equals C/H × 100% and is the hypothetical conversion of experimental dried polymer yield, compared with the predicted polymer yield (including trapped monomer).

CONCLUSIONS

In general, it was found that—by varying the extent of mixing, reaction time, and mold wall temperature—only a maximum of 81% conversion was achieved. Under the bulk conditions, it was discovered that the majority of the reaction was complete after 2 min and that the $Cp^*TiMe_3/B(C_6F_5)_3$ catalyst system was fairly robust in producing sPS polymer under the variety of conditions investigated. Lower mold wall temperatures increased the conversion; but, at both temperature extremes studied, the polymer properties deteriorated. A conversion limitation in the sPS polymerization is believed to exist and inherent to the nature of this semicrystalline polymer. FTIR investigations showed that the sPS polymer chains adopt a helical conformation during the polymerization, suggesting that SINC is occurring. DSC results and calculations indicate that the polymer produced has sufficient crystallinity to account for the entrapped monomer. It is believed that, during this SINC process, styrene monomer is being trapped within the crystalline chains that is preventing complete conversion of the sPS polymerization.

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