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# Effect of Sulfonation on the Crystallization Behaviour of Syndiotactic Polystyrene

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**Summary:** Syndiotactic Polystyrene (sPS) was sulfonated to different levels in a mixture of 1,1,2–trichloroethane and chloroform. Sulfonation levels were determined by nonaqueous titrations using phenolphthalein indicator. Thermal properties of sulfonated sPS (SsPS) ionomers depend on the sulfonation level. Incorporation of sulfonic acid groups in to the syndiotactic polystyrene backbone was found to affect the crystallization behavior of sPS. DSC data indicated that the melting temperature ($T_m$), heat of fusion, crystallization temperature ($T_c$), crystallization rate and degree of crystallization were lowered by the incorporation of sulfonic acid group on the syndiotactic polystyrene backbone. Thermal and FTIR data indicated that the sulfonic groups did not enter into the crystal lattice but remained in the amorphous phase.

**Keywords:** crystallization; functionalization; infrared spectroscopy; sulfonation; syndiotactic polystyrene

## Introduction

Highly stereoregular syndiotactic polystyrene has attracted much interest from the research community due to its high melting point, rapid crystallization rate, low density, excellent chemical resistance, enhanced mechanical properties and complex polymorphism.[1–5] It is used in automotive, electronic and packaging industries. However, it shows poor impact, tear resistance and low surface energy. Absence of polar groups restricts end uses like, adhesion to substrates and compatibility with polar polymers (i.e. nylons etc.). Therefore, modification of sPS is of interest and functionalization or grafting a polar group on sPS backbone is reported to address the above problems.[6,7]

Crystallization properties of sPS are strongly influenced by the incorporation of small quantities of ionic groups along the polymer backbone.[8] Even small amount of ionic groups show marked effect on polymer properties, for example, increase in modulus, melt and solution viscosity, glass transition temperature, hygroscopicity and decrease in melting point.[9]

Thermal crystallization and melting behavior of sPS can be modified by slight sulfonation of the styrene. Moore and coworkers[8,10] showed that sulfonation significantly reduces melting temperature, degree of crystallinity and the rate of crystallization. Neutralized SsPS ionomers containing alkali metal counter ion was found to have a significant effect on the thermal properties, for example, decrease in melting temperature, crystallization temperature and glass transition temperature. These changes are attributed to the rejection of sulfonated styrene from the crystal lattice. However, the glass transition temperature is shown to increase with increasing sulfonation level. Due to the presence of long-range strong electrostatic interactions and large size in comparison to nonpolar units, it is generally accepted that the pendant ionic groups interact or associate to form ion-rich regions in the nonpolar polymer matrix.[11]

The impetus for the present work came from the fact that sPS in the semi-crystalline form shows complex polymorphism. The nature of the polymorphism depends

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on the conditions of crystallization. It has been shown that sPS has four polymorphic forms, namely α, β, γ and δ. α and β forms, both containing planar zigzag chains having T4 all trans conformation, can be obtained from the melt or glassy state of sPS under different thermal crystallization conditions.[1–4] In γ and δ forms, the chains have T2G2 helical conformation and are formed under conditions where solvents are used for crystallization.[12–15] Another important aspect of sPS is that in gel state it forms fibrillar network.[16] In the fibrillar network sPS crystallizes in to δ form, which is nanoporous in nature and includes solvent[17,18] in the lattice. We modified sPS by sulfonation of the phenyl ring, hoping that such modification will have effect on the fibrillar network. In this paper we presented the initial data on the crystallization behaviour of sulfonated sPS.

## Experimental

Syndiotactic polystyrene was kindly supplied by DOW Chemicals. The weight average molecular weight was 2,75,000 and the melt index was 4.3. 1,1,2-Trichloroethane (TCE) (Aldrich), chloroform (Merck) and other reagents were of analytical reagent grade and were used as received.

Sulfonation of sPS was carried out according to the procedure followed by Li et al.[9] In a 1 L round bottom flask syndiotactic polystyrene (6.5 g) and TCE/chloroform (60/40, v/v) mixture (500 mL) were stirred at reflux temperature (ca. 115 °C) until all sPS dissolved. The solution was cooled to 70 °C and freshly prepared acetyl sulfate solution was added under vigorous stirring and stirring was continued for 3 h. The amount of acetyl sulfate required was determined by the desired degree of sulfonation. Ethanol (10 mL) was added to arrest the reaction and the polymer was precipitated by pouring the solution in to diethyl ether (2 L) and filtered. It was washed with hot distilled water and then dried in a vacuum oven at 70 °C for 24 h. The polymer was redissolved in TCE and precipitated in excess of diethyl ether, filtered and dried in a vacuum oven at 70 °C for 24 h. The degree of sulfonation was determined by nonaqueous titrations in a 95/5 (v/v) mixture of 1,2, 4-trichlorobenzene and ethanol using ethanolic KOH or NaOH titrant to phenolphthalein end point. The titrant was calibrated using benzoic acid standard. All titrations were carried out at 70 °C.

Room temperature and high temperature infrared spectra of these samples were taken using Perkin-Elmer FTIR Spectrometer (model: Spectrum GX) with DTGS detector at a resolution of 2 $cm^{-1}$ in the range of 400 to 4500 $cm^{-1}$. A total of 32 scans were used for signal averaging. Mounting the sample in the Mettler Toledo FP82HT hot stage and placing it in the sample compartment of the FTIR gave high temperature spectra. The sample, in the form of amorphous film was heated at the rate of 5 °C/min. Spectra were collected while the sample temperature was hold constant.

Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker (A C 200 MHz Spectrometry) in $CDCl_3$ and TFA mixture with tetramethylsilane (TMS) as an internal standard.

Thermal properties of the samples were analyzed by TA Instruments (modal: Q10) differential scanning calorimeter with a built in mass flow controller and an intra cooler for operation below ambient temperature. Samples were heated/cooled at the rate of 10 °C/min. The calorimeter was calibrated using standard protocols. The sample weight was maintained approximately at 5 mg for all the experiments.

***Table 1.***
Sulfonation levels of SsPS.

| Sample | Sulfonation level (mole%) |
|---|---|
| SsPS – 1 | 0.5 |
| SsPS – 2 | 2.0 |
| SsPS – 3 | 4.2 |
| SsPS – 4 | 5.0 |
| SsPS – 5 | 10.5 |

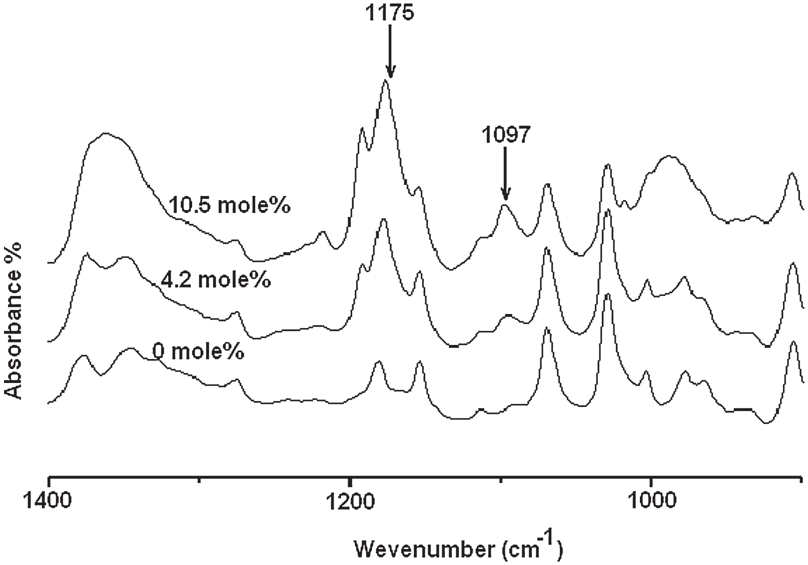

***Figure 1.***
FTIR spectra of sPS and SsPS samples.

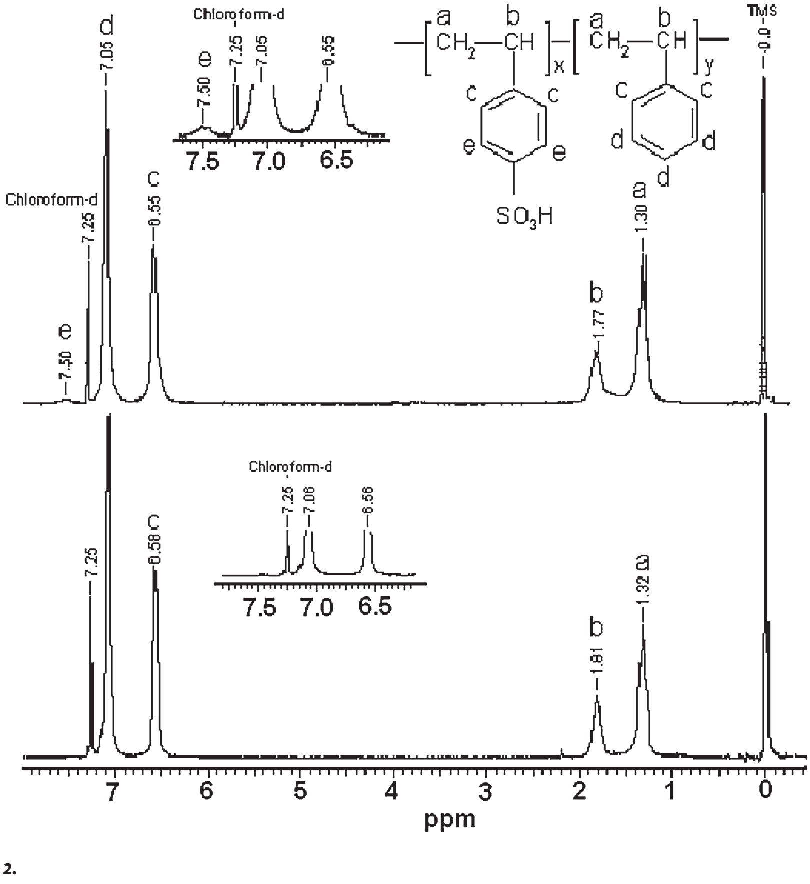

***Figure 2.***
$^1$H-NMR spectrum (CDCl$_3$+TFA) of sPS and SsPS (10.5 mol %).

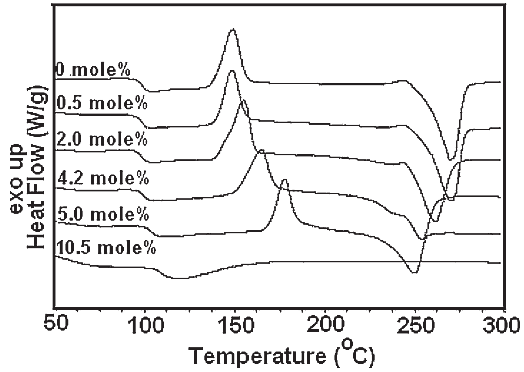

*Figure 3.*
DSC thermogram of SsPS amorphous samples.

## Results and Discussions

### Degree of Sulfonation

Syndiotactic polystyrene was sulfonated to different levels (i.e., 0.5, 2.0, 4.2, 5.0 and 10.5 mole%). The sulfonation procedure followed in the present work is according to the procedure by Li et al.[9] and is a modified procedure of Moore and coworkers.[8,10] Alkali salts of sPS (i.e., NaSsPS, KSsPS, etc.) have also been prepared by fully neutralizing the sulfonic acid groups with respective hydroxides. The degree of sulfonation was determined by nonaqueous titrations and the values are given in Table 1.

FTIR spectra of sPS and SsPS samples containing 4.2 and 10.5 mole% sulfonic acid group are shown in Figure 1. The bands at 1097 cm$^{-1}$ and 1175 cm$^{-1}$ are observed only for sulfonated samples and sPS sample does not show these bands. The band at about 1097 cm$^{-1}$ is attributed to the in-plane skeletal vibrations of the disubstituted benzene rings. The band at 1174 cm$^{-1}$ is assigned to symmetric stretching vibration of sulfonic acid group in polystyrene.[10] The presence of these bands in the sulfonated sample provides evidence of sulfonation.

Figure 2 compares the $^{1}$H-NMR spectra of sulfonated sPS (10.5 mole%) with that of

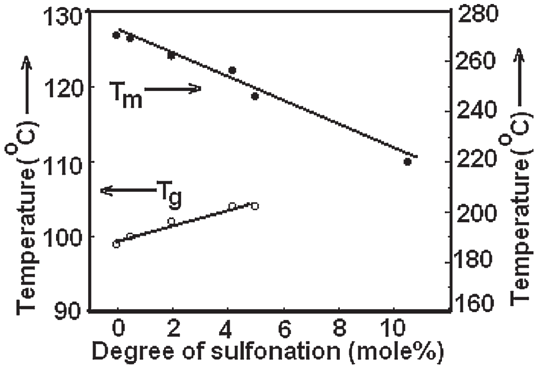

*Figure 4.*
$T_g$ and $T_m$ with sulfonation level.

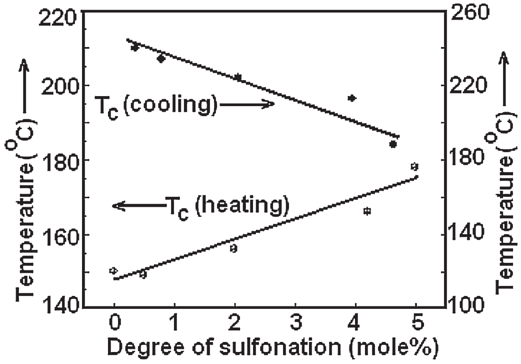

***Figure 5.***
Crystallization on heating and cooling.

neat sPS. The spectra exhibit peaks at about 1.3 ppm for $CH_2$ (a) and 1.8 ppm for CH (b) protons. The *ortho*-protons (c) appear at 6.5 ppm. The *meta* and *para*-protons (d) of the unsubstituted aromatic ring appear at about 7.0 ppm. The *meta*-protons (e) of the substituted aromatic ring appear at about 7.5 ppm [7,19] for the sulfonated sample but is absent in the sPS spectrum.

### Thermal Analysis

Thermograms obtained on heating amorphous SsPSsamples in DSC are shown in Figure 3. All samples except the sample with highest degree of sulfonation exhibit well defined glass transition temperature, cold crystallization temperature and finally the melting temperature. The sample having 10.5% sulfonation level does not crystallize on heating but clearly show glass transition temperature. Figure 4 and Table 2 shows the variation of glass transition and melting temperatures with sulfonation.

***Table 2.***
Summary of DSC data for SsPS

| Sulfonation level | $T_g$ | $T_m$ | ΔH | $T_c$ | ΔH |
|---|---|---|---|---|---|
| Mole% | °C | °C | g/J | °C | g/J |
| 0 | 99 | 270 | 35.7 | 240 | 27.2 |
| 0.5 | 100 | 269 | 34.8 | 234 | 23.6 |
| 2.0 | 102 | 263 | 33.9 | 224 | 24.3 |
| 4.2 | 104 | 259 | 27.2 | 213 | 21.6 |
| 5.0 | 104 | 249 | 19.4 | 188 | 10.1 |
| 10.5 | 110 | — | — | — | — |

Figure 5 and Table 2 shows the dependence of the heat of crystallization and heat of fusion with sulfonation. The glass transition temperature shows a linear increase in $T_g$ with increase in sulfonation indicating that the chain flexibity is decreased with the increasing $-SO_3H$ content in the chain. The loss in the flexibility of chain is also reflected in the crystallization behaviour of the sample.

The melt crystallization temperature decreases with increasing sulfonation. Along with the decrease in the crystallization temperature, the heat of crystallization also decreases indicating that the crystallizability

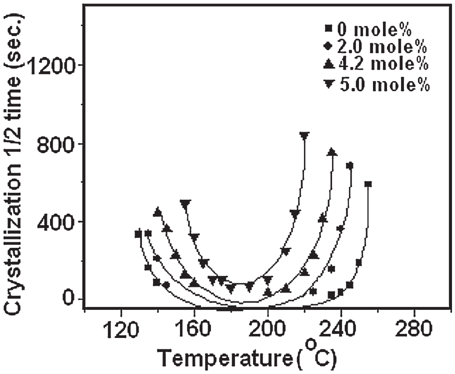

***Figure 6.***
Isothermal crystallization of SsPS.

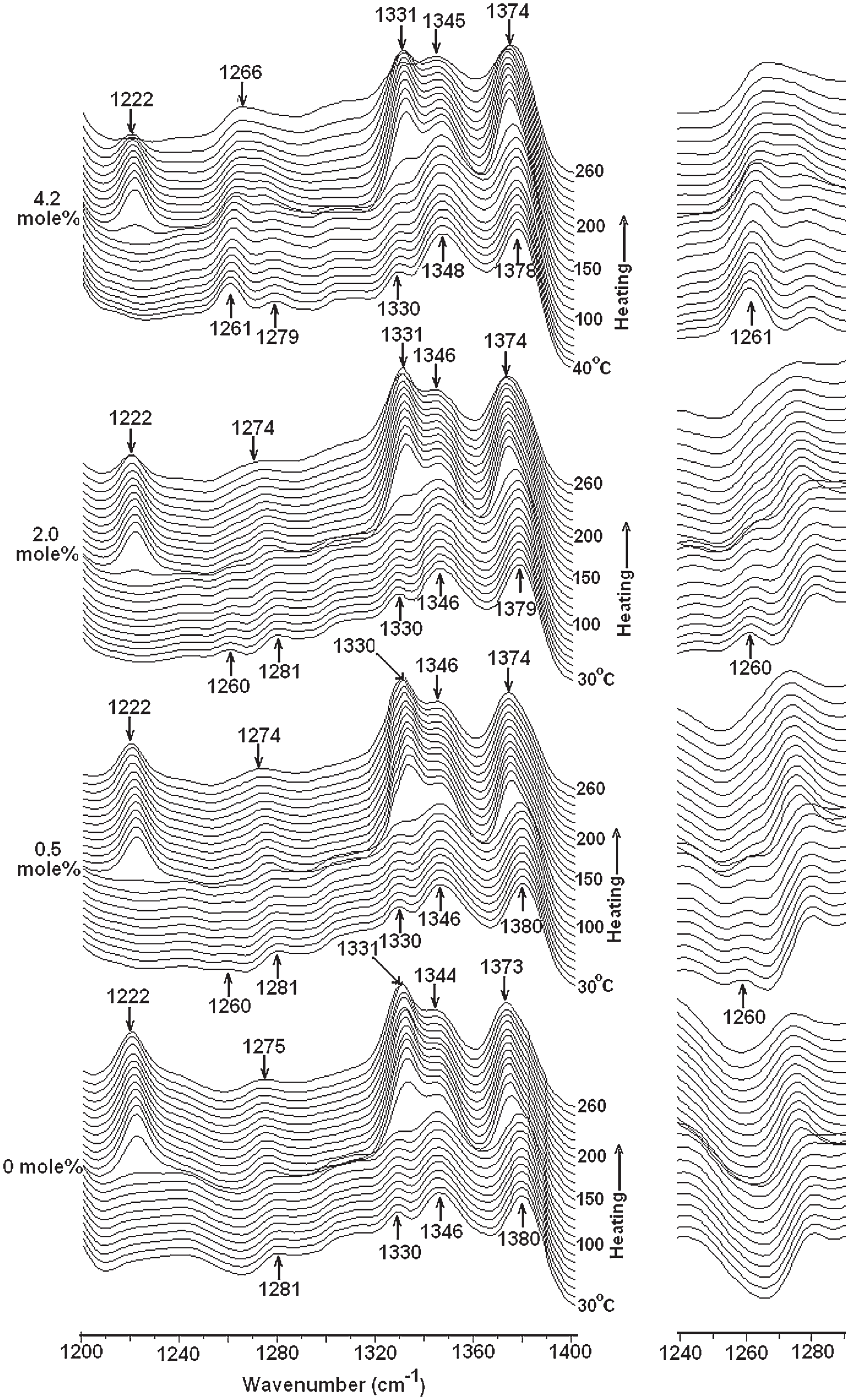

***Figure 7.***
Variable temperature FTIR spectra of SsPS.

decreases rapidly with increase in sulfonation; sample sulfonated to 10.5% does not crystallize at all. The melting temperature and heat of fusion also decreases with increasing temperature. The decrease in melting temperature indicates that the lamellar thickness decreases with increasing sulfonation levels. These results indicate that sulfonate groups are excluded from the lattice. The sequence of unsulfonated sections in the chain decreases with increasing sulfonation leading to a decrease in the lamellar thickness.

Figure 6 shows the dependence of crystallization half time on crystallization temperature. All the samples show typical inverted bell shaped curves and the effect of sulfonation is seen in the crystallization half times. The temperature range in which the samples can be crystallized decreases with increase in the sulfonation levels. One interesting aspect is that maximum crystallization rate temperature shifts to lower temperature with increasing sulfonation level.

Figure 7 shows the spectra in the region 1200 to 1400 $\text{cm}^{-1}$ during heating. The amorphous sPS and SsPS samples show bands at 1281, 1330, 1346 and 1380 $\text{cm}^{-1}$. On heating sPS crystallizes at about 130 °C and the band due to extended chain conformation (4T) appears at 1222 $\text{cm}^{-1}$. Also the bands at 1330 and 1380 $\text{cm}^{-1}$ shift to 1331 and 1373 $\text{cm}^{-1}$, respectively, and show sudden increase in absorbance. Sulfonation does not change the position of these bands but the appearance occurs at higher temperatures with increasing sulfonation level. The invariance of the band position indicates that the sulfonate groups are not included in the crystal lattice. However, the effect of sulfonation is seen in the spectra. The band at 1260 $\text{cm}^{-1}$ may be assigned to sulfonation because this peak does not appear for the sPS sample but is first seen in the 0.5% sulfonated sample and the peak absorbance increases with increasing sulfonation level. The band also shows a small change in absorbance and peak position after crystallization.

## Conclusion

sPS can be sulfonated and sulfonation influences the crystallization behavior of sPS. Melt crystallization, melting temperature and heat of fusion decrease with increasing sulfonation levels. These results indicate that the sulfonate groups do not enter into the crystalline lattice. The band at 1260 $\text{cm}^{-1}$ in the FTIR spectra is identified to arise from sulfonation.

[1] E.B. Woo, Y.S. Sun, and M.L. Lee, *Polymer* **1999**, *40*, 4425.

[2] V. Vittoria, A.R. Filho, F. De Candia, *J. Macromol. Sci. – Phys.* **1990**, *B29*(*4*), 411.

[3] S. Cimmino, E. Di Pace, E. Martuscelli, C. Silvestre, *Polymer* **1991**, *32*, 1080.

[4] C. De Rosa, M. Rapacciuolo, G. GuerraV. Petraccone, *Polymer* **1992**, *33*, 1423.

[5] E. Bhoje Gowd, S. Smitha Nair, C. Ramesh, *Macromolecules* **2002**, *35*, 8509.

[6] G. Yong, H.M. Li, *Polym. Int.* **2004**, *53*, 1436.

[7] A. Molner, A. Eisenberg, *Polym. Eng. and Sci.* **1992**, *32*, 1665.

[8] E.B. Orler, R.B. Moore, *Macromolecules* **1994**, *27*, 4774.

[9] H.M. Li, J.C. Liu, F.M. Zhu, S.A. Lin, *Polym. Int.* **2001**, *50*, 421.

[10] E.B. Orler, D.J. Yontz, R.B. Moore, *Macromolecules* **1993**, *26*, 5157.

[11] Z. Su, X. Li, S.L. Hsu, *Macromolecules* **1994**, *27*, 287.

[12] G. Guerra, E. Vitagliano, C. De Rosa, V. Petraccone V. Vittoria, *Macromolecules* **1990**, *23*, 1539.

[13] S. Rastogi, J.G.P. Goossens, P.J. Lemstra, *Macromolecules* **1998**, *31*, 2983.

[14] A. Immirzi, F. De Candia, P. Iannelli, A. Zambelli, V. Vittoria, *Makromol. Chem. Rapid Commun.* **1988**, *9*, 761.

[15] V. Vittoria, F. De Candia, P. Iannelli, A. Immirzi, *Makromol. Chem. Rapid Commun.* **1988**, *9*, 765.

[16] B. Ray, S. Elhasri, A. Thierry, P. Marie, J. M., Guenet, *Macromolecules* **2002**, *35*, 9730.

[17] C. Manfredi, M.A. Del Nobile, G. Mensitieri, G. Guerra. M.L. Rapacciuolo, *Polym Sci., Polym Phys. Ed.* **1997**, *35*, 133.

[18] G. Guerra, G. Milano, V. Venditto, P. Musto, C. De Rosa. L. Cavallo, Chem. Mater. **2000**, *12*, 363.

[19] A.J.F. Carvalho, A.J.S. Curvelo, *Macromolecules* **2003**, *36*, 5304.