 DOI: 10.1002/masy.201150507

Physical Gels of a Syndiotactic Polystyrene Derivative with a Large Side-Chain Group

Tomohiro Sago,[1] *Tomokatsu Tokami,*[2] *Hideyuki Itagaki,**[1,2] *Nobuhide Ishihara,*[3] *Christina Canter,*[4] *Jean-Michel Guenet*[4]

Summary: Gelation of syndiotactic poly(p-*tert*-butylstyrene) (sPTBS), a syndiotactic polystyrene (sPS) derivative having a larger side-chain group, was first examined with several solvents. The temperature-concentration phase diagram of sPTBS/*trans*-decalin gel clearly exhibited that sPTBS formed a polymer-solvent molecular compound with a ratio of 2.7 *trans*-decalin per one monomer unit. Our polarized fluorescence technique demonstrated that there appeared to exist more spacious free volume among sPTBS chains than sPS in a gel state. A cause determining the morphology of sPTBS with organic solvents was discussed in the present paper.

Keywords: fluorescence depolarization method; free volume; physical gels; polymer-solvent molecular compounds; syndiotactic poly(*p-tert*-butyl)styrene; syndiotactic polystyrene

Introduction

Syndiotactic polystyrene (sPS), which was first synthesized in 1986 by using metallocene catalyst,[1] is known to have a complex polymorphic behavior.[2–4] It has two stable conformations of polymer chain, all trans zigzag conformation and 2_1 helical conformation. Nonsolvated crystalline forms α and β consist of all trans conformation, while the other crystalline forms γ, δ and ε consist of 2_1 helical conformation. In particular, the δ and ε forms are quite interesting because they have cavities inside in spite of a crystalline form. They can cocrystallize with some organic molecules and host a functional guest molecule.[5] We have claimed that the size of the free volume between the polymer chains in gel form is a cause to produce a crystalline form with a cavity in sPS solids.[6] We thought that a syndiotactic polymer having a larger free volume among its polymer chains when it was aggregated would be able to host a larger guest molecule in its crystalline form. Therefore we have started with a study on an sPS derivative with a large side-chain group that is expected to have a larger free volume among its aggregated region. Our final aim is to obtain a film where cocryatalline region with a large functional guest molecule is highly orientated all over the film.

Then, syndiotactic poly(*p-tert*-buthylstyrene) (sPTBS) having a bulky side-chain was synthesized and examined in the present paper. We thought sPTBS was also able to produce a crystalline structure with a more spacious cavity than sPS does. The present study is the first step to know the physical properties of this new polymer, sPTBS. Because we believe that the information on gelation of sPTBS with some organic solvents should be related to the formation of its cocrystalline form together with the information on whether there exists free volume among sPTBS chains when they are aggregated, we started with the research on gelation process of

[1] Department of Chemistry, Graduate School of Science and Technology, Shizuoka University
[2] Department of Chemistry, School of Education, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan
Fax: +81-54-237-3354;
Email: edhitag@ipc.shizuoka.ac.jp
[3] Chemical Research Laboratory, Idemitsu Kosan Co., Ltd., 1-1 Anesaki-kaigan, Ichihara, Chiba 299-0193, Japan
[4] Institut Charles Sadron, CNRS UPR22, 23 rue du Loess, BP 84047, F-67083 Strasbourg Cedex2, France

sPTBS. We tried to prepare physical gels of sPTBS by changing solvents and observed morphologies of sPTBS gels/solutions by using scanning electron microscope (SEM). Moreover, we applied our original method using polarized fluorescence to sPTBS gel system as same as the case of other stereoregular polystyrene gels.[7–9] We try to show in this paper that molecular size and molecular shape of solvent compounds are dependent on the morphology of sPTBS in gels/solutions and on whether it forms a gel or not.

Experimental Part

Materials

SPTBS was prepared by the same manner described in ref.[10] and purified through repeated precipitation by dropping chloroform solution of SPTBS into methanol. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 145 °C was found to be $M_w = 2.24 \times 10^5$ with the polydispersity index, $M_w/M_n = 4.7$. ^{13}C nuclear magnetic resonance characterization of sPTBS in deuterated trichlorobenzene and benzene at 130 °C using JEOL Lamda 500 showed that the content of rrrrr was 99%. SPS was supplied by Idemitsu Kosan Co. Ltd. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic polystyrene triads was over 99%. The weight-average molar masses obtained by gel permeation chromatography (GPC) were found to be $M_w = 1.5 \times 10^5$ with the polydispersity index $M_w/M_n = 1.9$.

Method

Fluorescence spectra, fluorescence excitation spectra, and fluorescence polarization spectra were measured at 25 °C on a Hitachi F-4500 spectrofluorometer. Fluorescence measurements for the gels were carried out in a quartz cell with an optical path length of 1 mm for their aerated solutions. A cell and a film on a quartz disk were set at 45° to the exciting beam. Regarding measurements of fluorescence anisotropy, a Hitachi automatic polarizer was attached to a Hitachi F-4500 spectrofluorometer: the anisotropic values were determined by measuring values for 100 sec at some wavelengths more than three times and averaging them. Naphthalene (NP), 1,5-dimethylnaphthalene (DMNP), and anthracene (ANT) were used as fluorescent guest molecules. Excitation wavelengths were 280 nm for NP, 290 nm for DMNP and 342 nm for ANT. Scanning electron microscopy pictures were obtained using a JEOL JSM-6300 at Center for Instrumental Analysis of Shizuoka University. The thermal behavior of gels was investigated by means of a Perkin–Elmer DSC 7. Pieces of gel prepared beforehand in test tube were introduced into ''volatile sample'' pans that were hermetically sealed.

Results and Discussion

Morphology of sPTBS in Some Organic Solvents

SPTBS was found to form a physical gel with some organic solvents such as *trans*-decalin, L-menthol, and chlorobenzene. However, most other solutions of sPTBS rather turned out to show a sort of paste state or sherbet state that cannot be defined as a gel form. Figure 1 shows the morphology of freeze-dried sPTBS/organic solvents by using scanning electron microscope (SEM). The sPTBS gels/solutions after drying highlighted the occurrence of two types of morphology that should correspond to the macroscopic appearance: fibril structure for *trans*-decalin, L-menthol, and chlorobenzene, and lamellar/spherulitic structure for THF, D-limonene, citral, *cis*-jasmone and *cis*-decalin. The former solvents producing fibril structure gave rise to transparent gels, whereas the latter solvents produced paste-like or sherbet-like states of sPTBS.

This perfectly corresponds to the morphologies of sPS/organic solvents. Figure 2 shows two examples of morphol-

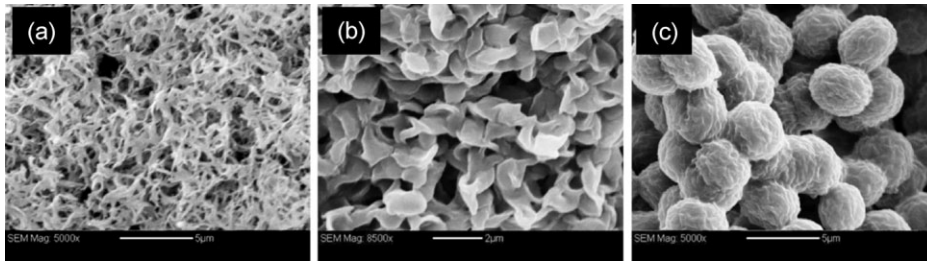

Figure 1.
SEM pictures of freeze-dried sPTBS/organic solvents. The morphology is of (a) fibril structure (*trans*-decalin), (b) lamellar structure (citral), and (c) spherulitic structure (*cis*-jasmone).

ogies, i.e., fibril structure and lamellar/spherulitic structure. The patterns of the morphology would be the same between sPS and sPTBS. However, this does not mean that the same organic solvent exhibits the same morphology with sPS and sPTBS. For instance, L-menthol produced fibril structure with sPTBS, while it produced lamellar/spherulitic structure with sPS as shown in Figure 2.

As is already known, the formation of the lamellar/spherulitic structure is quite natural because stereoregular polymer chains are ready to be folded. However, if solvent molecules can stay among side-chains and stabilizes linear fibril structure, folding of polymer chains are restricted more or less, resulting that fibril structures of polymer chains urge the formation of three-dimensional network as shown in Figure 1(a) and 2(a). Thus, the morphology is assumed to be greatly related to free volume among polymer chains aggregated in solutions and molecular size of solvent. Roughly speaking, if solvent molecules are small enough compared with the free volume among sPS or sPTBS chains that are aggregated and if it is settled down there, fibril structure is assumed to be produced in great quantities, forming a stable gel. In order to prove this, we tried to get information on whether sPTBS can form a polymer-solvent molecular compound in a solvent forming a gel, and also on the free volume among sPTBS polymer chains in a gel.

Formation of a Polymer-Solvent Molecular Compound in sPTBS/*Trans*-Decalin

We chose *trans*-decalin as a solvent and measured the thermal behavior of the gels in detail by DSC. The gelation process of sPTBS/*trans*-decalin was found to be very slow in contrast with sPS. The thermal motion of the *tert*-butyl group of side-chain appears to hinder the quick orientation of polymer chain and rapid formation of regular structure. Thus, we annealed all

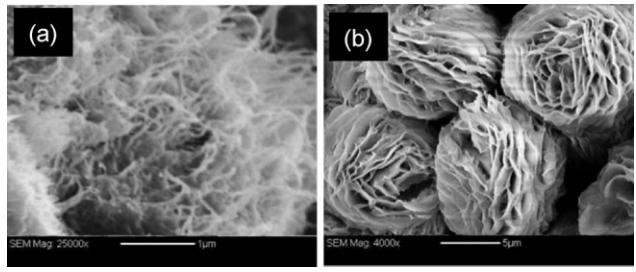

Figure 2.
SEM pictures of freeze-dried sPS/organic solvents. The morphology is of (a) fibril structure (carbon tetrachloride) and (b) lamellar/spherulitic structure (L-menthol).

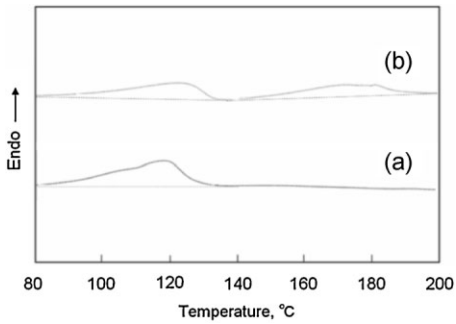

Figure 3.
Typical DSC traces obtained on heating sPTBS/*trans*-decalin gels at 20 °C/min. The concentrations of sPTBS were (a) 20.5 w% and (b) 40.3 w%.

the sample gels packed in stainless steel pans at 80 °C for at least 72 hrs to form structure homogeneously.

The typical DSC chart of sPTBS/*trans*-decalin system is shown in Figure 3 for two polymer concentrations. As is shown in Figure 3, there were two melting endotherm peaks: one was as low as 120 °C no matter how concentration was, whereas another was observed only for samples at higher concentrations than 23%.

Figure 4 shows the temperature-concentration phase diagram of sPTBS/*trans*-decalin. The temperature associated with the low-melting endotherm remains nearly constant in the range of concentrations investigated ($T_{low} = 118 \pm 3$ °C). The temperature associated with the high-melting endotherm appears at $T_{high} > 150$ °C. The variations of the enthalpies associated with each endotherm as a function of polymer concentration (Tamman's plots) are represented in the same figure. The enthalpy associated with the low-melting endotherm first increases linearly up to $C_p = 29\%$ and then decrease to become zero at about $C_p = 40\%$. On the other hand, the enthalpy associated with the high-melting endotherm increases continuously up to 45%.

The Tamman's plots and the phase diagram consist with the existence of two compounds C_1 and C_2 of different stoichiometries. The stoichiometric ratio of compound C_1 is given to be about 2.7 *trans*-decalin molecules per monomer unit of

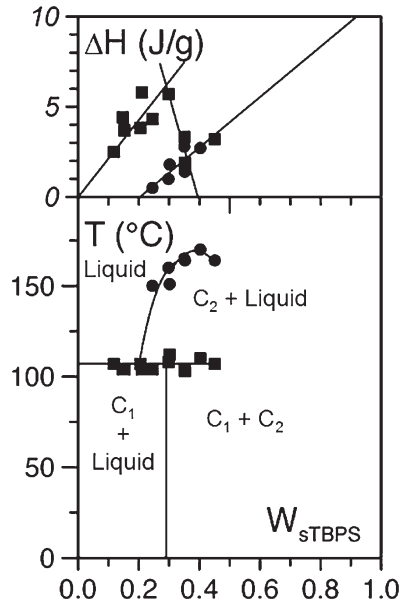

Figure 4.
Temperature-concentration phase diagram of sPTBS/*trans*-decalin system.

sPTBS. On the other hand, we could not determine stoichiometric information on C_2 because it is quite difficult to prepare homogeneous sPTBS samples at higher concentrations. The stoichiometric ratio of compound C_1 derived from the phase diagram may not reflect the correct stoichiometry of the organized part. It may arise from the degree of solvation of the amorphous phase like some sPS/solvent compounds.[11] So it is supposed to be "thermodynamic" stoichiometry of compound C_1. However, it is clear that this "thermodynamic" stoichiometry reflect the structure of the organized compound to some extent.

The complexation of sPTBS with solvent molecules such as C_1 was similar to sPS.[12,13] Thus, we were able to confirm that the characteristics of sPS are common to syndiotactic polystyrene derivatives to some extent.

Estimation of Free Volume Among sPTBS Chains Aggregated in a Gel Form

In general, when a chromophore is excited by polarized light, the emission of the

chromophore will be observed to be polarized if (I) the molecular motion of the chromophore is slow enough and (II) energy transfer and/or energy migration does not take place. Fluorescence anisotropy, r, is employed for evaluation of how much the fluorescence is polarized. When motion of a chromophore is fast enough or excitation energy can hop among molecules, the anisotropy of the emission falls to zero. When a chromophore is doped into amorphous plastic films such as poly(methyl methacrylate), it shows the highest absolute value of r because its molecular motion is perfectly suppressed. The comparison of r with this inherent value, r_0, gives the degree of depolarization. Energy migration can be avoided if the concentration of fluorescent molecules doped into a system is quite low and they are not aggregated. Accordingly, when we dope a small amount of fluorescent molecules into a system and excited them by polarized light, the degree of depolarization would give information on the motion of fluorescent molecules.

We have already shown that the anisotropy of a dye in plastic solution at 77K is almost identical with that at room temperature except for the situation where excitation energy migration occurs among dyes.[14] Molecular motion of a probe molecule is assumed to be suppressed in these plastic films. Thus, the r_0 values of probe molecules without molecular motion and energy transportation are determined to be 0.18 for naphthalene (NP), 0.14 for 1,5-dimethylnaphthalene (DMNP), 0.20 for anthracene (ANT) when they are excited at each wavelength of their absorption peaks. We also measured the fluorescence anisotropy of NP, DMNP, and ANT in chloroform and *trans*-decalin. All the fluorescence of probe molecules was found to be completely depolarized, although the viscosity of *trans*-decalin is relatively high.

The concept of our method is as follows. In a gel form, the possible location of a fluorescent molecule added into the gel can be divided to two: region I is the area where solvent molecules gather while region II is the area where polymer molecules associate together. Figure 5 shows the image of region II where there are some free volumes among polymer chains. If a guest molecule is larger than the free volume among polymer chains, it cannot penetrate into region II and has to be in region I where solvent molecules gather, resulting that its motion is quite free and the r value should be 0. However, if a guest molecule is smaller than the free volume among polymer chains, it can stay there and its molecular motion would be restricted compared with the motion of a guest molecule in fluid solution: the r values would not be 0.

We adjusted the concentrations of fluorescent guest molecules to be perfectly the same and only changed the concentra-

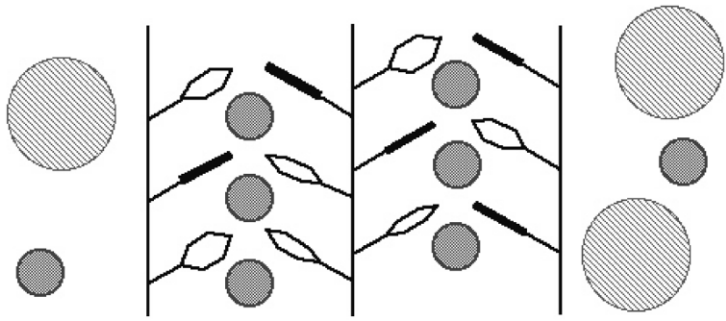

Figure 5.
The image of two different guest molecules in comparison with free volume among polymer chains that are aggregated in a gel form (region II).

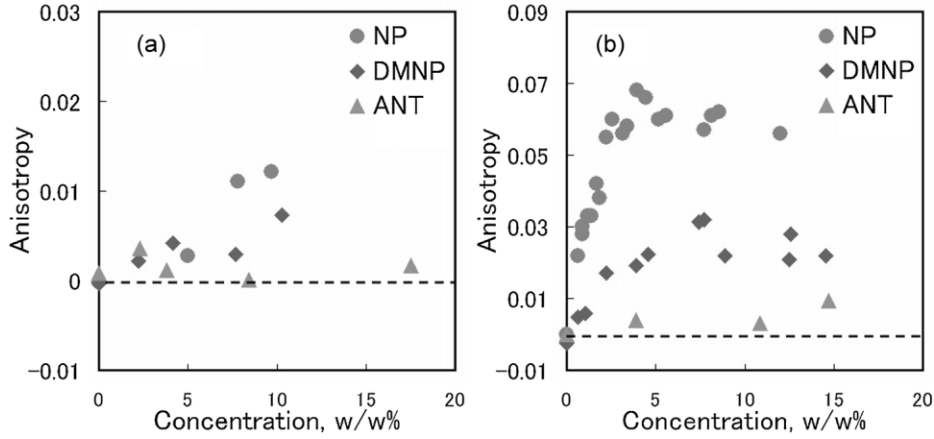

Figure 6.
Fluorescence anisotropy values of sPTBS/*trans*-decalin gel (a) and sPS/chloroform gel (b).[9]

tions of sPS and sPTBS. Figure 6 shows the change of *r* values with a change of polymer concentrations.

The sPS concentration dependence of the anisotropy of NP and DMNP in sPS/chloroform gels can be summarized as that the *r* value increased with increasing sPS content in the gels and then leveled off once the amount of sPS reached a particular level. Thus, it is concluded that (1) among the helical sPS rods in region II, there exist free volumes where some NP and DMNP molecules can penetrate and (2) the motions of the NP and DMNP staying among the side-chain phenyl groups of the sPS are suppressed. However, the *r* values of ANT doped into gels were found to be 0 no matter how many concentrations of sPS are. This means that ANT molecules cannot stay in the free volumes among sPS chains forming fibril structure, and that the free volume is smaller than the molecular size of ANT.

On the other hand, the sPTBS concentration dependence of the anisotropy of fluorescent guest molecules in sPTBS/*trans*-decalin gel is quite similar to that of sPS. The *r* values of NP and DMNP increased with increasing sPTBS content in the gels, while the *r* values of ANT doped into gels were found to be 0. However, the large discrepancy is that the *r* values for sPTBS/*trans*-decalin gels are by far smaller than those for sPS/chloroform gels. Here are two explanations possible. One is that the amounts of NP and DMNP molecules able to enter region II of sPTBS/*trans*-decalin gel are few. The other is that the motion of NP and DMNP molecules in region II of sPTBS/*trans*-decalin gel is not restricted so much. If NP molecules, which are the smallest molecules used in the present study, are difficult to enter region II, DMNP molecules would never enter region II like ANT molecules. However, it is clear that larger DMNP can enter region II because of *r* values being significant. Thus, it is deduced that NP molecules and DMNP molecules can enter region II of sPTBS/*trans*-decalin gel but that their molecular motions are not perfectly restricted by the polymer chains of sPTBS. Our polarized fluorescence method suggests that the free volume between sPTBS chains aggregated such as region II shown in Figure 5 is larger than that of sPS. Due to the bulky side chains of sPTBS, larger free volume is concluded to be produced. It is probable to form cocrystalline structure of sPTBS with a relatively larger guest molecule.

Conclusion

We prepared a syndiotactic polystyrene derivative in order to clarify some inter-

esting features of sPS and to develop a stereoregular polymer whose crystalline form can host a large functional guest molecule with high regularity in the same manner as sPS. As the first study of this derivative, sPTBS, we have examined its physical gelation with some organic solvents. Roughly speaking, the behavior of sPTBS gels is quite similar to that of sPS gels. For examples, sPTBS/*trans*-decalin gels were found to have fibril structure that formed three-dimensional network. The temperature-concentration phase diagrams of sPTBS/*trans*-decalin gel clearly exhibited there were two different types of polymer-solvent molecular compounds. On the other hands, solutions of sPTBS with some organic solvents looked like paste state or sherbet state. The SEM pictures of these states after freeze-drying showed that the morphologies of these sPTBS polymer chains were of lamellar/spherulitic structures. Then, we have tried to find a cause determining the morphology of sPTBS with organic solvents. Finally, the morphology turned out to depend on molecular size and molecular shape of solvent compounds. If a solvent is smaller than the free volume among sPTBS chains, it can enter and stay among the polymer chains following the formation of a polymer-solvent molecular compound. This could stabilize fibril structure very much, which results in the formation of the gel state together with the formation of three-dimensional network. Conversely, if a solvent is larger than the free volume among sPTBS chains, it cannot enter and stay among the polymer chains following the chain folding of sPTBS. This is assumed to produce chain-folded crystals having lamellar/spherulitic structures. Our polarized fluorescence method demonstrated that there appeared to exist more space among sPTBS chains than sPS. This conclusion was proved by a fact that sPS/L-menthol did not form gel and showed the morphology of spherulitic form with lamellar structure, although sPTBS/L-menthol forms gel with the morphology of fibril structure. This indicates that the free volume among sPTBS chains is large enough for an L-menthol molecule able to enter, though L-menthol cannot enter the free space among sPS chains in sPS/L-menthol solution. The difference of the free space was found to determine whether a gel form was produced or not.

Moreover, we would like to explain the morphologies of sPS and sPTBS with THF: THF gives a fibrillar structure with sPS while it gives a lamellar/spherulitic structure with sPTBS. This is the case where a stable polymer-solvent molecular compound is not always formed, even if a solvent molecule is able to enter the free volume among polymer chains. A THF molecule is small enough but it is supposed to move freely in sPTBS aggregated region because of too spacious free volume compared with its molecular size. The interaction of THF with sPTBS would not be enough to keep THF molecules in a stable polymer-solvent molecular compound. In this sense, the morphology could relate to mobility of solvent molecules and/or interaction of solvent with polymer. In any rate, because it is the first step to form gel that solvent molecules enter the free volume among polymer chains, the molecular size and shape of solvent should play an important role for determining the morphology.

Acknowledgements: This work was supported by Heiwa Nakajima Foundation and Grant-in-aid for Scientific Research (C) (21550206) from the Ministry of Education, Science, Sports and Culture of Japan. The research was partially carried out at the Center for the Instrumental Analysis, Shizuoka University, and Institut Charles Sadron, CNRS Strasbourg. H. Itagaki is indebted to CNRS for a three-month allowance as research fellow. J.M. Guenet is indebted to Heiwa Nakajima foundation for a visiting-professorship grant.

[1] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules*, **1986**, *19*, 2464.
[2] J. M. Guenet, *Polymer-Solvent Molecular Compounds*, **2008**, Elsevier, London.
[3] G. Milano, G. Guerra, *Prog. Mater. Sci.*, **2009**, *54*, 68.

[4] E. B. Gowd, K. Tashiro, C. Ramesh, *Prog. Polym. Sci.*, **2009**, *34*, 280.
[5] G. Guerra, M. V. Vitagliano, C. De Rosa, V. Petraccone, P. Corradini, *Macromolecules*, **1990**, *23*, 1539.
[6] H. Itagaki, *Macromol. Symp.*, **2008**, *273*, 9.
[7] H. Itagaki, in: "*Experimental Methods in Polymer Science: Modern Methods in Polymer Research and Technology*", T. Tanaka, Ed., Academic Press, New York **2000**, Chapter 3.
[8] H. Itagaki, Y. Nakatani, *Macromolecules* **1997**, *30*, 7793.
[9] H. Itagaki, J. Mochizuki, *Macromolecules* **2005**, *38*, 9625.
[10] N. Ishihara, M. Kuramoto, M. Uoi, *Macromolesules*, **1988**, *21*, 3356.
[11] S. Malik, C. Rochas, J. M. Guenet, *Macromolecules* **2006**, *39*, 1000.
[12] C. Daniel, A. Menelle, A. Brulet, J. M. Guenet, *polymer*, **1997**, *38*, 4193.
[13] S. Malik, C. Rochas, B. Deme, J. M. Guenet, *Macromol. Symp.*, **2005**, *222*, 73.
[14] H. Itagaki, K. Horie, I. Mita, M. Washio, S. Tagawa, Y. Tabata, H. Sato, Y. Tanaka, *Macromolecules* **1990**, *23*, 1686.

