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Clathrate Formation between Syndiotactic Polystyrene and Aromatic Compounds from Solution in Decalin

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Summary

In order to ascertain whether preferential inclusion of toluene and biphenyl into the δ phase of syndiotactic polystyrene occurs from solution in decalin, we investigate the crystal phase formation of this polymer from solution in decalin/toluene and decalin/biphenyl mixtures of varying composition. To this end, we performed a qualitative analysis of the solid formed upon quenching the solution and drying, with Fourier-transformed infrared spectroscopy and wide-angle x-ray diffraction. In all cases, the formation of T_2G_2 helical structures was observed. We find that the composition of the solvent mixture can have a strong effect on the X-ray spectrum of the solid, after quenching and drying. For syndiotactic polystyrene samples obtained from decalin/toluene mixtures, we find that little or no toluene inclusion occurs, unless the fraction of toluene in the solvent mixture is quite high. Conversely, biphenyl appears to be preferentially clathrated from solution in decalin, even if it is present in relatively small amounts.

Introduction

The complex morphological behavior of syndiotactic polystyrene (sPS) is well-documented [1-7]. sPS crystals (which make up a fraction of 30-50% of the polymeric solid [8,9]) can have two conformations, usually referred to as the zigzag (T_4) conformation, formed through nucleation-driven, conventional crystallization, and the helix (T_2G_2) conformation, formed through "gel-crystallization" [1,10,11]. The former conformation is generally obtained during crystallization from the melt, whereas the latter can be found upon crystallization from solution. In this paper, we focus on the latter class of crystal. Within this crystal class, two distinguishable helical phases exist. The first of these, named the δ phase, is a clathrate or inclusion compound, meaning that solvent molecules are present within the crystal lattice [12-15]. The second, known as the γ phase, has no such solvent inclusion [1,3,11,12,15-17].
Our interest is in studying the formation, from solution, of clathrates of sPS with species other than the solvent. As a first step toward this goal, we focus in this paper on the crystal structure formation of sPS from solvent mixtures, allowing us to

determine if preferential inclusion of either of the solvents takes place. Such preferential inclusion has recently been found for a mixture of good solvents for sPS, i.e., para-xylene and meta-xylene [18,19]. In contrast, the crystallization from mixtures of a good solvent with a poorer one has, to the best of our knowledge, not been investigated in detail.

In this paper, we present results of a qualitative study on the effect of using solvent mixtures consisting of decalin and aromatic compounds on the "gel-crystallization" of syndiotactic polystyrene. We focus first on decalin-toluene mixtures of varying composition. Toluene is a good solvent for sPS, and crystallization from toluene under the appropriate experimental conditions, is known to result in the formation of a clathrate δ phase [17,20]. Decalin, on the other hand, is a θ-solvent for the polymer. The effects of crystallization from this solvent are still debated in the literature, but the x-ray spectrum of sPS with this solvent is in any case quite distinguishable from that of the toluene δ phase [14,21-23]. This enables us to study whether the solvent composition has any effect on the crystallization of sPS, and hence to determine whether preferential inclusion of either solvent occurs. A more detailed and quantitative analysis of the crystal phases that form upon solidification from solution is left for future work.

Because the use of a non-volatile substance could conceivably lead to clathrates that are more stable at room temperature than those obtained with volatile solvents, we also studied the preferential inclusion of biphenyl. To this end, we induced crystal formation in solutions of sPS in decalin-biphenyl mixtures of varying composition. Additionally, these experiments may give us an indication of the size of the molecules that can be accommodated in the clathrate phase, as it is known that the size and bulkiness of the solvent molecules can cause them to be excluded form the crystal [24]. Similar investigations on the inclusion of compounds that are also solid at room temperature have been reported recently in the literature [25,26].

Experimental

Materials

We obtained the sPS used for this study from Dow Chemical, in pellet form and with a syndiotacticity of over 96%. Its mass-averaged molar mass is $3 \cdot 10^5$ g/mol, whereas its polydispersity index lies below three. Toluene was obtained from Chem-lab N.V. with a purity of over 99.5%, and decalin was purchased from ACROS as a mixture of cis- and trans-decahydronaphthalene with a purity of 98%. Biphenyl was purchased from Aldrich with a purity of over 98%. All chemicals were used without further purification.

Methods

We prepared a ten weight-percent solution of syndiotactic polystyrene in the appropriate solvent mixture at elevated temperatures (120-180 °C) in a flask fitted with a cooler. Note that while biphenyl is in the solid state at room temperature, at these elevated temperatures it melts and can serve as a solvent for sPS. After a homogeneous solution was obtained, we quenched it in an ice bath. This was done because studies have shown that solidification at high temperatures yields T_4-type crystals, whereas low temperatures promote the formation of T_2G_2 conformations

[22]. The samples were then ground into powder, and allowed to dry at room temperature until their weights were no longer found to decrease appreciably over a 24-hour period.

In the cases where the solvent mixture contained relatively high fractions of biphenyl, the dried polymer was subsequently washed with cold decalin over a two-hour period to remove the excess of solid biphenyl. Wide-angle X-ray diffraction (WAXD) served to verify that the solid biphenyl was succesfully removed, since no signals of pure biphenyl were detected. Clathrated biphenyl, on the other hand, was still present, as we were also able to verify by WAXD (to be discussed in Sections III.2 and III.3).

We determined the conformation of the sPS chains and the amounts of decalin and toluene in the crystals by Fourier-transformed infra-red spectroscopy (FTIR) measurements, performed on a Perkin-Elmer 2000 FTIR apparatus. These measurements of the transmittance were performed with KBr tablets, at a resolution of 1 cm^{-1}.

In order to study the crystals that form after quenching the sPS solution and allowing it to dry, we performed static WAXD measurements at room temperature using Ni-filtered Cu $K\alpha$ radiation from a Rigaku Rotaflex RU 200B rotating anode. Samples covered by thin aluminium foils were mounted in a horizontal Bragg-Brentano diffractometer with a scintillation counter. Experiments were performed in the transmission mode, covering the angular range $5° < 2\theta < 60°$ with 2θ the scattering angle, and with 5 s of irradiation at each 0.05°.

Results and Discussion

1. Conformation of sPS chains: FTIR spectroscopy

We performed FTIR spectroscopy on sPS samples that were obtained by quenching solutions of sPS in toluene-decalin mixtures of varying composition, and that were subsequently allowed to dry at room temperature. All solutions we prepared contained ten weight percent sPS. In Figure 1, we show the results of these measurements in the form of FTIR spectra (these have been truncated at 1000 cm^{-1} for clarity). We note that signals at 541, 858, 901 and 911 cm^{-1}, indicative of the formation of the T_4 "zigzag" structure, are absent. However, we find signals at 501, 535, 548, 571, 601, 769, 779, 932 and 943 cm^{-1}, which peak positions are associated with the formation of a T_2G_2-type molecular conformation. All these signals are present for all investigated solvent compositions. The same conclusions can be drawn from the parts of the spectrum not shown here. They, too, present signals associated with a helix structure, whereas those connected with a zigzag structure are absent. The signal at 1224 cm^{-1}, which is considered to be the strongest indication of a T_4-type structure, is completely absent in most cases, although a few of the spectra do show a very small signal near this frequency.

Any differences in the spectra corresponding to different solvent compositions are due to differences in solvent content, and not to changes of the chain conformation in the crystals. The decrease of the toluene content, for instance, results in a decrease of the signals at 465 and 729 cm^{-1}, while the change in the intensity of the signals at 668, 792, 823, 853, 872 and 923 cm^{-1} is connected to the amount of decalin that is present. We conclude that the solvent composition has no effect on the conformation of the sPS chains under the circumstances of our experiments, and that a T_2G_2-helix conformation is formed in all cases.

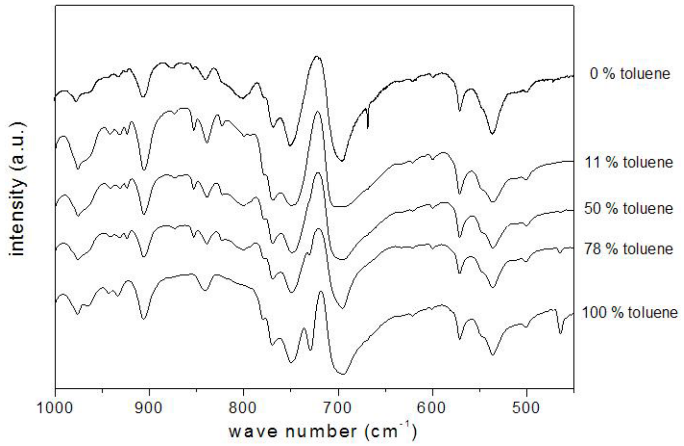

Figure 1. Partial infrared spectra of dried samples, for several solvent compositions, as indicated. In all cases 10 weight percent of sPS is present.

In the solidification of sPS from mixtures of decalin and biphenyl, we again detected no evidence of the formation of T_4 conformations. Only the signals characteristic for the T_2G_2 conformation are found. The corresponding spectra are similar to those represented in figure 1 and are therefore not shown. Since biphenyl is solid at room temperature, a quench of a liquid solution of biphenyl and sPS in decalin yields a solid that contains both pure biphenyl crystals and crystalline sPS, which may contain clathrated biphenyl. In order to eliminate the pure biphenyl, an extraction with decalin at room temperature was performed. to FTIR spectroscopy was used to determine that there was still (clathrated) biphenyl present after our standard period of extraction, i.e., two hours.

2. WAXD results: crystallization from pure solvents

To determine whether clathrates are formed, we performed wide-angle X-ray diffraction measurements. The WAXD patterns we obtain for sPS quenched from the three pure solvents are compared in Figure 2. For the solid obtained from toluene, we observe reflections at $2\theta = 8.0$, 10.1, 17.1, 20.0 and 23.3 degrees, as well as weaker reflections at 13.8 and 28.5 degrees. This agrees closely to results found in literature [23,27], and it is generally accepted that these reflections correspond to a clathrate δ phase.

For the solid that is obtained after quenching a solution of sPS in decalin, we find (for the conditions under which we have performed our experiments) reflections at 10.2, 16.2 and 19.7 degrees, with weaker ones at 7.1, 23.0 and 28.5 degrees. This corresponds quite closely to the spectrum found by Gowd and co-workers, who interpret it as a clathrate phase [27]. De Rudder and co-workers, on the other hand, note that the signal at 16 degrees is typical for a γ phase and interpret their results as representative of this phase [22]. Indeed, our spectrum is reminiscent of that of the γ phase, which has reflections at 9.1, 10.2, 13.7, 15.9, 19.6, 23.2 and 28.0 degrees [23]. While our spectrum apparently lacks the reflections at 9.1 and 13.7 degrees, inspection of Figure 2 shows that these signals may in fact be present, but obscured by the presence of the strong signals at 10.2 and 16.2 degrees. Deconvolution of the spectrum could eventually bring an answer to this question.

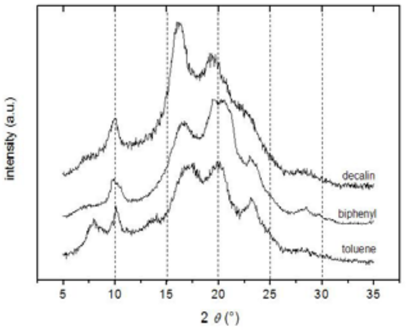

Figure 2. WAXD spectra of dried sPS samples, obtained by quenching from solution in toluene, biphenyl and decalin, as indicated.

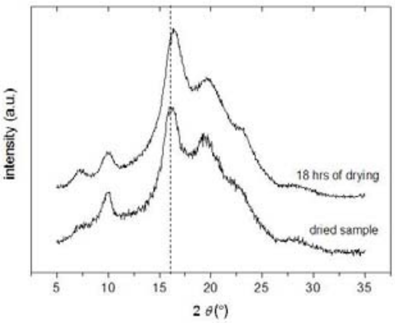

Figure 3. WAXD spectra of sPS samples, crystallized from solution in decalin. Bottom curve: fully dried sample (after a week of drying), top curve: sample after 18 hours of drying.

The interesting question whether the γ or/and the δ phase is formed, is irrelevant for our current investigation. In fact, to determine whether preferential inclusion of toluene or biphenyl occurs from a solution in decalin, we only need the spectrum of the solid induced by decalin to be distinguishable from those induced by the aromatic compounds.

We would like to note, however, that we observed differences between the WAXD spectrum of a sample that has been thoroughly dried and that of one that has been allowed to dry for only 18 hours (see Figure 3). The changes we see consist of an increase of the signal at 7 degrees, and a shift of the peak at 16 degrees to slightly higher values. As we shall discuss below, these same changes occur if one compares a sample solidified from pure decalin to one obtained from a toluene/decalin mixture. This could indicate that a δ-to-γ transition occurs during the drying process. Clearly, this deserves further study.

For the solid obtained by quenching a solution of sPS in melted biphenyl and subsequently washing it with decalin for two hours in order to remove excess biphenyl (and then drying it extensively), we find reflections at $2\theta = 10.3$, 16.7, 20.2 and 23.1 degrees, and a weak one at 28.5 degrees, see Figure 2. The peaks at 10.3 and 20.2 degrees appear to have shoulders at 9.9 and 19.6 degrees. These are likely due to a small amount of remaining solid, non-clathrated biphenyl, as we found signals near these same locations in the WAXD spectrum of pure biphenyl, see Figure 4.

When we compare the spectrum to that of a γ phase [23], we note that the signals around 17 and 20 degrees show a significant deviation from the positions characteristic for the γ phase. We must therefore conclude that the crystals we find do not represent a pure γ phase. Whether the sample we have prepared corresponds to a pure δ phase or a mixture of the two phases, we cannot conclude from this measurement alone. It seems clear, however, that at least some biphenyl has been incorporated in the crystal structure, and we can conclude that the size of the biphenyl molecules does not prevent the clathrate formation. Again, we note that the determination of the identity of the crystal phase is not the focus of this work. We refer to recent work by Guenet and co-workers for a more detailed description of the clathrate formation of sPS with biphenyl [26].

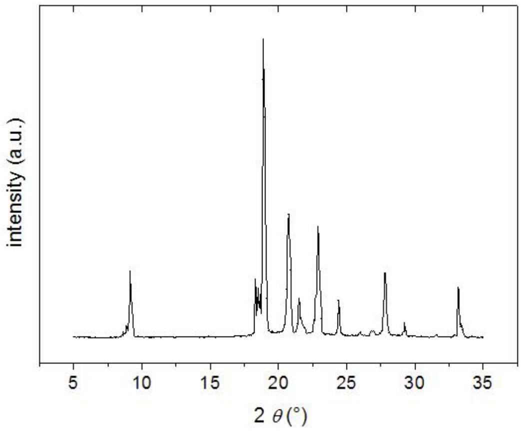

Figure 4. WAXD spectrum of biphenyl.

3. WAXD results: crystallization from solvent mixtures

The WAXD patterns of the solids that form upon quenching a solution of sPS in a mixed solvent are generally found to change with the composition of the original solvent mixture (Figures 5 and 6).

For toluene-decalin mixtures (Figure 5) we see that the δ-phase spectrum observed in the solid obtained from pure toluene (the bottom curve) changes gradually to that of the solid obtained from pure decalin (the top curve). This manifests itself in a shift of the peak at 17 degrees, and a change in the intensity of the peaks at 7-8 and 23 degrees, and implies that at intermediate compositions, both the toluene clathrate phase and the decalin-induced phase are present to some degree.

We note that, even at relatively low fractions of decalin (22%), the spectrum already strongly resembles that of the solid obtained from pure decalin (note especially the locations and relative heights of the reflections between 15 and 25 degrees). Hence, it would seem that a rather limited amount of decalin (< 22% of the solvent mixture) already inhibits the formation of a toluene δ phase. We conclude that above this

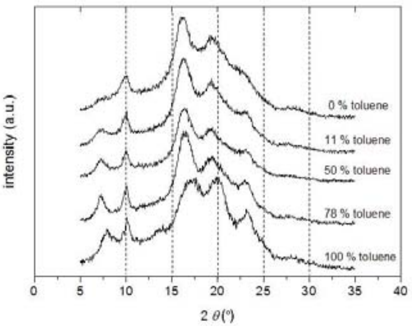

Figure 5. WAXD spectra of dried sPS samples, prepared from 10% sPS solution in a toluene-decalin mixture, containing an amount of toluene indicated by % toluene.

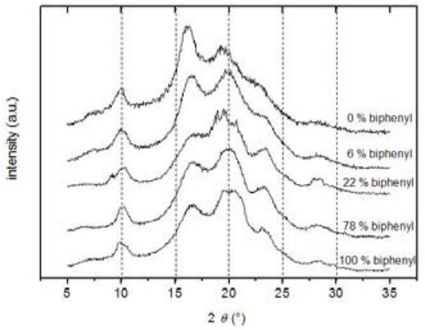

Figure 6. As Figure 4, but with sPS from biphenyl-decalin mixtures.

limiting concentration of 22% decalin, no preferential inclusion of toluene takes place from a decalin solution, under the conditions of our experiments.

For decalin/biphenyl mixtures, the WAXD spectra (Figure 6) also show a gradual change from a solid in which the biphenyl-induced phase dominates, to one in which the decalin-induced phase becomes more important. This change is characterized by a shift to lower angles of the peak at 17°, and an increase in the intensity of this same peak, as well as a decrease of the intensity of the peak at 23°. However, now the spectrum strongly resembles that of the biphenyl-induced phase for solutions with a decalin content of up to 78 weight percent. This seems to indicate that preferential inclusion of biphenyl does occur up to quite high fractions of decalin in the solvent mixture, and that the biphenyl-sPS clathrate crystallized from solution is likely more stable than the toluene-sPS one.

While solidification from mixtures containing a large fraction of biphenyl necessitates the removal of the excess biphenyl in order for us to be able to detect the sPS WAXD signals, for solutions where the fraction of biphenyl is modest, this need not be necessary. Indeed, wherever possible, we have omitted the extraction, as the additional contact with decalin may influence the crystal structure. Specifically, we have performed the extraction only on the sPS samples obtained from solvent mixtures containing more than 22 percent of biphenyl. Due to this, the WAXD spectrum of the solid obtained from a solution containing 22 percent of biphenyl is somewhat rougher in appearance than the others, and displays more signals. The extra signals around 9 and 28°, as well as in the region between 15 and 22 degrees, are due to some solid biphenyl still present in the sample we analyzed (see also Figure 4).

4. FTIR study of solvent inclusion from solvent mixtures

Besides WAXD, it is also possible to use FTIR to get a tentative indication of the inclusion of solvent molecules. This is shown in Figure 7 for the solid obtained from toluene-decalin mixtures. Here, we have plotted the intensity of the toluene signal at 465 cm^{-1}, divided by that of the signal at 1583 cm^{-1}. This latter signal is present in the spectrum of sPS, but not in those of the solvents, and its intensity can hence be expected to be independent of the solvent content of the sample. We see in Figure 7 that the amount of toluene rapidly (and non-linearly) decreases with an increasing fraction of decalin in the solution. In fact, for a sample where the solution contained 55 % toluene, we no longer see any evidence of this solvent in our FTIR measurements. Even at relatively small decalin fractions, we see a large decrease in the intensity of the toluene signal.

Note that, in order to draw any conclusions regarding the preferential toluene inclusion from Figure 7, we need to invoke several assumptions. The first is that our drying procedure ensures that any "free" toluene has evaporated, so that the signal at 465 cm^{-1} corresponds to the amount of clathrated toluene, and hence to the amount of toluene δ phase in our sample. In addition, we have to assume that the fraction of amorphous material that forms upon quenching the solution does not change with the composition of the solvent. Because these assumptions have not been verified for our system, the FTIR results of Figure 7 should not be regarded as a quantitative indication of the formation of the toluene δ phase, but rather as a qualitative corroboration of our WAXD results of Figure 4, and of our conclusion that a small amount of decalin serves to inhibit the inclusion of toluene under the conditions of our experiments.

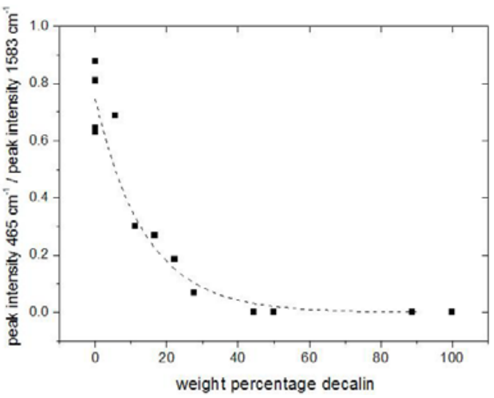

Figure 7. Relative intensity of the toluene peak at 465 cm^{-1} as a function of solvent composition. The line serves to guide the eye.

Similarly, we also determined the relative intensity of the decalin signal (defined as the intensity of the decalin signal at 853 cm^{-1}, divided by that of the sPS signal at 1583 cm^{-1}) as a function of solvent composition. In contrast to the case of toluene, we observe no clear trend here. We did find that decalin was present in all samples. This decalin may in principle be present in the amorphous portion of the sPS, or clathrated in the crystal phase, or in both. To gauge whether some decalin may indeed remain in the amorphous phase after the drying procedure we apply, we have dissolved atactic polystyrene (which does not crystallize) in decalin and in toluene and quenched these solutions. We found a much smaller decrease in mass after drying for the decalin sample than for the toluene one. This seems to indicate that decalin may indeed linger in the amorphous solid, and that our drying procedure does not suffice to remove all decalin. This of course makes sense when one takes into account the much higher boiling point of decalin, when compared to toluene.

Conclusions

We have performed a qualitative investigation of the formation of clathrates between syndiotactic polystyrene and toluene and between syndiotactic polystyrene and biphenyl, from solution in decalin. To this end, we quenched 10 percent solutions of this polymer in toluene-decalin and biphenyl-decalin mixtures of varying composition, and analyzed the resulting solid, after extensive drying, using Fourier transform infrared spectroscopy and wide-angle X-ray diffraction. We find that only T_2G_2 helix conformations are present in the solids (as opposed to T_4 zigzag conformations). For polystyrene crystallized from mixtures of toluene and decalin, and for that obtained from mixtures of biphenyl and decalin, we find a gradual change in the wide-angle x-ray spectra with increasing decalin content, from one that corresponds to the clathrate with the aromatic compound to one that corresponds to the crystal phase induced by decalin. For the toluene/decalin mixture, a small fraction of decalin in the solvent mixture suffices to significantly reduce the amount of toluene δ phase that is formed. Consequently we conclude that toluene is not preferentially included from solution in decalin. For syndiotactic polystyrene crystallized from biphenyl-decalin mixtures, on the other hand, we find that the biphenyl-induced phase dominates up to quite high fractions of decalin in the solvent mixture, i.e., biphenyl is preferentially clathrated under the conditions of our experiments. It appears possible to produce stable clathrates of sPS with a compound that is solid at room temperature, even from a solution in which this compound is present only in a relatively low concentration. WAXD measurements on sPS obtained from solution in pure decalin seem to suggest the possibility of a transition from a δ phase to a γ phase during drying for this solvent.

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References

1. Immirzi A De Candia F Ianelli P Zambelli A Vittoria V (1988) Makromol Chem Rapid Commun 9:761
2. Vittoria V, Russo R, De Candia F (1991) Polymer 32 3371
3. Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P (1990) Macromolecules 23:1539
4. Doherty D, Hopfinger J (1989) Macromolecules 22:2472
5. Prasad A, Mandelkern L (1990) Macromolecules 23:5041
6. Vittoria V, De Candia F, Ianelli P, Immirzi A (1988) Makromol Chem Rapid Commun 9:765
7. Vittoria V, Filho A (1993) J Appl Polym Sci 49:247
8. De Candia F Filho A Vittoria V (1991) Colloid Polym Sci 269:650
9. Musto P Tavone S Guerra G De Rosa C (1997) J Polym Sci B Polym Phys 35:1055
10. De Rudder J, Berghmans H, De Schryver FC, Bosco M, Paoletti S (2002) Macromolecules 35:9529
11. Tashiro K, Ueno Y, Yoshioka A, Kobayashi M (2001) Macromolecules 34:310
12. Daniel C, Menelle A, Brulet A, Guenet JM (1997) Macromol Symp 114:159
13. Berghmans H, Aerts L, Buyse K, Deberdt F, Roels T, de Rudder J, Vereecke S (1998) Ber Bunsenges Phys Chem 102:1654
14. Roels T, Rastogi S, De Rudder J, Berghmans H (1997) Macromolecules 30:7939
15. Roels T, Deberdt F, Berghmans H (1994) Macromolecules 27:6216
16. Daniel C, Guerra G, Musto P (2002) Macromolecules 35:2243
17. Daniel C, Menelle A, Brulet A, Guenet JM (1997) Polymer 38:4193
18. Sivakumar M, Yamamoto Y, Amutharani D, Tsujita Y, Yoshimizu H, Kinoshita T (2002) Macromol Rapid Commun 23:77
19. Tsutsui K, Katsumata T, Fukatsu H, Yoshimizu H, Kinoshita T, Tsujita Y (1999) Polym J 31:268
20. Chatani Y, Shimane Y, Inagaki T, Ijitsu T, Yukinari T, Shikuma H (1993) Polymer 34:1620
21. De Rudder J (2001) PhD Thesis Katholieke Universiteit Leuven
22. De Rudder J, Bergé B, Berghmans H (2002) Macromol Chem Phys 203:2083
23. De Rosa C, Guerra G, Petraccone V, Pirozzi B (1997) Macromolecules 30:4147
24. Rizzo P, Albunia AR, Guerra G (2005) Polymer 46:9549
25. Malik S, Rochas C, Guenet JM (2005) Macromolecules 38:4888
26. Malik S, Rochas C, Guenet JM (2006) Macromolecules 39:1000
27. Gowd EB, Nair SS, Ramesh C (2002) Macromolecules 35:8509