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Polymer 44 (2003) 5293–5302

polymer

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WAXD and FTIR spectroscopy studies on phase behavior of syndiotactic polystyrene/1,1,2,2-tetrachloroethane complexes

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Received 26 February 2003; received in revised form 12 June 2003; accepted 23 June 2003

Abstract

Crystal polymorphism, conformation, and transformation of syndiotactic polystyrene (sPS) thin films cast from 1,1,2,2-tetrachloroethane were investigated via wide angle X-ray diffraction, transmission electron microscopy, electron diffraction, differential scanning calorimetry, and Fourier-transform infrared spectroscopy (FT-IR). The solvent-induced crystallization of sPS yielded an ordered crystalline γ-form packed with a helical conformation of lower degrees of perfection. The 1,1,2,2-tetrachloroethane solvent was unique in that, instead of forming a meso crystalline δ-form (which is a polymer-solvent complex) for most other solvents, it could induce sPS to develop a crystalline γ-form. The unique behavior was attributed to the discrepancies in the location of solvent molecules after solvent casting. As evidenced by FT-IR characterization, the solvent molecules within the polymer-solvent complex were identified being mainly trapped in the non-crystalline/amorphous phase. The solvent-induced crystalline γ-form exhibited a crystalline morphology having small crystal aggregates with an average size less than 100 nm. Upon heating, the crystalline γ-form gradually grew into much perfect packing, and finally went through a $\gamma \rightarrow \alpha'$ transformation at temperature of 200 °C.

Keywords: Syndiotactic polystyrene; Solvent-induced crystals; Wide angle X-ray diffraction; Fourier-transform infrared spectroscopy; 1,1,2,2-Tetrachloroethane

1. Introduction

Syndiotactic polystyrene (sPS) possesses complex polymorphism in its crystalline region, and previous work has shown that there are four common crystalline forms (α-, β-, δ-, and γ-forms) in polymorphism of sPS subjected to various thermal or solvent-induced crystallization [1–3]. The two crystalline forms, α and β, have been shown to possess an all-*trans* planar-zigzag (designated as a TTTT conformation) chains, while the crystalline δ and γ-forms consist of s(2/1)2 helical-chain conformations of regular repetition of *trans–trans* (TT) and *gauche–gauche* (GG) on the backbones. In addition to the crystal transitions already widely known and reported earlier for solution-cast sPS [1–3], the crystalline α-form can also be found easily in cold-crystallized sPS (i.e. crystallization at above T_g from rubbery amorphous chains). Cold-crystallization of neat amorphous sPS produces only the crystalline α-form (α′ and α″), whereas both crystalline α- and β-forms (in various fractions depending on temperatures) can be found in melt-crystallized sPS [4–6]. Two sub-forms of the (-form are known; usually, cold-crystallization at temperatures below 200 °C leads to the α′-form whereas the α″-form is favored at high temperatures greater than 200 °C [5].

The solvent-induced crystalline δ-form and solvent-free crystalline γ-forms are both of helical structural conformations, and the crystalline δ-form is obtained in sPS when freshly cast from solvent at low temperatures below 100 °C or so, while the solvent-free crystalline γ-form is obtained by subjecting the solvent-cast sPS to thermal annealing at medium temperatures to drive out the solvent molecules, leaving the same monoclinic crystal structure [3,7–11]. The crystal with helical conformation is not quite stable and crystal transition (δ-form → γ-form → α′-form, or δ-form → β′-form) can occur via a melting and re-crystallization process upon annealing when temperatures are greater than 200 °C [2–11]. In addition, the emptied δ-form

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0032-3861/03/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0032-3861(03)00563-9

can go into a mesomorphic form of the same chains in the helical conformation. This unstable mesomorphic form can transform finally into the γ-form with further annealing at a medium temperature of 110 °C, as determined by wide-angle X-ray diffraction (WAXD) and Fourier-transform infrared spectroscopy (FT-IR) [7]. Phase transition mechanism is seen commonly in semicrystalline polymers.

FT-IR has been commonly used for analyzing molecular interactions and molecular packing in many semi-crystalline polymers. Vibrational modes are quite sensitive to molecular symmetry so that the different conformations are directly reflected in the spectrum [12–34]. In addition, Kaji et al. [18] have studied the nucleation mechanism in the crystallization process by using time-resolved FT-IR characterizations on sPS during the induction period of crystallization from the glass state. Many studies also have pointed out that polymorphism such as the crystalline α- and β-forms in sPS can be determined with FT-IR characterization [2,21–24]. The various thermal treatment of the melt produced samples with different degree of crystallinity, where the structure organization was analyzed using IR spectroscopy by examining the conformation-sensitive IR bands [19–25]. More recently, a number of studies have investigated on subjects of IR vibration spectra changes with polymorphism alteration in sPS [18]. A characteristic peak at 1222 cm^{-1} has been assigned to the presence of the all-*trans* planar zigzag conformation which do not exist in the helical form [1,28]. Spell [26] have shown that the increase in the 940 cm^{-1} absorbance peak is due to disordering of the packing of the helical chains in the crystalline δ-form prior to reformation as the helices in the crystalline γ-form, and the absorbance peaks of 934 and 943 cm^{-1} can be seen in freshly solvent-cast sPS samples containing only the crystalline δ-form. For annealing temperatures above 120 °C, reduction of the 934 and 943 cm^{-1} peak intensities is apparent, while a third peak of 940 cm^{-1} became merged, indicating occurrence of a transition from the solvent-trapped δ-form to the solvent-free γ-form [26]. However, the detailed mechanism is yet to be clarified. Rastogi et al. [27] have studied the phase behavior of sPS cast from three different solvents (decalin, benzylmethacrylate, and cyclohexylmethacrylate) using in situ SAXS, WAXS, and Raman/IR spectroscopy. They found two different crystal modifications in solution-cast sPS (denoted as δ′ and δ″ that incorporate ordered and disordered solvent molecules in the solvent-induced crystalline (-form with helical chains), but they claimed that no solvent-free γ-form was resulted upon further heating. Crystal units in sPS also possess an interesting crystalline polymorphism behavior depending on processing conditions of solution-cast, melt crystallization, or cold crystallization. Normally, the crystalline δ-form can be obtained by sorption (or solution-casting) in suitable solvents/compounds in amorphous or semicrystalline sPS materials that initially contains the α or γ-forms [1–3,7–9,26–40]. This implies that the helical conformation can only be prepared in the presence of a solvent, and this leads to the formation of δ-form. Kobayashi et al. [1,29] and Roels, et al. [30] have suggested that highly ordered sequences of the TTGG-type skeletal conformation are formed in a physical-gel state of sPS. It is known that the crystallization behavior and crystal forms of sPS in solutions can be affected by the type of solvents used, which are also known to influence the gelation rates [2,29].

Our preliminary studies showed that the types of solvents used in preparing the polymer solutions might have an influence on the helical phase peaking in solution-cast sPS. Our investigation on the sPS whose crystallization was induced by three different solvents led to different unique morphologies in the polymers [41]. These three different solvents were, respectively, 1,1,2,2-tetrachloroethane, 1,2-dichloroethane, and *o*-dichlorobenzene. Various phases in the solution-cast sPS samples were identified through an analysis of the IR spectra and X-ray scattering patterns. After complete removal of the solvent, two different structural modifications exist within the solvent-free crystalline γ-form, respectively. The disordered γ-form, in which the helical chains disappears, and transforms into the α′-form at temperatures of 160 °C upon slow heating. By comparisons, thermal treatments at high temperatures above 195 °C imposed on the ordered γ-form (of helical chains) lead to a transition into the α′-form.

In this study, differential scanning calorimetry (DSC) and X-ray diffraction experiments as well as FT-IR spectroscopy were used to identify the crystal transformation behavior and heating-induced structural changes in thin-film samples obtained by solution casting of sPS from 1,1,2,2-tetrachloroethane. On the basis of these experimental evidences, this study attempted to describe the structural evolution and the conformation changes as a function of temperature and to interpret the thermal behavior of the unique morphology in solution-cast sPS. Here, our aims are to explore the metastability of sPS polymorphism, particularly the crystals with helical chain conformations, and thus to clarify the origins of the formation of γ-form for polymer-solvent complex.

2. Experimental

2.1. Materials and procedures

Semicrystalline sPS was obtained as a courtesy sample material from Idemitsu Petrochemical Co., Ltd (Japan) with a high $M_\mathrm{w} = 241{,}000$ g/mol and PI $(M_\mathrm{w}/M_\mathrm{n}) = 2.3$. The solution-cast samples for IR, X-ray diffraction and DSC experiments were prepared by the following process. The polymer was dissolved in 1,1,2,2-tetrachloroethane ($Cl_2C_2H_2Cl_2$) in a sealed glass tubes at about 130 °C (below the boiling point of 146.2 °C at atmospheric pressure). A polymer concentration of 4 wt% in the solvent was determined from the amounts of the polymer and solvent weighed into the sample tubes. After complete dissolution of sPS in 1,1,2,2-tetrachloroethane, the sPS solutions were cooled at 60 °C for about 30 min. The sPS solutions were then cast into films at 60 °C and dried for 6 h. The solution-cast sPS films were then subjected to various thermal schemes, as specified in Section 3.

Thin sPS films with a thickness ranging between 0.01 and 0.1 μm were prepared for transmission electron microscopy (TEM) characterization by casting a 0.1% (w/w) solution of sPS/$Cl_2C_2H_2Cl_2$ onto carbon-coated glass slides. After different crystallization conditions were applied, the films were stripped and floated onto the water surface and then picked up using copper grids.

2.2. Apparatus

Fourier-transform infrared spectroscopy (FT-IR, Nicolet Magna-560) was used for investigating conformations and crystal types in sPS. Spectra were obtained at 2 cm^{-1} resolution and average were obtained from at least 64 scans in the standard wavenumber range of 400–4000 cm^{-1}. Thin films for FT-IR studies were obtained by casting the sPS solutions onto potassium bromide (KBr) disks at 60 °C and then the solvent were removed in vacuum at 60 °C. Thermal annealing of specific schemes was then imposed on the KBr-cast sPS films.

A differential scanning calorimeter (DSC-7, Perkin–Elmer) equipped with a mechanical intracooler was used for analyzing thermal behavior of sPS. The instrument was calibrated with indium and zinc standards at 10 °C/min on the temperature and heat of transitions. A scan rate of 20 °C was used in characterization of glass transitions.

Wide-angle X-ray instrument (WAXD) was Shimadzu XRD-6000 with copper K_α radiation (30 kV and 40 mA) and a wavelength of 1.542 Å. The scanning 2(angle ranged between 3 and 30° with a step scanning rate of 2°/min. The XRD characterizations for all samples were performed after the samples were subjected to solvent-induced crystallization. Further thermal treatments of the solvent-crystallized sPS were performed in situ directly in the XRD high-temperature oven (VOS-200SD) with a PID controller with temperature accuracy of ±1.5 °C from 60 °C to various holding temperatures: 80, 100, 120, 140, 160, 180, 200, 220, and 240 °C.

sPS crystal morphology and electron diffraction (ED) patterns were observed via a JEOL (1200 ×) TEM using a 120-kV accelerating voltage. The sPS films were shadowed by Pt and coated with carbon for TEM morphological observation. Calibration of the ED spacing was carried out using Au and TlCl (d-spacing < 0.384 nm, the largest spacing for TlCl). Spacing value larger than 0.384 nm was calibrated by double the d-spacing of those reflections based on the spacing of their first-order reflections.

3. Results and discussion

3.1. IR characterization of conformational changes

More information regarding temperature-induced polymorphism/conformation changes can be obtained by using FT-IR. The annealed sPS samples (at various isothermal temperatures) were then characterized by using FT-IR. Fig. 1(A) and (B) shows the FT-IR spectra in the frequency range of 440–640 cm^{-1} corresponding to out-of-plane modes of the phenyl C–H bending for the solvent-cast sPS samples subjected to post-cast heating (at 1 °C/min) to various temperatures as indicated on the traces. The thermal structural changes are evidenced by the IR result in Fig. 1(A), showing the conformational changes after crystal phase transition. By examining the bands of 502, 510 and 572 cm^{-1} attributed to the TTGG sequences, one can see that they all exhibit a slight decrease for samples annealed at temperatures below 200 °C, and they finally disappear at complete helix-to-*trans* phase transition. By comparisons, the band at 539 cm^{-1} exhibits an increasing trend solely at the helix-to-*trans* phase transition. For clearly observing the conformational changes on slow-heating, the absorption profile in the 440–640 cm^{-1} range was separated into five components and the integrated intensity of each band was plotted against temperatures, after normalization using the 1069 cm^{-1} peak which is generally regarded as a ring in-plane CCH bending vibration for both all-trans and helical conformation [42] and unaffected by conformational changes [26]. The result is shown in Fig. 1(B). A decrease in intensity at temperatures behind the right-hand dotted line is observed for the 502, 510, and 572 cm^{-1} bands associated with the TTGG conformation, while the 539 cm^{-1} band attributed to an all-trans planar zigzag structure shows a greater intensity. The increase in IR absorbance of 539 cm^{-1} peak (associated with the TTTT/GTTG conformation) at temperatures of 195–205 °C indicates that a structure change associated with the proportion of all-*trans* local conformation has occurred. Unlike other bands, the band at 547 cm^{-1} attributed to the GTTG conformation exhibits a stepwise decrease at these two transition points. The significant decrease was first observed at temperatures (marked as left-hand dotted line) above T_g (onset, at 20 °C/min) of ca. 95 °C, while it maintained a constant intensity at temperatures of 150–195 °C. As a matter of fact, the band of 547 cm^{-1} is not only attributed to the molecular vibration of the polymer chains in the GTTG conformation [9,18] but also related to the molecular motion of 1,1,2,2-tetrachloroethane solvent (from software database of the IR spectrum for 1,1,2,2-tetrchoroethane). Further annealing imposed on the sPS sample led to removal of the solvent from non-crystalline regions in the annealing temperatures range of ca. 95–150 °C. Upon annealing the samples to high temperatures greater than 195 °C, the band of 547 cm^{-1} showed a decreasing intensity owing to a helix to all-*trans* conformation transition.

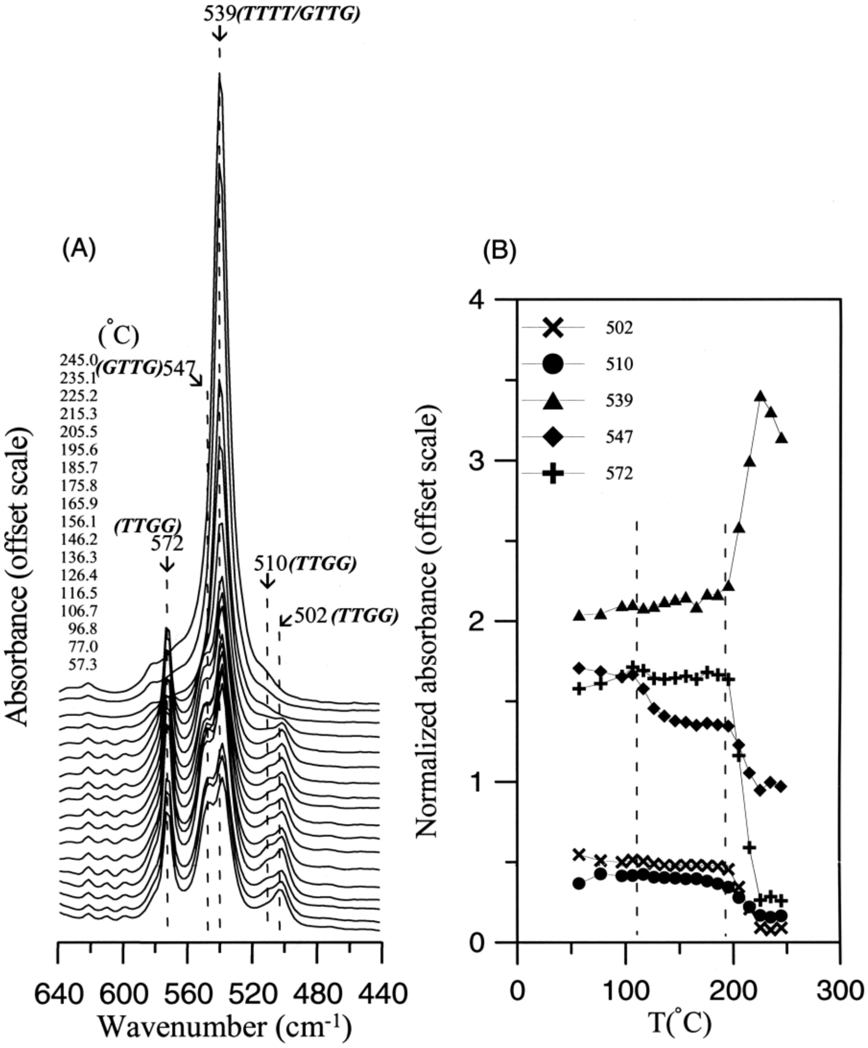

Fig. 1. FTIR spectra of solution-cast sPS sample having been subjected to step-wise increase of 10 °C in the range 60–245 °C.

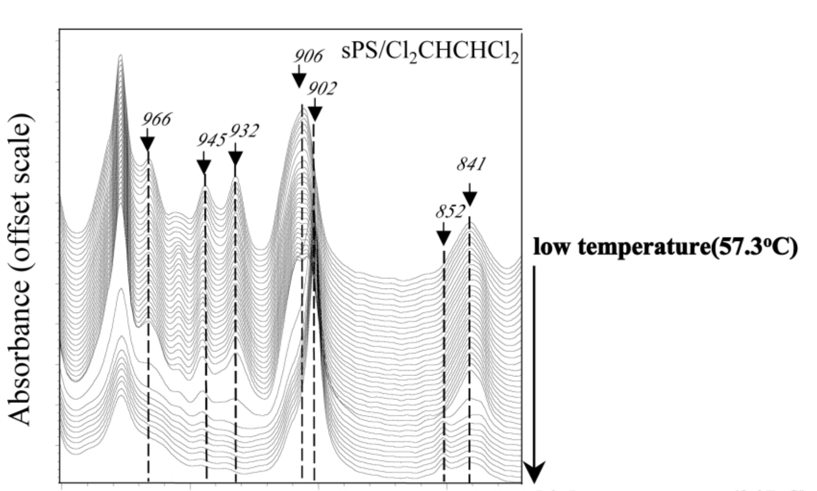

Fig. 2. FTIR spectra in the frequency ranging from 820 to 1000 cm^{-1} for the sPS sample subjected to step-wise increase of 5 °C in the temperature range 60–245 °C.

Fig. 2 shows the FT-IR spectra in the frequency range of 820–1000 cm^{-1} for the solution-cast film sPS sample subjected to similar thermal treatments. Obviously, the bands at 841 and 906 cm^{-1} are present in the sPS containing helical conformation. No significant spectral changes were observed in the temperature range of 60–195.6 °C before a helix to all-trans transition temperature was reached. Above 200.5 °C, two bands at 852 and 902 cm^{-1} start to emerge. Its intensity becomes stronger with the increasing annealing temperatures (> 200.5 °C) while the intensity of the bands at 841 and 906 cm^{-1} is increasingly depressed. It suggests a transition from a crystal with helical chains to a different crystal with a zigzag structure [11]. Additionally, note that the absorbance peaks at 932 and 945 cm^{-1}, attributed to the vibration of the helical chains packed in the crystalline form, showed no significant differences in the intensities and peak positions for samples annealed at temperatures ranging from 60 to 200 °C. For clearly identifying the IR band spectral changes as a function of annealing temperature, the temperature dependence of the normalized intensity of the bands at 932, 945 and 1222 cm^{-1} is shown in Fig. 3. Three regions labeled as Region-(II), -(III) and -(IV) are shown in the figure. Step-wise decease in the intensity is seen in the peaks of 932 and 945 cm^{-1} in region-(III). As for the peak at 1222 cm^{-1}, one can see a step increase in the same region. The changes of these three peaks whose intensity and position are sensitive for the conformation changes clearly indicate that the helical conformation is present in Region-II while the zigzag all-trans conformation is present in Region-IV. In Region-III, the helix-to-*trans* conformation change occurs via a rapid melting/re-crystallization process.

The interesting phenomenon needs to be clarified. Spell [26] have suggested that the peaks 934 and 943 cm^{-1} show greater sensitivity to the helical chains packed in the crystalline δ-form and the third peak at 940 cm^{-1} is solely caused by the packing of the helical chains in the crystalline γ-form. The increasing shift of the band from 943 to 944 cm^{-1} as well as the decreasing shift from 934 to 932 cm^{-1} is clearly seen at the δ- to γ-form transition. This is presumed from the increased inter-chain interaction as the unit cell *b* dimension is reduced during removal of the solvent from the δ-form. In this present case, apparently, these two bands (932 and 945 cm^{-1}) stay at approximately the same frequency regardless of annealing temperature as long as the temperature is lower than 200 °C, indicating that the crystalline form with helical conformation retained unchanged during the removal of the solvent.

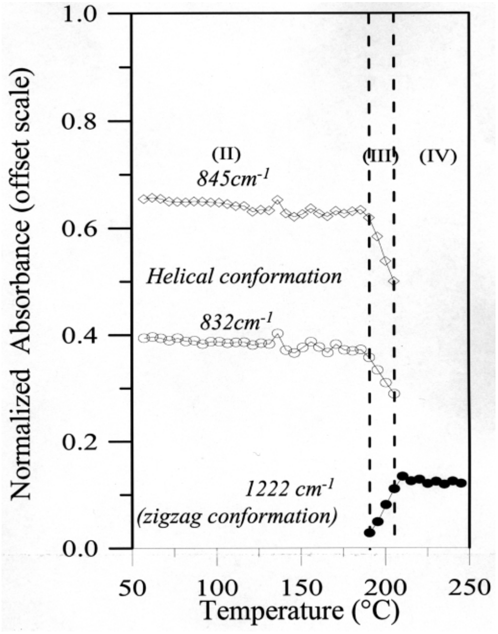

Fig. 3. Normalized relative intensities of the 832, 845 and 1222 cm^{-1} bands of cast sPS samples post-annealed at various temperatures.

It is reasoned that the solvent was trapped mainly in the non-crystalline domain and not in the crystalline domain of sPS. For proving that the solvent molecules are mainly in the amorphous chains, a model of miscible aPS with sPS was used for investigation. Samples of the blends of sPS with aPS of various compositions of sPS/aPS: (a) 100/0, (b) 90/10, (c) 75/25 and (d) 50/50 were prepared by subjecting to the same solution-cast treatments as those for neat sPS. The IR evidence in Fig. 4 shows that the 1203 cm^{-1} peak as well as 547 cm^{-1} attributed to molecular vibration of 1,1,2,2-tetrachloroethane in sPS/aPS blends becomes greater in intensity with an increase in the contents of aPS in the blends.

To identify the metastability and phase transformation of solvent-induced sPS crystals, thin film sample of sPS was examined by DSC measurement. The thermogram of DSC (scanned at 20 °C/min) is shown in Fig. 5. An endothermic peak at 199.2 °C designated as T_{m1} was identified, and the endothermic peak is attributed to the melting of crystalline

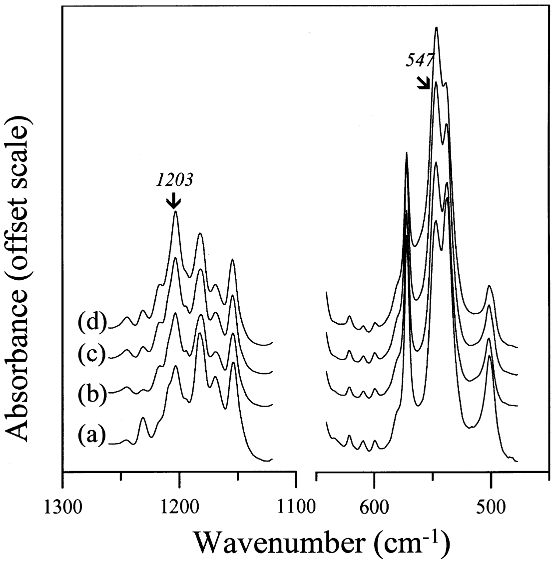

Fig. 4. IR spectra in two interested ranges for: (a) as-cast sPS film sample, and its miscible sPS/aPS blend (also solution-cast) of compositions: (b) 90/10, (c) 75/25, and (d) 50/50.

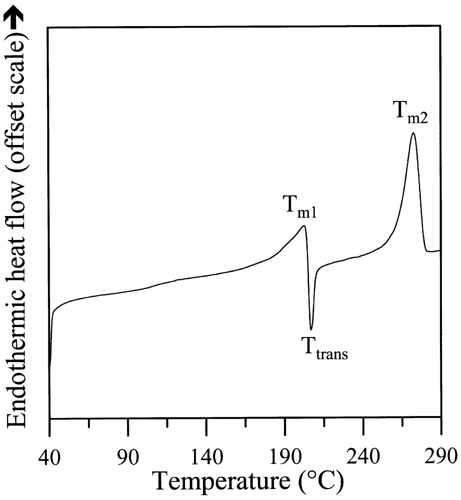

Fig. 5. DSC traces (20 °C/min) revealing the melting of γ-form crystal in sPS sample cast from 1,1,2,2-tetrachloroethane.

γ-form with helical conformation [3,7]. Several previous studies have pointed out that the melting of crystalline γ-form occur in a temperature range of 180–200 °C [3,7]. Interestingly, above this melting peak, a small exothermic peak at 205 °C designated as T_{trans} was observed. At an even higher temperature, a broad endothermic peak designated as T_{m2} was observed, which is attributed to regular α or β forms.

To further clarify the phase transition as a result of thermal-induced crystalline form changes in solution-cast sPS samples subjected to slow heating treatment, the structure of the heated/annealed samples was examined by using XRD. Fig. 6 shows the XRD patterns of the sPS sample occluding solvent initially subjected to step-increase of the temperature of 20 °C in the range 80–240 °C. The X-ray diffraction pattern of sPS samples solution-cast from 1,1,2,2-tetrachloroethane is shown in bottom spectrum. In particular, the reflection peaks at $2\theta = 9.5, 15.6, 17.2, 19.9, 21.2$ and 28.3°, attributed to the characteristics of γ-form, were observed in the X-ray diffraction pattern. This result indicated that the γ-form formed directly in as-cast sPS thin-film samples. Also, the reflection peak at 9.54°, assigned as the (010) reflection by Wang et al. [32], is broad and the (200) reflection peak is absent. This reflects that the perfection and/or crystallinity of γ-crystal packing is rather poor so as to cause the decrease and/or loss in intensity of major diffractions. Earlier literature reports have shown that the γ-form can be yielded only after drying off residual solvent from originally formed δ-type modification [1–3,7–9,26–41]. It is interesting that the sPS polymorphism is strongly dependent upon the selection of solvent for solution-casting, particularly the use of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrachloroethane. In comparison, the use of 1,1,2,2-tetrachloroethane induces the formation of γ-form whereas the 1,1,2,2-tetrachloroethane induces the δ-form [34]. For the consideration of phase metastability, the γ-form is, in principle, more stable than the δ-form due to the higher packing density of γ-form than that of δ-form [32]. It has been proposed that de-complexation of δ-form by removal of solvent leads to a decrease on the *b*-axis dimension of chain packing [32]. Under specific conditions, the δ-form rather than γ-form stabilized by the solvent in the sPS gels in the solution is preferred [43]. Berghmans, et al. [44–45] found that the phase stability of the δ-form changes with the selection of solvent. More recently, Gowd et al., however, found that the stability of the δ-crystal showed a dependency on the amount of solvent absorbed but not on the nature of the solvent [46]. Our preliminary study indicated the existence of solvent effect on the phase stability of the γ-forms, obtained by desiccating various complexes of sPS [41]. We speculate that the phase stability of the δ-form may be extremely low. The δ → γ transition might have occurred at lower temperatures such as room temperature, where solvent-plasticized sPS (or ambient room temperature) chains possess sufficient mobility to undergo such a transformation.

On the other hand, the sPS samples annealed at lower temperatures showed broader γ-form reflection peaks, being indicative of the existence of the γ-form of either poorly formed crystallites or very small crystalline domains. When the samples were annealed at higher temperatures, e.g. above 140 °C, the imperfect crystals were gradually reorganized into more perfect γ-form as indicated by an increase of diffraction intensities of the peaks at $2\theta = 9.5$ and 10.3°. In addition, the degree of perfection of crystallites increases with further increase of the annealing temperature in the range 140–200 °C, showing that reorganization of the γ-form has brought about an increase in crystallinity. Further increase of annealing temperature was imposed on the samples. The reduced intensity of the peaks at 15.9 and 20.0°, attributed to the typical reflections of the γ-form, were present at higher temperatures above 200 °C. The

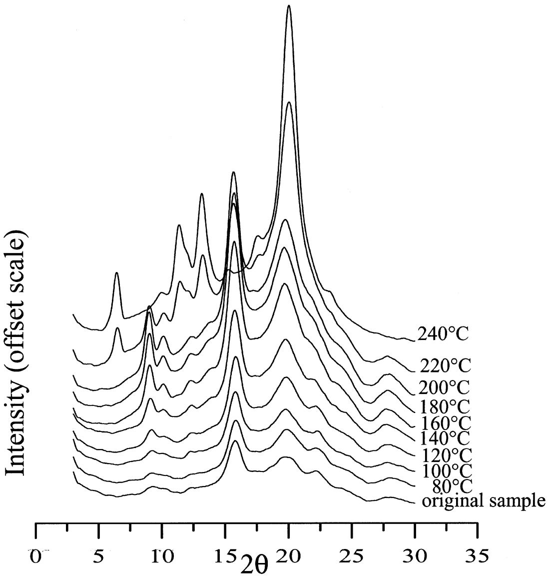

Fig. 6. XRD patterns of a solution-cast sPS film further subjected to stepwise temperature increase of 20 °C from 80 to 240 °C.

peaks at $2\theta = 6.9$, 12.2, 13.5 and 20.2°, which is related to the characteristics of the α′-form, exhibited an opposite trend, implying that a transition from γ- to α′ form occurs. At the temperature where the γ-to-α′ phase transition took place, the crystallinity seemed to exhibit a significant increase in intensities in XRD diffractogram. We believe that the remaining amorphous chains as well as the melting of the γ-from re-crystallize into the α′-form. That is, upon heating, the γ-form of a helical-chain conformation can transform into the α-form of planar zigzag chains via a melting/re-crystallization process. As evidenced by the results of in situ WAXD experiments, the exothermic response is in accordance with the phase transformation from γ-form to α′-form where the melting of γ-form coincides with the re-crystallization process to form the α′-form. The higher temperature endotherm is attributed to the melting of the α′-form.

3.2. Molecular structural changes versus annealing temperatures

A peak decomposition process is imposed on the IR spectra in the range of 720–820 cm^{-1} to reveal several separated peaks, shown in Fig. 7. Three separated components at 779, 769 and 750 cm^{-1}, respectively, are clearly seen for initially solution-cast sample in the bottom spectrum. Upon slow heating, the peaks at 779 and 769 cm^{-1} are evident in the spectrum-a–d. At 210.4 and 245.0 °C, the 750 cm^{-1} peak becomes sharper whereas the peaks at 778 and 767 cm^{-1} disappear completely. Additionally, the intensity of the 767 cm^{-1} band increases gradually with the increasing temperatures, while at the same time, the intensity of peak at 750 cm^{-1} seems to reveal a decreasing trend prior to the helix-to-*trans* transition.

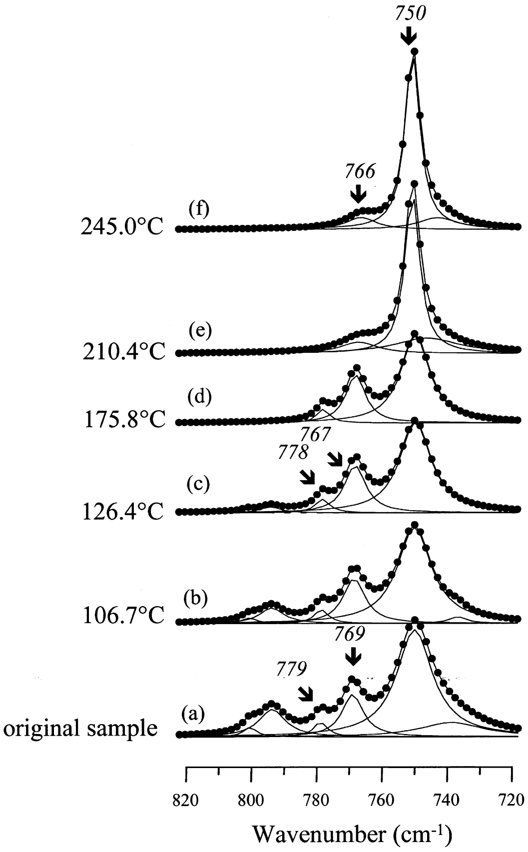

Fig. 7. IR spectra (a) as-cast sample, and cast sPS samples post-annealed at various temperatures of (b) 106.7, (c) 126.4, (d) 175.8, (e) 210.4, and (f) 245 °C.

In order to observe intensity changes of two peaks at 750 and 767 cm^{-1}, a relative intensity ratio of two peaks was plotted to analyze the transition mechanism. Fig. 8 shows the changes of intensities of these two IR bands (750 and 767 cm^{-1}), plotted as A_{767}/A_{750} and I_{767}/I_{750}, where the symbol A and I represent the relative absorbance and integrated absorbance, respectively. It was found that an initial γ-form with helical conformation could be obtained by solution-casting, and that further post-annealing at higher temperatures caused the γ-form to transform into a more perfect one with higher degrees of crystallinity. Thus, the increasing values of A_{767}/A_{750} and I_{767}/I_{750} with respect to the annealing temperature provide a piece of evidence for the fact. The figure shows that at temperature of ca. 200 °C, corresponding to a helix-to-all-*trans* transition temperature, a stepwise decease in both ratios is obvious. This shows that the polymer chains of a helical conformation go through a transformation into another crystalline form packing with chains of a zig–zag planar conformation as the annealing temperature reaches 200 °C or higher.

The ED patterns and TEM morphology of the γ-form are shown in Fig. 9 (A) and (B). Owing to low crystallinity and poor orientation, three diffused and weak ring reflections were observed. The d-spacing values were determined as $d_{\text{obs}} = 5.71(2\theta = 9.5°)$, $9.67(2\theta = 16.1°)$ and 12.25 Å $(2\theta = 20.6°)$, respectively. The results of observed reflections suggest that the formation of γ-form. Very fine crystallites with an average size of less than 100 nm were observed by TEM. To increase the crystallinity, selected

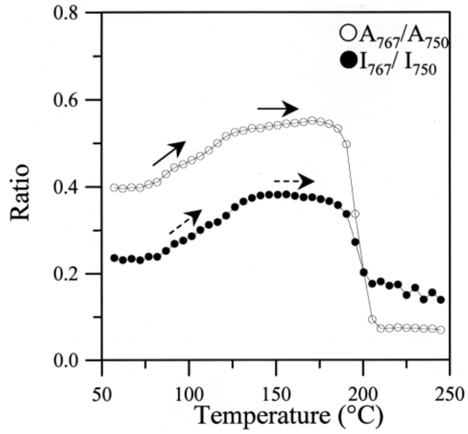

Fig. 8. Ratios of A_{767}/A_{750} and I_{767}/I_{750} for sPS films post-annealed at various temperatures. Symbols I and R represent the integrated intensity and relative intensity, respectively

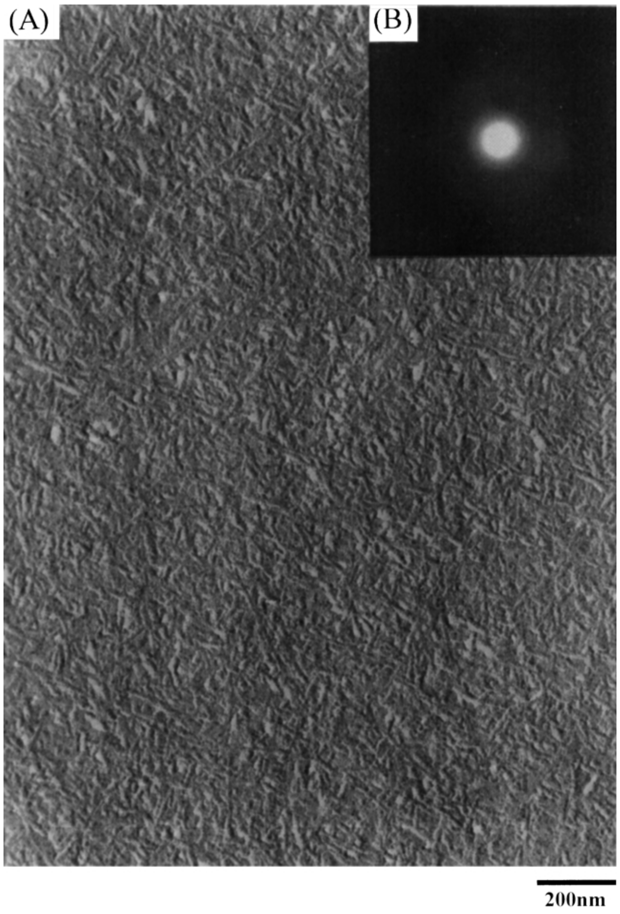

Fig. 9. (A) TEM graph, and (B) ED pattern of the γ form in sPS film solution-cast at 60 °C.

solution-cast film samples were further exposed under vapor of the solvent. For those solvent vapor-exposed samples, much stronger reflections in ED pattern were found. Similar results are also shown in Fig. 10(A) and (B), which reveals the ED pattern and morphology of the γ-form subjected to isothermal annealing at a temperature of 130 °C for 12 h in order to acquire maximum crystallinity. In comparison with the non-annealed samples, the morphology exhibited typical crystallites with slightly larger sizes of 100–200 nm in the figure. The enlarged size of the crystallites by isothermal annealing has led to a clearer powder-like ED pattern.

3.3. Effect of solvent absorbed

The original δ-form in most solution-cast sPS is usually first transformed into the γ-form crystal before subsequently into the α′-form when heated at low heating rates, but a direct transition from the δ- to β″-forms becomes possible as the cast sPS sample containing the original (-form was subjected to annealing rapidly (instead of slow heating) to a high temperature [2–3,7–11]. However, both transformations from δ- to β-form and γ- to β-form upon heating have been found to be probable [44–45]. Thus, it seems likely that the (-form could transform into not only α′-form but also β″-form depending on situations.

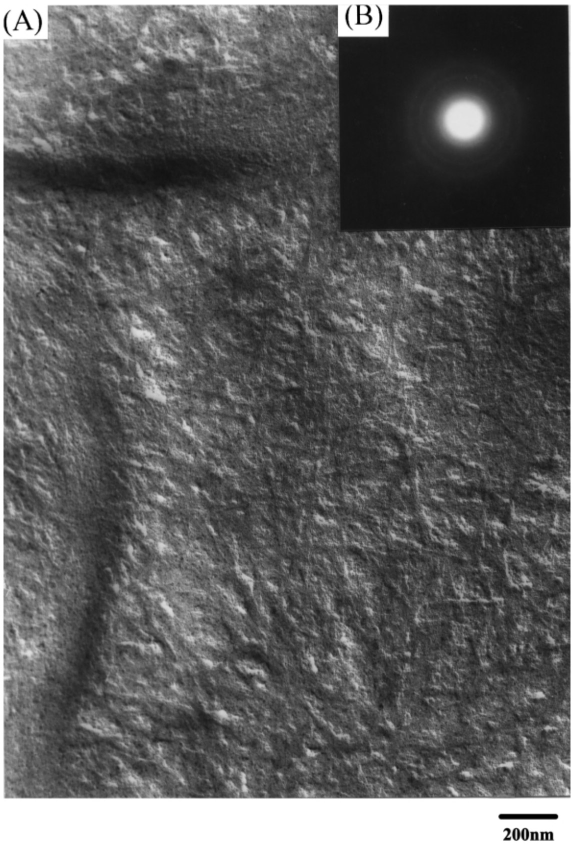

Fig. 10. (A) TEM graph, and (B) ED pattern of the γ-form in sPS film subjected to extended isothermal annealing at 130 °C for 12 h.

It is reasoned that the amounts of solvent trapped in the helical or amorphous chains might have some effects on the routes of phase/crystal transitions. To further identify whether the solvent content might affect the transition of the helical chains in the crystalline γ-form into an all-trans conformation in the orthorhombic or hexagonal α or β form, the γ-form crystals with various contents of the guest (solvent) molecules dominated within the amorphous phase were subjected to 240 °C-thermal annealing for 1 h. The result is shown in Fig. 11. Apparently, the 858 and 910 cm^{-1} bands associated with the vibrational motion of the chains in the crystalline β-form are present with a great intensity as isothermal annealing is imposed on the thin film samples including 17.7% solvent. By comparison, the 852 and 902 cm^{-1} peaks due to crystalline α′-form became more obvious by annealing the desiccated samples being initially the γ-form. It suggests that the crystal could transform from the γ-form into β-form rather than into the α-form as the contents of the solvent resident in solution-cast sample reached a certain level. This demonstrates clearly that the fractions of the crystalline β-form transformed from the crystalline γ-form are increasing with an increase of the content of the solvent molecules trapped in the samples (in the non-crystallized domain),

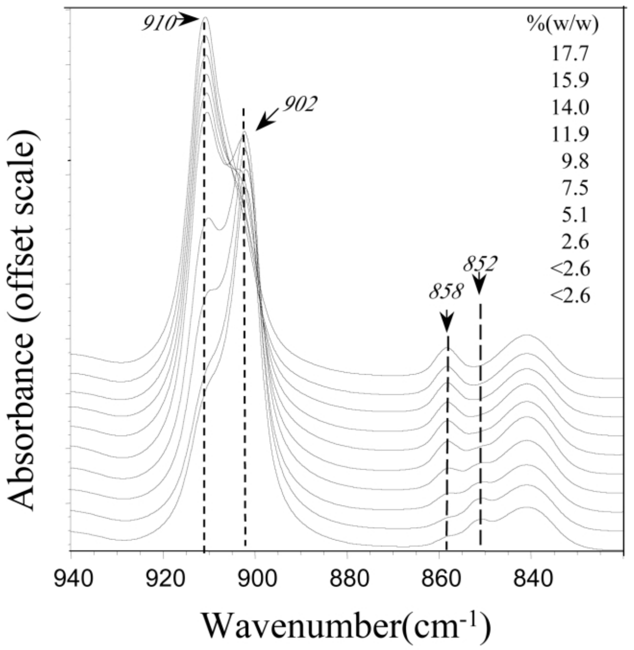

Fig. 11. IR spectra for a series of sPS samples initially occluding various contents of solvent molecules then subjected to post-annealing at 240 °C for 1 h.

indicating that the solvent trapped in sPS is favorable for the orthorhombic-packing of β-type as the samples were rapidly brought to annealing at high temperatures.

According to the DSC, XRD, TEM evidences in association with the FT-IR analysis, a visual illustration of the structural change is shown in Fig. 12, which is proposed for explaining the evidences obtained by carrying out the combination of the various measurements (FTIR, DSC and WAXD). The helical chains packed in the crystalline γ-form are illustrated as a crystalline domain of long helices. Upon heating to successive increases of the temperature in the range100–160 °C, the gradual removal of the solvent from amorphous glassy chains occurred. The crystalline γ-form can finally transform into crystalline α′-form with an all-trans conformation when the as-cast sPS was further subjected to heating to higher temperatures above 200.5 °C (in sequence of crystalline γ-form → crystalline α′-form). By contrast, a direct transition of γ → β′ was effected depending on the amount of solvent resident in the solvent-cast samples as the sPS was rapidly brought to isothermal annealing at a high temperature of 240 °C.

4. Conclusion

Previous literature reports have documented that crystalline γ-form is always proceeded by the crystalline δ-form in most solvent-cast sPS, and only after post-annealing at high temperatures of the solvent-cast sPS, the crystalline γ-form can go through a transformation into a crystalline γ-form. In this study, however, it was found that the γ-form, not δ-form, was directly obtained in thin films of sPS cast from solution in the 1,1,2,2-tetrachloroethane solvent with no post-annealing at high temperatures required. That is, no transformation from a meso crystal of δ-form into final crystal of γ-form was observed in 1,1,2,2-tetrachloroethane-cast sPS. The crystalline γ-form so directly obtained in the solution-cast sPS was isolated for various characterizations, and its morphology was found to be of imperfect crystallites with typically small sizes (< 100 nm). In addition, by using a model of miscible aPS/sPS blend system, it was proven that the solvent molecules were mainly trapped in the non-crystalline domains rather than in the crystalline phase of γ-form.

Furthermore, when the solvent-cast sPS films were brought to higher temperatures, the γ-crystal could undergo transition into other more stable crystal phases (i.e. α′ or β′) depending on the thermal schemes of annealing. It was found that, upon gradually slow heating, a γ → α′ transition took place via rapid re-crystallization (i.e. a melting/re-crystallization process) of the melted γ-crystal as well as further crystallization of the initially amorphous chains. As a result, the crystallinity increased significantly after the phase transition, which was proven by XRD equipped with in situ temperature chamber. By contrast, a direct transition of γ → β′ was effected as the sPS was rapidly brought to

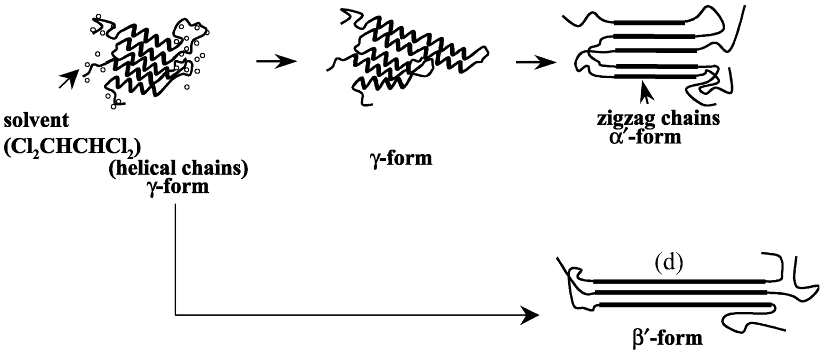

Fig. 12. Schemes illustrating the structural changes in solution-cast sPS films: (a) initial γ-from occluded with 1,1,2,2-tetrachloroethane molecules, (b) desiccated γ-form, (c) α-form, and (d) β-form.

isothermal annealing at a high temperature of 240 °C. The solvent molecules trapped in sPS during rapid temperature rising might have acted as plasticizers and eased the polymer chain motion in going from the γ-crystal to a more stable β'-crystal. This is interestingly different from the more commonly encountered phenomenon where a slow heating led to transition from γ to α'-crystal.

Acknowledgements

The work was supported by basic research grants from Taiwan's National Science Council in consecutive years (#NSC91-2216-E006-004, NSC90-2216-E006-011, and NSC 89-CPC-7-006-003). The authors are grateful to Dr Masahiko Kuramoto of Idemitsu Petrochemicals Co. Ltd (Japan), who kindly supplied the research-grade sPS material. The very helpful comments by the referees during reviewing stages have significantly improved the contents, readability, and styles of this paper.

References

[1] Kobayashi M, Nakaoki T, Ishihara N. Macromolecules 1989;22:4377.
[2] Guerra G, Musto P, Karasz FE, Macknight WJ. Macromol Chem 1990;191:2111.
[3] Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P. Macromolecules 1990;23:1539.
[4] Sun YS, Woo EM. J Polym Sci Polym Phys 2001;38:3210.
[5] Sun YS, Woo EM. Polymer 2001;42:2241.
[6] Woo EM, Sun YS, Lee ML. Polymer 1999;40:4425.
[7] Manfredi C, De Rosa C, Guerra G, Rapacciuolo M, Auriemma F, Corradini P. Macromol Chem Phys 1995;196:2795.
[8] Reynolds NM, Savage JD, Hsu SL. Macromolecules 1989;22:2867.
[9] Nakaoki T, Kobayashi M. J Mol Struct 1991;242:315.
[10] Reynolds NM, Stidham HD, Hsu SL. Macromolecules 1991;24:3662.
[11] Sun YS, Wang C, Woo EM. J Polym Res 2001;8:59.
[12] Tashiro K, Ueno Y, Yoshioka A, Kobayashi M. Macromolecules 2001;34:310.
[13] Reynolds NM, Hsu SL. Macromolecules 1990;23:3463.
[14] Rastogi S, Gupta VD. J Macromol Sci Phys 1994;B33:129.
[15] Nakaoki T, Yamanaka T, Ohira Y, Horii F. Macromolecules 2000;33:2718.
[16] Guadagno L, D'Arienzo L, Vittoria V. Macromol Chem Sci 2000;201:246.
[17] Kimura T, Ezure H, Tanaka S, Ito EJ. Polym Sci Part B: Polym Phys 1998;36:1227.
[18] Matsuba G, Kaji K, Nishida K, Kanaya T, Imai M. Macromolecules 1999;32:8932.
[19] Vittoria V, Ruvolo Filho A, De Candia FJ. Macromol Sci Phys 1990; B29:411.
[20] Vittoria V, Ruvolo Filho A, De Candia FJ. Macromol Sci Phys 1991; B30(1 and 2):155.
[21] Musto P, Tavone S, Guerra G, De Rosa C. J Polym Sci B: Polym Phys 1997;35:1055.
[22] Wu HD, Wu ID, Chang FC. Macromolecules 2000;33:8915.
[23] Wu HD, Wu SC, Wu ID, Chang FC. Polymer 2001;42:4719.
[24] Bu W, Li Y, He J, Zeng J. Macromolecules 1999;32:7224.
[25] Kellar EJC, Evans AM, Knowles J, Galiotis C, Andrews EH. Macromolecules 1997;30:2400.
[26] Moyses S, Spell SJ. Macromolecules 1999;32:2684.
[27] Rastogi S, Goossens JGP, Lemstra PJ. Macromolecules 1998;31:2983.
[28] Ishihara N, Seimiya T, Kuramoto M, Uoi M. Macromolecules 1986;19:2465.
[29] Kobayashi M, Yoshioka T, Imai M, Itoh Y. Macromolecules 1995;28:7376.
[30] Roels T, Rastogi S, De Rudder J, Berghmans H. Macromolecules 1997;30:7939.
[31] Kobayashi M, Nakaoki T, Ishihara N. Macromolecules 1990;23:78.
[32] Wang YK, Savage JD, Yang D, Hsu SL. Macromolecules 1992;25:3659.
[33] Savage JD, Wang YK, Stidham HD, Corbett M, Hsu SL. Macromolecules 1992;25:3164.
[34] De Rosa C, Rizzo P, de Ballesteros OD, Petraccone V, Guerra G. Polymer 1999;40:2103.
[35] Immirzi A, de Candia F, Iannelli P, Vittoria V, Zambelli A. Macromol Rapid Commun 1988;9:761.
[36] Vittoria V, de Candia F, Iannelli P, Immirzi A. Macromol Rapid Commun 1988;9:765.
[37] Vittoria V, Russo R, de Candia F. Polymer 1991;32:337.
[38] Chatani Y, Shimane Y, Inoue Y, Inagaki T, Ishioka T, Ijitsu T, Yukinari T. Polymer 1992;33:488.
[39] Chatani Y, Shimane Y, Inoue Y, Inagaki T, Ishioka T, Ijitsu T, Yukinari T, Shikuma H. Polymer 1993;34:1620.
[40] Chatani Y, Inagaki T, Shimane Y, Shikuma H. Polymer 1993;34:4841.
[41] Sun YS. PhD Thesis. Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan; 2002
[42] Nyquist RA, Putzig CL, Leuger MA, McLachlan RD, Thill B. Appl Spectrosc 1992;46:981.
[43] Daniel C, Guerra G, Musto P. Macromolecules 2002;35:2243.
[44] De Rudder J, Berghmans H, Arnauts J. Polymer 1999;40:5919.
[45] Roels T, Deberdt F, Berghmans H. Macromolecules 1994;27:6216.
[46] Gowd EB, Nair SS, Ramesh C. Macromolecules 2002;35:8509.