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Miscibility of syndiotactic polystyrene/atactic polystyrene blends by crystallization kinetics and enthalpy relaxation

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The miscibility of syndiotactic polystyrene (sPS)/atactic polystyrene (aPS) blends, whose constituent polymers have close T_gs was investigated by crystallization kinetics and enthalpy relaxation. It was observed from crystallization kinetics experiment that both the spherulite growth rate and the overall crystallization rate of sPS in blends decrease with an increasing amount of aPS, indicating that sPS is diluted with aPS. When enthalpy relaxations of the blends are examined, it is revealed that the enthalpy recovery of sPS/aPS blends shows a single peak whose relaxation time is intermediate between those of sPS and aPS, and that the relaxation time of the blends gradually increases with the amount of aPS. From these results, it is concluded that sPS/aPS blends are completely miscible over the entire composition. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Since syndiotactic polystyrene (sPS) with a very high degree of stereospecificity (>96%) has been successfully synthesized by stereospecific polymerization[1], characterization of this new material has been of considerable interest[2–13]. Improved mechanical properties of sPS are expected as compared with atactic polystyrene (aPS), especially at high temperature, due to its crystalline structure. Furthermore, a larger crystallization rate of sPS relative to that of isotactic polystyrene (iPS) and its high tensile modulus lead to a potential engineering plastic.

It is well known that polymer blends give an efficient way of developing new materials with tailored properties and have received much attention from both scientific and commercial points of view. Both aPS/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends and aPS/poly(vinyl methyl ether) (PVME) blends have been reported to be miscible at room temperature[14,15]. On the other hand, iPS is miscible with PPO or aPS but not with PVME[16–18]. Recently, it was reported that sPS/PPO blends are completely miscible in the amorphous phase, whereas sPS/PVME blends form a phase-separated structure[19–23]. To our knowledge, however, there is no concrete evidence concerning the miscibility of sPS/aPS blends. sPS is a crystallizable polymer whose glass transition temperature (T_g, 97.5°C) is very close to that of aPS (103.8°C). It is generally believed that most thermoanalytical techniques, e.g. d.s.c., are not adequate for examining the miscibility of polymer blends whose constituent polymers have T_g in close proximity to each other (10–20°C apart).

In this study, the miscibility of sPS/aPS blends is examined by two methods, crystallization kinetics and enthalpy relaxation. For crystallization kinetics, the following assumptions were made[24]. The crystallization of crystalline polymer (in this study, sPS) in a miscible crystalline/amorphous polymer blend is disturbed by blending with amorphous polymer (in this study, aPS) owing to a dilution effect, and hence the crystallization rate of the crystalline polymer depends upon the amount of amorphous polymer, whereas the crystallization of crystalline polymer in an immiscible blend is not influenced by blending with amorphous polymer because the crystalline polymer phase separates from the amorphous polymer phase. The use of enthalpy relaxation for miscibility is based on the fact that relaxation of polymers at temperatures below the glass transition temperature results in changes in many physical properties such as enthalpy and density. By relying on the inherent structural dependence of the kinetics of physical ageing in the form of enthalpy recovery[25,26], it has been shown that an analysis based on this phenomenon is a sensitive method of probing phase behaviour in blends whose constituent polymers have close T_g[27–30]. Assuming that a miscible blend shows a single ageing peak whose ageing kinetics is intermediate between those of component polymers, whereas an immiscible blend exhibits two ageing peaks corresponding to each of component polymers, the miscibility of sPS/aPS blends is examined.

EXPERIMENTAL

Materials and blend preparation

sPS ($M_w = 3.6 \times 10^6$ g mol^{-1}, $T_g = 97.5$°C, $T_m = 271.0$°C) was obtained from Idemitsu Kosan Co., Ltd., Japan. aPS ($M_w = 2.8 \times 10^5$ g mol^{-1}, $T_g = 103.8$°C) was purchased from Aldrich Chemical Co. The sPS/aPS blends were melt-mixed at 300°C for 7 min in a Mini-Max moulder (CS-183 MMV, Custom Scientific Instruments, Inc.). The

samples were compression-moulded into a thin film by a hot press at 300°C (except pure aPS, 200°C) for 10 min, and then quenched in a liquid nitrogen bath. All films are completely amorphous, which is confirmed by X-ray diffraction pattern.

Optical microscopy

Isothermal spherulite growth rate (*G*) was measured using a polarizing optical microscope (Nikon Microphot FXA) fitted with an automatically controlled hot-stage. For the measurement of the spherulite growth rate, films were sandwiched between two glass slides, heated at 300°C for 5 min, and then rapidly cooled to the pre-determined crystallization temperature (T_c) followed by an isothermal crystallization. The radial growth of sPS spherulite was monitored during isothermal crystallization by taking photographs at appropriate time intervals. Isothermal spherulite growth rate was obtained from the slope of plot of the radius of the growing spherulite *versus* time.

Calorimetric measurements

Overall kinetics of crystallization and enthalpy relaxation were analysed by a differential scanning calorimeter (Perkin–Elmer DSC 7). All scans were run under a nitrogen gas purge to minimize thermo-oxidative degradation and calibrated for temperature and enthalpy using indium and zinc. For isothermal crystallization, samples were heated to 300°C, held at this temperature for 5 min, and quenched to a pre-determined T_c followed by an isothermal crystallization. For enthalpy relaxation, as-quenched films were immediately sealed in a d.s.c. pan, and aged at 80°C (T_a) for various ageing times (t_a) in a heating block. Subsequently, the samples were heated from room temperature to 300°C (except pure aPS, 200°C) at a heating rate of 20°C min^{-1} to obtain thermograms of aged samples, held at this temperature for 5 min, and then quenched to room temperature. The samples were immediately reheated to 300°C (except pure aPS, 200°C) at a heating rate of 20°C min^{-1}. For a completely amorphous polymer, the enthalpy difference, $\Delta H(t_a, T_a)$ resulting from ageing, has been conventionally

measured by subtracting the d.s.c. thermogram of the second scan from that of the first scan of a sample. For a crystalline/amorphous polymer blend, however, this conventional method may lead to an overestimation of the value of $\Delta H(t_a, T_a)$ owing to underestimation of the amorphous fraction of the unaged sample. Since the crystallization rate of sPS is very fast, the amorphous fraction of the second scan samples can be much lower than that of the first scan samples owing to an increase in crystallinity of the former (see *Figure 1*). Therefore, in the present study, the enthalpy differences in pure sPS and sPS/aPS blends were obtained by subtracting the weight-normalized d.s.c. thermogram of the first scan of unaged sample from that of the first scan of aged sample, whereas $\Delta H(t_a, T_a)$ of pure aPS was measured by the conventional method.

RESULTS AND DISCUSSION

Crystallization kinetics

For all blends investigated, the spherulite radius was found to increase linearly with time until spherulites impinge upon each other, indicating a constant growth rate throughout the crystallization process. The growth rate was determined from the slope of plot of the radius of growing spherulite *versus* time. *Figure 2* shows the variation of radial growth rates of sPS spherulites with crystallization temperature for various sPS/aPS blends. As shown in *Figure 2*, the spherulite growth rate of sPS in blends decreases with increasing amount of aPS in blends at a given crystallization temperature. For example, at $T_c = 242$°C, the growth rate of sPS decreases by a factor of 1.2 and 2.5 when 10 wt% and 40 wt% of aPS are added to sPS, respectively. In general, the spherulite growth rate of the crystallizable polymer, at a given T_c, is dependent on two energetic terms[31,32]: the activation free energy required for the transport process through the liquid–solid interface, ΔF^*, and the free energy for the formation of a nucleus of critical size, $\Delta \phi^*$. For a miscible crystalline/amorphous polymer blend, the amorphous polymer, as a diluent, might influence both the transport term (ΔF^*) and the thermodynamic term
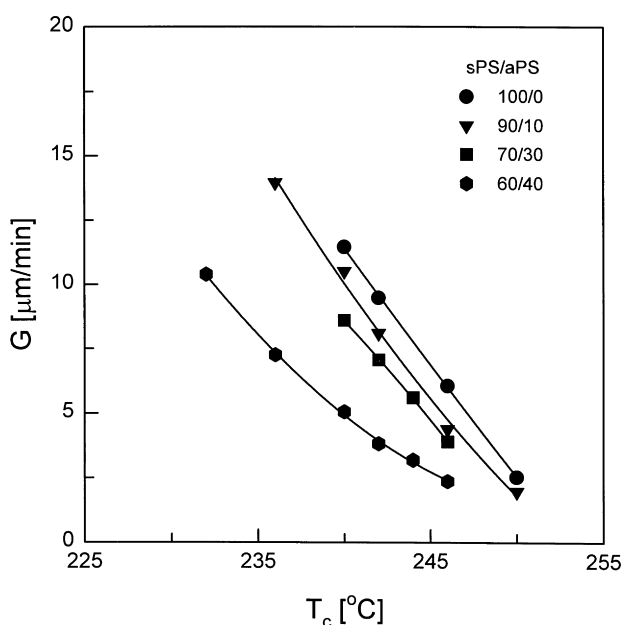

Figure 1 Representative DSC thermograms of pure sPS aged at 80°C for various ageing times. Thick and thin lines represent the first and second scans, respectively
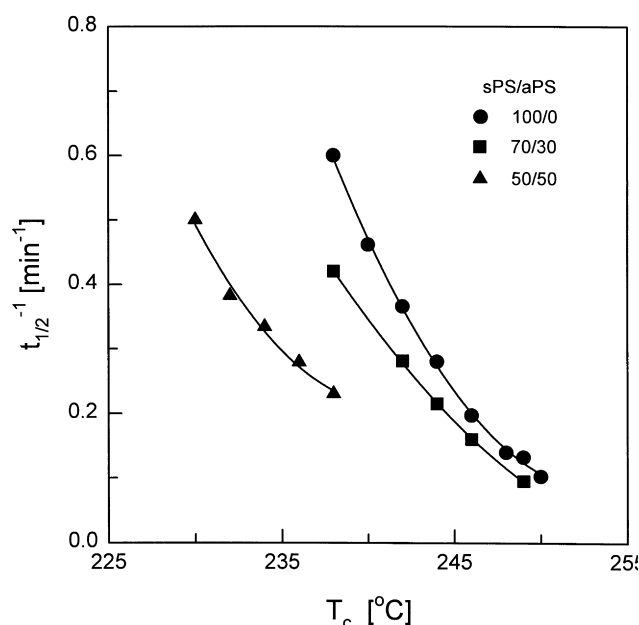

Figure 2 Plots of spherulite growth rate *versus* crystallization temperature for sPS/aPS blends

($\Delta\phi^*$). The effect of a diluent on ΔF^* may be accounted for by considering the difference between the glass transition temperature of the blend and that of the crystallizable component: when T_g (blend) is higher than T_g (crystallizable component), ΔF^* (blend) may be higher than ΔF^* (crystallizable component), resulting in a decrease in spherulite growth rate of the blend; conversely, when T_g (blend) is lower than T_g (crystallizable component), ΔF^* (blend) becomes lower than ΔF^* (crystallizable component), implying an increase in spherulite growth rate of the blend. For sPS/aPS blends, the variation of T_g with composition is not discernible because of the proximity of T_gs of two component polymers. Therefore, it is evident that the growth rate reduction of sPS/aPS blends is not related to changes in transport process that may be of importance in blend systems showing a wide variation of T_g with blend composition[33]. Thus, the decrease in spherulite growth rate of sPS/aPS blends is due to an increase of $\Delta\phi^*$ which may arise from a dilution effect associated with a diminished concentration of crystallizable components at the crystal growth front[34].

The kinetics of isothermal crystallization from the melt of sPS is analysed by the well-known Avrami equation[35]:

$$1 - X_t = \exp(-kt^n) \tag{1}$$

where X_t is the weight fraction of crystallinity at time t, k is the overall kinetic rate constant, and n is the Avrami exponent related to the nucleation mechanism and growth dimensions. equation (1) is rewritten as

$$\log[-\ln(1 - X_t)] = \log k + n \log t \tag{2}$$

A plot of the left-hand side of equation (2) versus $\log t$ should yield a straight line from which the Avrami exponent and $\log k$ can be determined. The values of Avrami exponent of sPS/aPS blends, contrary to the theoretical prediction, are not integers and range between 2 and 3, indicating mixed nucleation mechanisms which are similar to those of sPS/PPO blends[21]. The inverse of half-time of crystallization, $t_{1/2}^{-1}$, can be used as a measure of overall crystallization rate of sPS. From the plot of $t_{1/2}^{-1}$ *versus* T_c
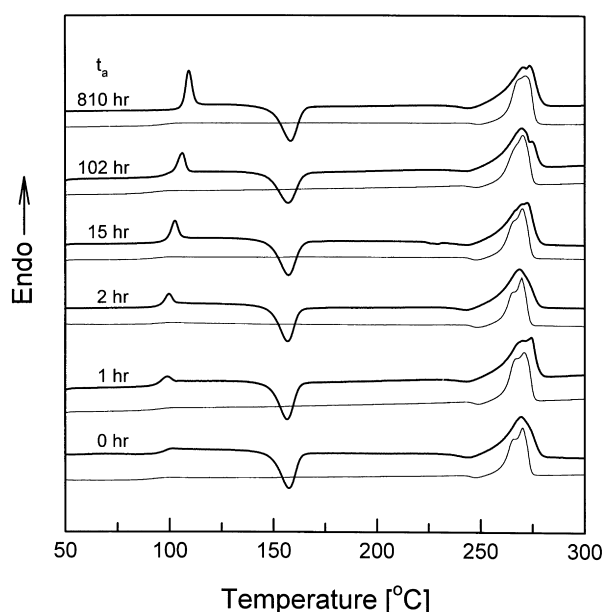
as shown in *Figure 3*, it is observed that the addition of aPS to sPS, at a given T_c, causes a decrease in $t_{1/2}^{-1}$, which is very similar to the behaviour of *Figure 2*. These results may provide evidence that sPS is miscible with aPS, since it is generally known that for a miscible crystalline/amorphous polymer blend, the crystallization rate of the crystalline polymer in blends depends upon the amount of amorphous polymer.

Enthalpy relaxation

To gain further insight into the miscibility of sPS/aPS blends, the behaviour of enthalpy relaxation of sPS/aPS blends was investigated. *Figure 1* shows d.s.c. thermograms of pure sPS aged at 80°C for the indicated ageing times, t_a. For the first scan after ageing, the aged samples usually show three peaks: an endothermic overshoot peak at near T_g, which results from enthalpy recovery; a crystallization exothermic peak at 157°C; a melting endothermic peak at 271°C. As the ageing time increases, the maximum of the enthalpy recovery peak (T_{max}) shifts towards higher temperatures and the magnitude of the peak area increases, which is typical of enthalpy relaxation phenomena[25–30]. For the second scan, the enthalpy recovery peaks and crystallization peaks completely disappear, indicating that the enthalpy lost on ageing is fully recovered during the first scan and that the crystallinity of the second scan sample is much larger than that of the first scan sample. It is also observed that the melting enthalpy of sPS is slightly larger than the crystallization enthalpy and that a small exotherm appears just before melting. This implies that recrystallization of sPS occurs during heating scan, as also observed by other workers[36]. *Figure 4* shows representative d.s.c. thermograms of sPS/aPS blends aged at 80°C for 4 h. As mentioned in the Introduction, a miscible blend generally shows a single peak where its ageing kinetics is intermediate between those of component polymers, whereas an immiscible blend exhibits two ageing peaks corresponding to each of the component polymers. In *Figure 4*, sPS/aPS blends show a single overshoot peak intermediate between those of the two component polymers, suggesting that the blends are miscible. When T_{max} is plotted against the logarithm of t_a for

Figure 3 Plots of overall crystallization rate *versus* crystallization temperature for sPS/aPS blends. The overall crystallization rate is represented by the reciprocal crystallization half-time
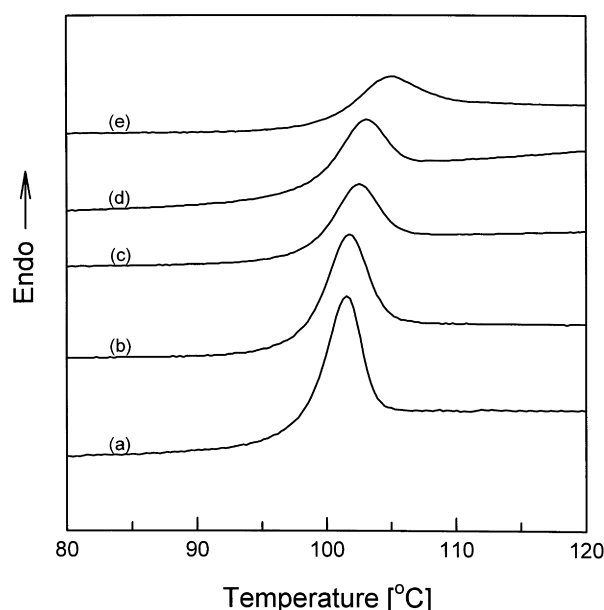

Figure 4 Representative DSC thermograms of sPS/aPS blends aged at 80°C for 4 h: (a) 100/0; (b) 70/30; (c) 50/50; (d) 30/70; (e) 0/100

sPS/aPS blends, as shown in *Figure 5a*, it is revealed that T_{max} is approximately proportional to log t_a for all samples. The linear relationship between T_{max} and log t_a is well established for aged glass when the thermodynamic state of aged glass is not too close to equilibrium[26]. When T_{max} is plotted against the concentration of aPS in blends as shown in *Figure 5b*, T_{max} gradually increases with the concentration of aPS at a given t_a, suggesting that the sPS/aPS blends are miscible because T_{max} could be used as a measure of the glass transition temperature of the blends. According to the model of Cowie and Ferguson[37,38], the relaxation of enthalpy toward an equilibrium state can be described by the following equation:

$$\Delta H(t_a, T_a) = \Delta H(t_\infty, T_a)[1 - \Phi(t_a)] \qquad (3)$$

where $\Delta H(t_a, T_a)$ and $\Delta H(t_\infty, T_a)$ represent the enthalpy lost on ageing for t_a at T_a and on reaching the equilibrium structure at T_a, respectively. In equation (3), the relaxation function $\Phi(t_a)$ is often expressed by the Kohlrausch–Williams–Watts (KWW) form:

$$\Phi(t_a) = \exp\left[-\left(\frac{t_a}{t_c} \right)^\beta \right] \qquad (4)$$

where β is the non-exponentiality parameter, and t_c is a relaxation time. The relaxation function describes the kinetics of the approach of the system to the equilibrium state. The three parameters, $\Delta H(t_\infty, T_a)$, β and t_c, are determined by fitting experimental data to equations (3) and (4). *Figure 6* shows the enthalpy difference of sPS/aPS blends as a function of ageing time. It is observed
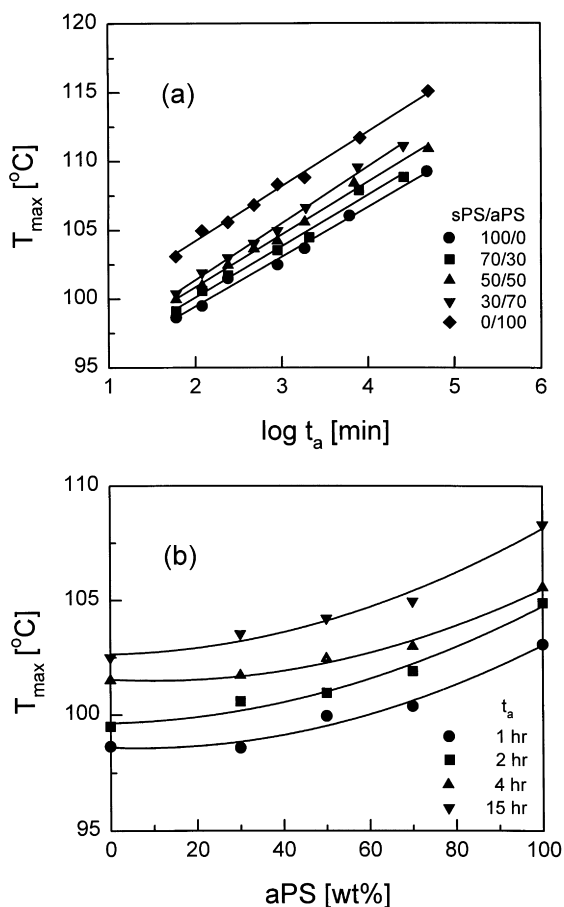
Figure 6 Plots of $\Delta H(t_a, T_a)$ *versus* log t_a for sPS/aPS blends aged at 80°C. Symbols and lines represent the experimental data and the non-linear curve-fitting by equation (3) and equation (4), respectively

Figure 5 Variation of T_{max} with (a) log t_a and (b) the concentration of aPS, when the samples are aged at 80°C
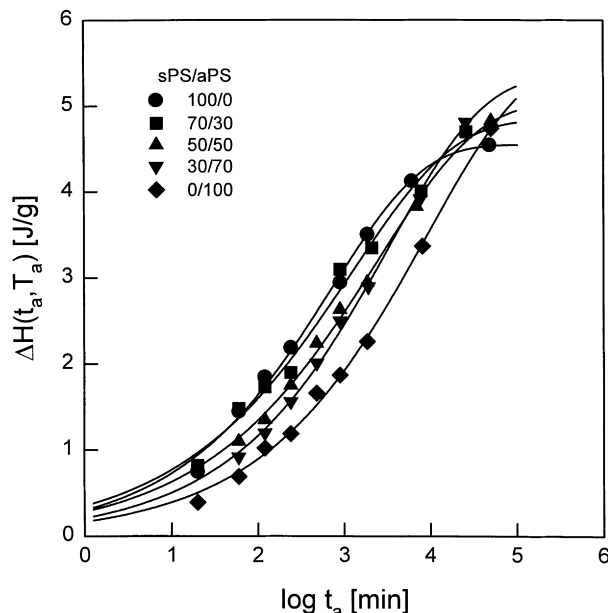
Figure 7 Plots of $\Phi(t_a)$ *versus* log t_a for sPS/aPS blends aged at 80°C. Symbols and lines represent the experimental data and the non-linear curve-fitting by equation (3) and equation (4), respectively
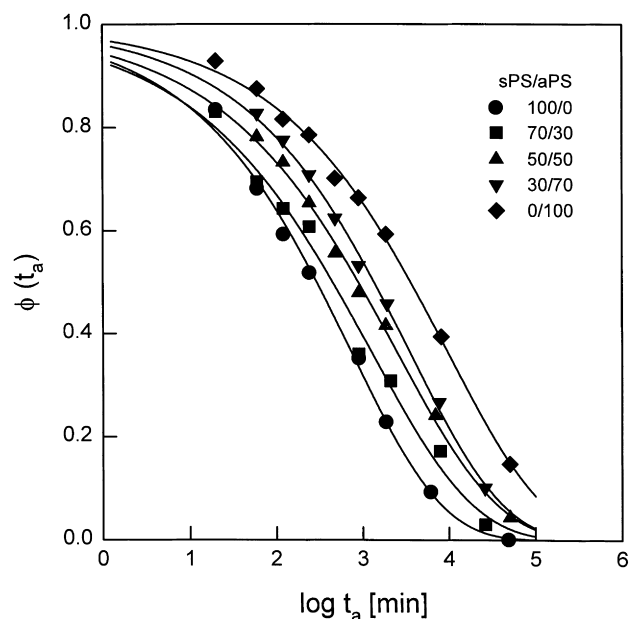
that $\Delta H(t_a, T_a)$ increases with logarithm of t_a and that it decreases with increasing the amount of aPS in blends at a given t_a. The corresponding plots of $\Phi(t_a)$ as a function of log t_a for sPS/aPS blends are shown in *Figure 7*. The relaxation of sPS/aPS blends becomes slower as the amount of aPS increases, indicating that the blends are miscible over entire composition. The fitting values of $\Delta H(t_\infty, T_a)$, β and log t_c are listed in *Table 1*. It is shown that both values of $\Delta H(t_\infty, T_a)$ and t_c increase with the amount of aPS in blends owing to an increase of the temperature difference between the glass transition and the ageing temperature, $(T_g - T_a)$, while the parameter β is approximately constant (≈ 0.383) for all samples examined here. When the relaxation times of

Table 1 Parameters in equations (3) and (4), and error limits determined by non-linear least-squares curve fit for sPS/aPS blends

sPS/aPS	$\Delta H(t_\infty, T_a)$(J g)	β	$\log t_c$ (min)
100/0	4.533 ± 0.115	0.408 ± 0.024	2.858 ± 0.067
70/30	4.844 ± 0.333	0.364 ± 0.041	3.091 ± 0.188
50/50	5.049 ± 0.163	0.367 ± 0.020	3.386 ± 0.087
30/70	5.350 ± 0.267	0.396 ± 0.022	3.536 ± 0.115
0/100	5.559 ± 0.376	0.382 ± 0.022	3.975 ± 0.157
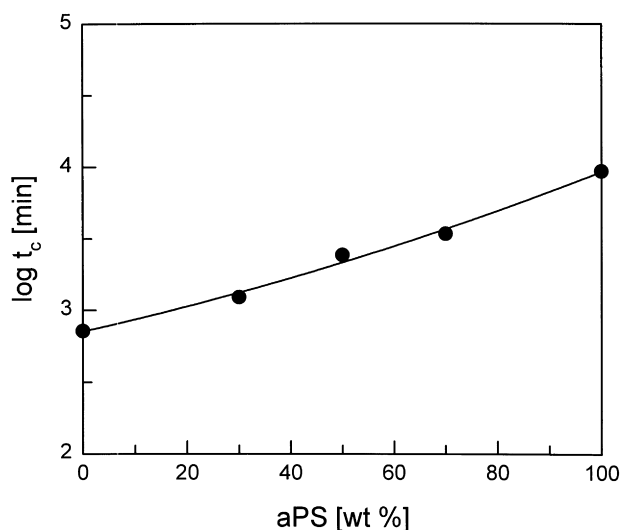
Figure 8 Composition dependence of $\log t_c$ for sPS/aPS blends aged at 80°C

sPS/aPS blends are plotted against the concentration of aPS as shown in *Figure 8*, it is clear that the relaxation times are composition-dependent. Consequently, it is suggested that sPS/aPS blends are completely miscible over the entire composition examined.

CONCLUSIONS

The miscibility of sPS/aPS blends was investigated by two methods, the crystallization kinetics and enthalpy relaxation. It is observed from crystallization kinetics experiment that both the spherulite growth rate and the overall crystallization rate of sPS in blends decrease with increasing the amount of aPS, indicating that sPS is miscible with aPS. For enthalpy relaxation, the enthalpy recovery of sPS/aPS blends shows a single peak where the relaxation time is intermediate between those of sPS and aPS. It is observed that both the enthalpy recovery peak (T_{max}) and $\Delta H(T_\infty, T_a)$ increase with the amount of aPS in the blends. It is also observed that the relaxation times of sPS/aPS blends gradually increase with the amount of aPS. From these results, it is concluded that sPS/aPS blends are completely miscible over the entire composition.

REFERENCES

1. Ishihara, N., Seimiya, T., Kuramoto, M. and Uoi, M., *Macromolecules*, 1986, **19**, 2464.
2. Guerra, G., Vitagliano, V. M., De Rosa, C., Petraccone, V. and Corradini, P., *Macromolecules*, 1990, **23**, 1539.
3. Vittoria, V., de Candia, F., Iannelli, P. and Immirzi, A., *Makromol. Chem. Rapid Commun.*, 1988, **9**, 765.
4. Wang, Y. K., Savage, J. D., Yang, D. and Hsu, S. L., *Macromolecules*, 1992, **25**, 3659.
5. Hong, B. K., Jo, W. H., Lee, S. C. and Kim, J., *Polymer*, 1997, in press.
6. Greis, O., Xu, Y., Asano, T. and Petermann, J., *Polymer*, 1989, **30**, 590.
7. Sun, Z. and Millar, R. L., *Polymer*, 1963, **1993**, 34.
8. De Rosa, C., Rapacciuolo, M., Guerra, G., Petraccone, V. and Corradini, P., *Polymer*, 1992, **33**, 1423.
9. Chatani, Y., Shimane, Y., Inoue, Y., Inagaki, T., Ishioka, T., Ijitsu, T. and Yukinari, T., *Polymer*, 1992, **33**, 488.
10. Chatani, Y., Shimane, Y., Inagaki, T., Ijitsu, T., Yukinari, T. and Shikuma, H., *Polymer*, 1993, **34**, 1620.
11. Roels, T., Deberdt, F. and Berghmans, H., *Macromolecules*, 1994, **27**, 6216.
12. Kellar, E. J. C., Galiotis, C. and Andrews, E. H., *Macromolecules*, 1996, **29**, 3515.
13. de Candia, F., Russo, R. and Vittoria, V. J., *Polym. Sci.: Part C: Polym. Lett.*, 1990, **28**, 47.
14. Stoelinting, J., Karasz, F. E. and Macknight, W. J., *Polym. Eng. Sci.*, 1970, **10**, 133.
15. Bank, M., Leffingwell, J. and Thies, C., *Macromolecules*, 1971, **4**, 43.
16. Plans, J., Macknight, W. J. and Karasz, F. E., *Macromolecules*, 1984, **17**, 810.
17. Yeh, G. S. Y. and Lambert, S. L., *J. Polym. Sci., Part A-2*, 1972, **10**, 1183.
18. Amelino, L., Martuscelli, E., Sellitti, C. and Silvestre, C., *Polymer*, 1990, **31**, 1051.
19. Cimmino, S., Di Pace, E., Martuscelli, E. and Silvestre, C., *Polym. Commun.*, 1991, **32**, 251.
20. Cimmino, S., Di Pace, E., Martuscelli, E., Silvestre, C., Rice, D. M. and Karasz, F. E., *Polymer*, 1993, **34**, 214.
21. Cimmino, S., Di Pace, E., Martuscelli, E. and Silvestre, C., *Polymer*, 1993, **34**, 2799.
22. Guerra, G., De Rosa, C., Vitagliano, V. M., Petraccone, V., Corradini, P. and Karasz, F. E., *Polym. Commun.*, 1991, **32**, 30.
23. Guerra, G., De Rosa, C., Vitagliano, V. M., Petraccone, V. and Corradini, P. J., *Polym. Sci.: Part B: Polym Phys.*, 1991, **29**, 265.
24. Sasaki, H., Bala, P. K., Yoshida, H. and Ito, E., *Polymer*, 1995, **36**, 4805.
25. Struik, L. C. E., *Physical Aging in Amorphous Polymers and Other Materials*. Elsevier, Amsterdam, 1978.
26. Hodge, I. M. and Berens, A. R., *Macromolecules*, 1981, **14**, 1599.
27. Bosma, M., ten Brinke, G. and Ellis, T. S., *Macromolecules*, 1988, **21**, 1465.
28. Grooten, R. and ten Brinke, G., *Macromolecules*, 1989, **22**, 1761.
29. Oudhuis, A. A. C. M. and ten Brinke, G., *Macromolecules*, 1992, **25**, 698.
30. Ellis, T. S., *Macromolecules*, 1990, **23**, 1494.
31. Wunderlich, B., *Macromolecular Physics*, Vol. II. Academic Press, New York, 1976.
32. Martuscelli, E., *Polym. Eng. Sci.*, 1984, **24**, 563.
33. Wang, T. T. and Nishi, T., *Macromolecules*, 1977, **10**, 421.
34. Boon, J. and Azcue, J. M., *J. Polym. Sci., Polym. Phys. Ed.*, 1968, **6**, 885.
35. Avrami, M. J. J., *Chem. Phys.*, 1939, **7**, 1103.
36. de Candia, F., Russo, R. and Vittoria, V., *Macromol. Chem. Phys.*, 1994, **195**, 735.
37. Cowie, J. M. G. and Ferguson, R., *Macromolecules*, 1989, **22**, 2307.
38. Cowie, J. M. G. and Ferguson, R., *Macromolecules*, 1989, **22**, 2312.