

Polymer Communication

Preparation of physical gel consisting of syndiotactic polystyrene and poly(ethylene glycol)

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Abstract

Syndiotactic polystyrene (s-PS) was blended with poly(ethylene glycol) (PEG) in 1,2-dichloroethane (DCE) solvent. The mixture became a homogeneous solution at 155 °C depending on the composition ratio of PEG to DCE. When the solution was cooled at the rate of 5 °C/min to room temperature, a thermoreversible gelation was occurred. Wide angle X-ray diffraction (WAXD) measurements revealed that the polymer chain of s-PS in the obtained gel was crystallized with a helical conformation, while that in the non-gelated sample was done with an all-trans planar zigzag conformation.

After drying gelated samples at 70 °C for 24 h, a novel polymer blend type of the physical gel consisting of s-PS and PEG was obtained. Dynamic mechanical analysis (DMA) revealed that the physical gel had a high modulus and a long elastic plateau in the temperature range of –80–270 °C.

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1. Introduction

Thermoreversible gelation of syndiotactic polystyrene (s-PS) has been widely studied in the past decade [1–4]. When s-PS is swollen by a small molar mass solvent such as toluene or chloroform, polymer chains of s-PS are crystallized with a helical conformation by clathrating the solvent of a suitable size [4]. Intermolecular associations of these helical chains are reported to play an important role as a network junction in the thermoreversible gel [5,6].

More recently, thermoreversible gelation of s-PS using binary solvent mixtures has investigated by several researchers in order to clarify a solvent selectivity during the formation of clathrate compounds [7–11]. Daniel et al. reported that 1,2-dichloroethane (DCE) was preferred in the binary solvent system of DCE and 1-chlorotetradecane (CTD) for the clathrate formation of s-PS [7]. They also reported that a physical gel consisting of s-PS and CTD was obtained by removing DCE which was temporarily existed

as a preferential guest compound for the clathrate structure [8]. Since the helical crystal structure of s-PS was still remained after removing DCE, it acted as a network junction in the physical gel. Both the existence of the network junction and the non-volatile solvent such as CTD which was localized in the amorphous part of s-PS polymer chains improved the mechanical property of the physical gel.

In this communication, we demonstrate that a thermoreversible gel consisting of s-PS and polyethylene glycol (PEG) is obtained in an existence of DCE which is acted as a guest compound for the formation of the clathrate structure of s-PS. We also reports that a novel polymer blend type of the physical gel consisting of s-PS and PEG is obtained by removing DCE completely.

2. Experimental part

2.1. Materials

s-PS ($M_w = 1.12 \times 10^6$, $M_w/M_n = 2.41$) was kindly supplied by Idemitsu Petrochemical Corporation. A series of PEGs (M_n was 200, 1000, and 4000, relative density = 1.

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127 g/ml) was purchased from WAKO Pure Chemicals and used without further purification. DCE (molecular mass = 98.96, relative density = 1.256 g/ml) and other reagents were purified by conventional methods.

2.2. Preparation of a thermoreversible gel and a polymer blend typed gel

s-PS (0.3 g, 2.1×10^{-5} mol/l) prepared in amorphous state by quenching from melt was mixed with a various composition ratio of PEG to DCE by weight in a Taiatsu Glass Co. V-300 type glass reactor at room temperature. The mixture was heated at 155 °C for 1 h and a transparent homogeneous solution was obtained. Cooling it to the room temperature at the rate of 5 °C/min, we confirmed that it became clouded and lost the fluidity at a temperature around 100 °C. After drying the thermoreversible gel at 70 °C for 24 h in a vacuum oven, a novel type of the physical gel consisting of s-PS and PEG was obtained.

2.3. Characterization

Thermal properties of an obtained physical gel consisting of s-PS and PEG were measured on a Rigaku DSC 8230B at a heating rate of 10 °C/min in nitrogen atmosphere. WAXD measurements were carried out using a rotating-anode X-ray generator (Rigaku-Denki, RU-300) operated at 40 kV, 240 mA at room temperature. The specimen was irradiated by Cu K α radiation (1.542 Å) monochromatized with a graphite monochromator. Each two-dimensional diffraction pattern was recorded onto an imaging plate (IP) and read out as digital data for a computational process using an IP-system (MAC Science, DIP-220).

To investigate mechanical properties of the physical gel, DMA measurements were performed using a rheometer (MR500) at the temperature range from –100 to 280 °C at a frequency of 1 Hz under a N₂ atmosphere.

3. Results and discussion

3.1. Preparation of a thermoreversible gel

s-PS (2.1×10^{-5} mol/l) was mixed with a various composition ratio of PEG ($M_n = 200$) to DCE in a reactor at room temperature. A transparent homogeneous solution was obtained at 155 °C when the ratio of PEG to DCE was 0:10, 1:9, 2:8, 3:7, and 4:6 (w/w). A homogeneous solution of s-PS was also obtained with a high molecular weight PEG ($M_n = 1000$ or 4000) at the constant ratio of PEG to DCE (1:9). Taking that s-PS is hardly miscible with PEG into consideration, we assume that the temporary presence of the DCE solvent gives a significantly influence on the miscibility between s-PS and PEG chains as a co-solvent [12]. When the ratio of PEG to DCE was 5:5, 7:3, and 10:0 (w/w), on the other hand, a phase separation between s-PS

and PEG was remained at 155 °C. Even if the mixture was heated at 200 °C, no homogeneous solution was obtained. It indicates that the formation of a homogeneous solution depends on the composition ratio of PEG to DCE against s-PS. We suggest that the degree of inhomogeneity is increased with an increase of the composition ratio of PEG due to the decrease of its solubility against the s-PS solution.

When the homogeneous solution was cooled at the rate of 5 °C/min to room temperature, it became an opaque uniformly and lost the fluidity. While it was heated to 155 °C, it became transparent again. It indicates that the thermoreversible gelation was occurred upon the cooling process. Table 1 shows the result of the gel formation. Gelation was occurred from the homogeneous solutions except for one prepared at the ratio of PEG and DCE of 4:6 (w/w) which was separated into two phases i.e. a gel part and a transparent solution macroscopically. It is noted that no gelation was occurred from the inhomogeneous solutions containing a separated s-PS. A further study on the effect of the molecular weight and the dosage of PEG upon its gelation mechanism is now in progress and published later.

Fig. 1 shows WAXD diffractograms of a gelated (a), an extracted (b), a phase-separated (c) and a neat (d) s-PS sample after drying at room temperature for 48 h in a vacuum oven. In a diffraction pattern of the gelated s-PS sample prepared at the ratio of PEG and DCE of 1:9 (w/w), a sharp peak at $2\theta = 8.1^\circ$ and a broad peak in the range between $2\theta = 13$ and 30° were observed. The latter peak is attributed to the amorphous hallow scattered from PEG chain. In order to elucidate the former one, s-PS was extracted from the gelated sample by acetone and methanol each for 2 h. After extraction, several peaks at $2\theta = 8.1, 13.5, 17.5, 20.3, 24.0,$ and 28.6° were observed as shown in Fig. 1(b). These peaks were identified by a typical diffraction pattern of δ_e -form of s-PS which had cavities in crystal structure consisting of helical polymer chains [9]. From these results, we suggest that the sharp peak at $2\theta =$

Table 1
Results of physical gels of s-PS

PEG:DCE ^a	Gel formation ^b	
	After reaction	After drying ^c
0:10	○	Powder
1:9	○	○
2:8	○	○
3:7	○	○
4:6	×	×
5:5	–	–
7:3	–	–
10:0	–	–

s-PS: 0.3 g, 2.1×10^{-5} mol/l, $M_w = 1.12 \times 10^6$, $M_w/M_n = 2.41$.

^a PEG: $M_w = 200$, $d = 1.127$ g/ml.

^b ○: The physical gel was formed, ×: The phase separation was observed, –: The mixture was immiscible.

^c Resulting polymers were dried at room temperature for 48 h in a vacuum oven.

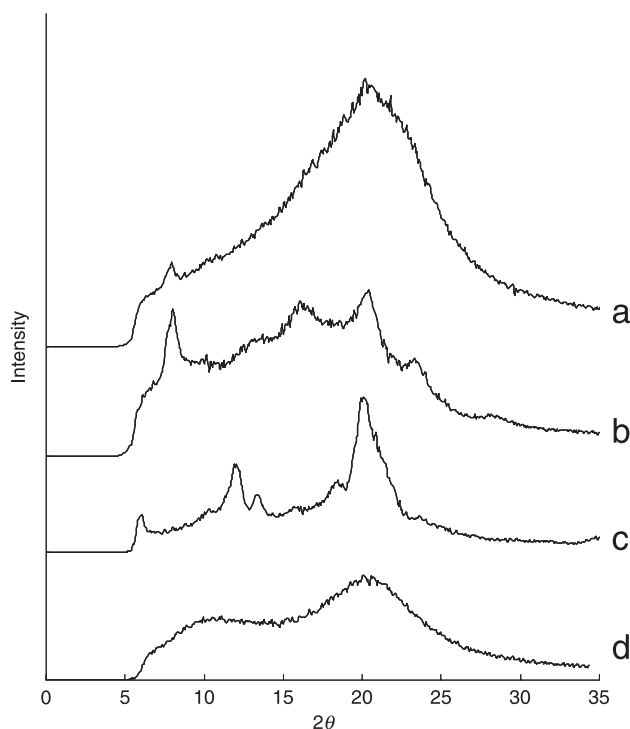


Fig. 1. WAXD diffractograms of a gelated (a), an extracted (b), a phase-separated (c) and a neat (d) s-PS sample after drying at room temperature for 48 h in a vacuum oven.

8.1° in Fig. 1(a) is one of the diffraction peaks of the δ -form of s-PS with $2\theta = 8.1, 10.5, 17.5, 20.3, 24.0,$ and 28.6° and is corresponded to 010 reflection of the crystal structure of s-PS [10].

In a diffraction pattern (c) of a phase-separated s-PS sample, several sharp peaks between at $2\theta = 6.2^\circ$ and ca. 20° were observed, which showed the typical reflections of the orthorhombic β -form of s-PS crystal structure in which polymer chains adopt an all-trans planer zigzag conformation [11]. It indicates that the thermoreversible gelation of s-PS is occurred only when the s-PS crystal structure is configured as δ -form by clathrating a solvent. On the other hand, two broad peaks with maximal values at $2\theta = 10$ and 20° were observed in the neat s-PS as shown in Fig. 1(d). These peaks were attributed to the amorphous hallow scattered from s-PS chain. The thermoreversible gelation of s-PS in combination with PEG in DCE solution is related closely to the crystallization of s-PS from a homogeneous solution, supposing that the s-PS crystal region plays a role as a network junction in the thermoreversible gel.

3.2. Mechanical properties of the physical gel

As shown in Table 1, obtained thermoreversible gel remains to be a gel after removing DCE by drying under vacuum at 70°C for 24 h. It may be due to the fact that PEG with a low T_g approximately -80°C , which is confirmed by DSC measurement, exists in the matrix consisting of an amorphous part of s-PS polymer chains in the physical gel.

It is reasonable that a thermoreversible gel consisting of only s-PS and DCE (i.e. PEG:DCE=0:10) become powder states after drying. Fig. 2 shows the result of the DMA measurement of a resulting physical gel consisting of s-PS and PEG prepared at the ratio of PEG and DCE of 2:8 (w/w). In the range of the temperature from -100 to 280°C , the values of storage modulus (G') were higher than that of loss modulus (G'') throughout the entire range of investigated frequencies, indicating that the physical gel had a high elasticity. We also confirmed the frequency dependence of G' and G'' for the same gel sample measured at 25°C . G' was much larger than G'' and both of them were independent on the frequency between 0.01 and 10 Hz. These features were in agreement with the mechanical definition of a gel which should display a solid-like behavior [13]. A broad peak in $\tan \delta$ was observed at 120°C , which was corresponded to the endothermic peak observed in DSC chart, supporting that a transition of the morphology could be occurred in this point. Further investigation on the crystal morphology at this temperature is necessary.

It is interesting to note that a long plateau region was observed in the both G' and G'' between the T_g of PEG at -80°C and the T_m of s-PS approximately at 270°C . This unique long plateau was observed in all physical gels consisting of s-PS and different dosage of PEG obtained in this work. It suggests that a crystal region of s-PS forms a network junction three-dimensionally in a matrix consisting of PEG and s-PS polymer chains in the physical gel. In fact, we confirmed that both G' and G'' were drastically dropped down when the temperature went beyond the melting point of s-PS. It indicates that the network junction of the physical gel is crystallites. From these results, we suggest that the physical gel obtained from the polymer blend of s-PS and PEG has a good mechanical property in the wide range of the temperature.

4. Conclusion

A thermoreversible gel was obtained from a homogeneous solution consisting of s-PS and PEG in DCE when it was cooled at the rate of $5^\circ\text{C}/\text{min}$ from 155°C to room temperature. The WAXD measurements revealed that the crystal structure of s-PS in the obtained gel was the clathrate crystal structure with a helical polymer chain. Taking that s-PS is immiscible with PEG into consideration, we suggests that the temporarily existed DCE can behave as a co-solvent of each component in a polymer blend as well as a guest compound for the formation of the clathrate structures of s-PS.

After drying gelated samples at 70°C for 24 h, a novel polymer blend type of the physical gel consisting of s-PS and PEG was obtained with no macroscopic phase separation. DMA measurements revealed that the novel type of a physical gel consisting of s-PS and PEG was found to have a strong mechanical property and a high thermal

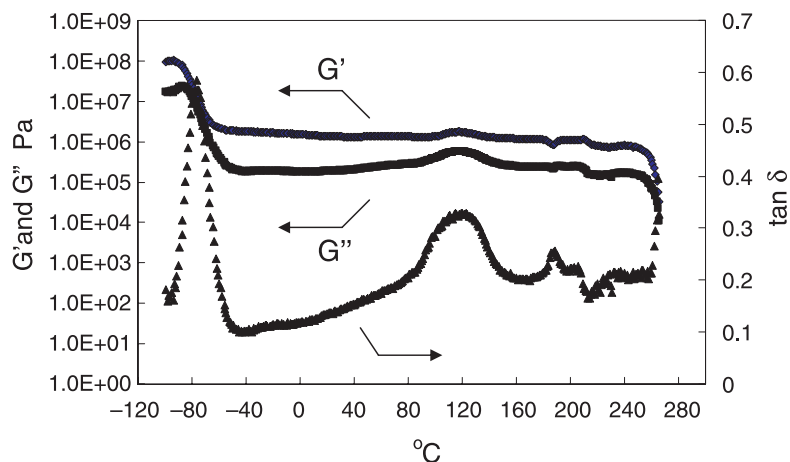


Fig. 2. DMA charts for the physical gel consisting of s-PS and PEG obtained by drying the thermoreversible one prepared at the ratio of PEG and DCE of 2:8 (w/w).

stability. One of the most important suggestions here is that the crystallite of s-PS not only plays a role of the network junction in the physical gel but also prevents the macroscopic phase separation between s-PS and PEG.

References

- [1] Ishihara N, Seimiya T, Kuramoto M, Uoi M. *Macromolecules* 1986; 19:2464.
- [2] Tashiro K, Sasaki S. *Prog Polym Sci* 2003;28:451.
- [3] Woo EM, Sun YS, Yang CP. *Prog Polym Sci* 2001;26:945.
- [4] Kobayashi M, Nakaoki T, Ishihara N. *Macromolecules* 1990;23:78.
- [5] Daniel C, Dammer C, Guenet JM. *Polymer* 1994;35:4243.
- [6] Matsuba G, Kaji K, Kanaya T, Nishida K. *Phys Rev* 2002;E65: 061801.
- [7] Daniel C, Alfano D, Guerra G, Musto P. *Macromolecules* 2003;36: 1713.
- [8] Daniel C, Alfano D, Guerra G, Musto P. *Macromolecules* 2003;36: 5742.
- [9] De Rosa C, Guerra G, Petraccone V, Zpirossi B. *Macromolecules* 1997;30:4147.
- [10] Daniel C, Guerra G. *Soft Mater* 2004;2:47.
- [11] Uda Y, Kaneko F, Kawaguchi T. *Macromol Rapid Commun* 2004;25: 1900.
- [12] Dewal L, Ouyang H, Dimonie V. *J Appl Polym Sci* 1995;58:265.
- [13] Flory PJ. *Faraday Discuss Chem Soc* 1974;57:7.