Viscoelastic and Gelation Studies of SEBS Thermoplastic Elastomer in Different Hydrocarbon Oils

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Abstract: Poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) triblock copolymer was studied by dissolving the ethylene butylene midblock in selective hydrocarbon oils. These oils differ in their aromatic, paraffinic and naphthenic content. Dynamic rheological studies showed that the storage modulus (G') exceeded the loss modulus (G'') for all the gels over the entire range of frequency, thereby confirming them as physical gels. However, the behavior of G' and G'' as a function of frequency depended primarily on the oil type. The gelation melting temperature decreased drastically with increased oil aromaticity. Small angle X-ray scattering studies revealed that the maximum interdomain interference shifted to a higher angle depending on the composition and type of hydrocarbon oil.

Keywords: physical gel, viscoelastic properties, triblock copolymer, SEBS.

Introduction

Poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) is a thermoplastic elastomer which polystyrene in the range between 20 to 35%. This thermoplastic elastomer is obtained by the hydrogenation of triblock copolymers of styrene and butadiene (SBS). It has glass transition temperature (T_g) of its rubber block below -50 °C, thereby retaining the rubbery properties even at low temperatures. The triblock copolymer of styrene and ethylene-butylene (SEBS) and styrene and isoprene (SIS) are widely used for the modification and compatibilization of blends.[1] The major applications are in adhesives, sealants, coatings, footwear industry, automotive parts and others. In recent years, physically associating thermoplastic elastomer (TPE) gels have attracted scientific and technical interest. These gels are formed when a triblock copolymer of styrene is dissolved in selective solvents for the midblock, wherein the solvent is not able to dissolve the endblocks. TPE gels are hydrophobic and can be processed as thermoplastic materials at high temperature.[2,3] The ability of the TPE gels to establish bridges between micelles which in turn can form three-dimensional network in a matrix of solvent and dissolved midblocks has been a subject of great investigation. If the micelle forming block is a glassy polymer such as polystyrene, then the PS micelles serve as physical crosslink sites and the resultant copolymer/solvents solution behaves as physical gels. Since the

formation of the micelles is a thermoreversible process, these TPE gels have a unique network behavior providing high elasticity. The temperature where it shows rubber like behavior can be easily adjusted by changing the polymer concentration. Numerous significant researches have been done in understanding the structural morphologies,[4-11] viscoelastic and thermal properties[12-18] of these systems in different solvents like extender oil, *n*-octane, etc. The results showed that gels exhibited a pronounced superstructure and rheological properties, which is a function of the block copolymer concentration, molar mass, end/block ratio, deformation and temperature.

The purpose of this particular study is to ascertain the effect of different types of hydrocarbon oils whose content differs in the concentration of aromatic, paraffinic and naphthenic hydrocarbon on the properties of thermoreversible physical gels. The linear viscoelastic properties of SEBS triblock copolymer gels was taken for study and investigated as a function of temperature and frequency. Gelation melting temperature and swelling behavior of TPE gels were also studied. Small angle x-ray scattering (SAXS) was employed to confirm the arrangement of microdomains of TPE gels.

Experimental

Materials. The poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) triblock copolymers, Kraton G1652 employed in this study was produced by the Shell Co. Ltd (USA), with styrene/rubber ratio of 29/71, as reported by the manufac-

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turer.[19] The chemical structure is shown in Figure 1. According to GPC analysis, the number-average molecular weight (M_n) and polydispersity index was 76,000 and 1.03 respectively. Four different hydrocarbon mineral oils with varying mixtures of aromaticity, paraffinic and naphthenic hydrocarbon content were used in this study, supplied by Michang Oil Industrial Co. Ltd, South Korea. The hydrocarbon type and its molecular weight of extender oil are presented in Table I. Its molecular weight was discerned from the ASTM D2502 testing procedure. These oils were blended with the triblock copolymer SEBS without further purification and designated as P1, P2, P3, and P4 respectively. These oils have a solubility parameter close to that of the elastomeric midblocks and believed to be incompatible with the polystyrene end blocks of the triblock copolymers.[20]

Gels Preparation. Sample gels were prepared by dissolving the triblock copolymer in hydrocarbon mineral oil at 150 °C using a mixer under vacuum condition until homogeneous clear solutions were obtained and then allowed to cool to room temperature in order to form transparent and highly elastic gels. Sample TPE gel used in this study has weight fraction of 0.65, 0.75, and 0.85 by using different hydrocarbon mineral oils. Sheets were molded in a hydraulic press at 150 °C and cooled rapidly in running water to room temperature.

Viscoelastic Behavior. The dynamic rheological measurements were conducted on a rheometrics mechanical spectrometer (RMS) Stresstech HR model, Rheologica Instruments, USA operated with 25 mm parallel plate geo-

Figure 1. Chemical structure of poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) triblock copolymers.

metry and a 1.5 or 2.5 mm gap heights. The moduli were measured at two different via low frequency range 10^{-1}-20 rad/s and a higher frequency range of 1-10^2 rad/s both at a constant strain (γ_o) of 1% at three different temperatures (25, 80, and 100 °C). The values of the dynamic storage and loss modulus (G' and G'') were also recorded at the temperature range 30-180 °C with increments of 10 °C/min.

Gelation Melting Temperature. The gelation melting temperature was determined by two methods. The first method is by tilting a test tube containing the gel heated to its melting temperature.[17] The temperature at which the solution no longer flows was taken as the gelation melting temperature, T_{GM}. The second method is by measuring the elastic storage modulus (G') and loss modulus (G'') as a function of temperature at a frequency of 1 Hz in the RMS Stresstech HR model, Rheologica Instruments, USA. The temperature at which G' crosses G'' was considered gelation melting temperature, or softening point since it marks the transition from a solidlike state to a viscoelastic liquid-like state.[17]

Small-Angle X-ray Scattering (SAXS) Measurement. The isothermal SAXS measurements were carried out in a D8 Discover instrument with GADDS, system of Bruker AXS (Germany). The scattering experiments use the radiation from a sealed X-ray tube with copper anode and a Siemens generator (Kristalloflex 760). The distance between the sample and the linear detector was 30 cm. The scattered intensity is recorded and analyzed with Hi Star detector. Since SAXS measurement was conducted at different testing time, the scattering patterns and xyz frame were also different. The scattering patterns were collected as 3600 s frames for P1, P2, P3 sample gels and neat SEBS, and 600 s for P4 sample gel. For neat SEBS, P1, P2, P3 sample gels, SAXS frame was at x=-1.94, y=19.234, and z=2.737 and while x=-0.308, y=20.424, and z=9.545 for P4 gel.

Swelling Experiment. Swelling studies were done by measuring the sample weight before and after immersing in excess oil until it reached equilibrium at room temperature (25 °C). The swelling ratio was calculated as follows: Swelling ratio, $S = P/P_o$, where P is the weight after immersion, P_o is the weight of original sample before immersion.
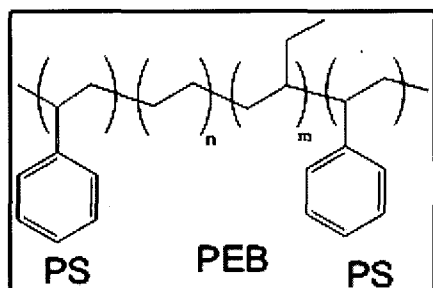
Table I. Compositions of Different Hydrocarbon Oils

TPE Gels Code	Type of Oil	Hydrocarbon Type, %*			Molecular Weight	Kinematic Viscosity (S.U.S) 40 °C cSt
		C_A	C_N	C_P		
P1	P1	4	48	48	380	8.0
P2	White oil 4060	0	52	48	400	10.2
P3	White oil 1100	0	36	64	500	20.5
P4	P100	0	29	71	680	137

*C_A=aromatic, C_N=naphthenic, and C_P=paraffinic.
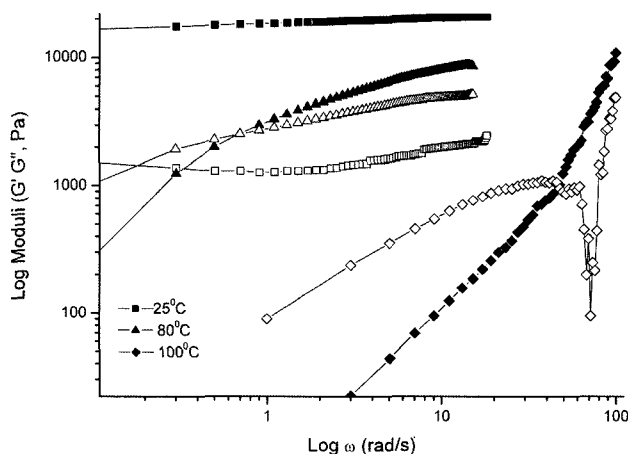
Results and Discussion

Viscoelastic Behavior. In order to get a better idea on the rheological properties of TPE gels with respect to their concentration, composition and type of hydrocarbon oil, SEBS TPE gels were subjected to rotational dynamic mechanical studies, the sample material was strained sinusoidally, both the in-phase and out-of-phase components of stress was measured as a function of frequency and temperature. The storage modulus (G') is a measure of the stored (and recoverable) elastic energy in a cyclic deformation, while loss modulus (G'') is a measure of the energy lost as heat.

Effect of Frequency. The sample gels have been measured as a function of frequency at a temperature of 25, 80, and 100 °C. Shown in Figure 2 are the frequency spectra obtained at 25 °C from P4 TPE gels with different amounts of P4 oil, which is expressed as weight fraction of oil 0.65, 0.75, and 0.85. All the gels were confirmed to behave as physical gels. Here, we mean physical gel as a liquid-rich system exhibiting solid-like behavior, with the characteristics of showing flat mechanical spectrum in an oscillatory shear experiment.[21] The results show G' exceeds G'' over the entire frequency range, and G' is virtually independent of frequency at this 1% strain. On the other hand, G'' is only independent of frequency at oil weight fraction of 0.75 and 0.65. Since the material formed with oil weight fraction of 0.85 is a soft gel, which flows like high viscosity solution, G'' has the tendency to become frequency dependent at very low frequency. Both moduli (G', G'') decrease monotonically with increasing oil content. This characteristic, as discussed by Laurer[13,14] reflects due to the presence of increase fraction of mineral oil (a viscous liquid) in which the distance
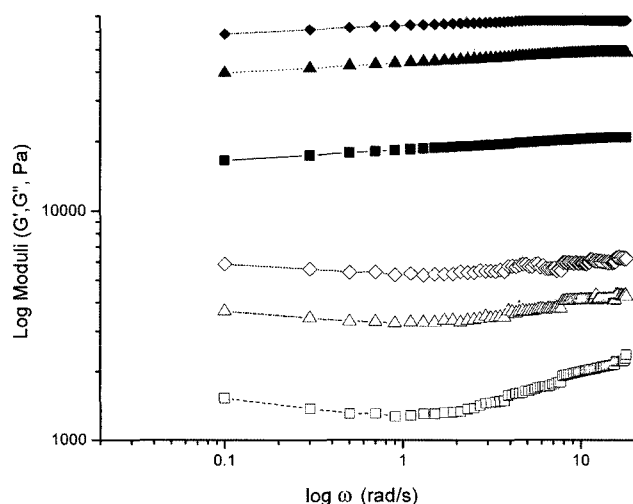
between micelles increases and the bridge midblocks become more highly stretched. The energy penalty associated with the formation of midblock bridges results in an increase in looped and dangling midblocks thereby resulting in the corresponding reduction in the elastic copolymer network.[20] The effect of frequency at different temperatures (25, 80, and 100 °C) for TPE gels with 0.85 weight fraction of P4 oil is shown in Figure 3. The spectra for gel measured at 25 °C indicate that G' remains independent of frequency and consistently greater than G'', which is a typical characteristic of a gel. A further increase in temperature to 80 °C causes G' to become frequency dependent, which implies that the gel is no longer a physical gel at this temperature. Since 80°C is above the gelation melting temperature of this type of gel as shown later, the gel is in the liquid-like state. As expected, similar behavior is observed for TPE gel heated at 100 °C. An increase in both moduli (G' and G'') for TPE gels heated at 80 and 100 °C exhibited temporary entanglement network due to topological constraints they impose to each other.[22] For entanglement networks (pseudogel) at low frequency $G' \sim \omega^2$ and $G'' \sim \omega^1$, while as the frequency is decreased there is a cross-over in G' and G''. At the very low frequencies, in the terminal zone they flow as high viscosity liquids.[21] The behavior of the gel is like isolated solid particles in the liquid environment. With further increase in frequency, a big depth in G'' and continues increase of G' are observed, indicating plateau region is obtained.[21] In this region, the entangled rubbery chains relax due to the movement of hard phases acting as glassy solid. Therefore G'' decreases with frequency until the frequency becomes less than the relaxation time of the midblock soft phase. Again with further increase in frequency, the G'' increases once again as the molecules do not have enough time to relax. In Figure 4,


Figure 2. Dynamic storage modulus, G', (close symbols) and loss modulus, G'', (open symbols) presented as a function of oscillatory frequency (ω) at a strain amplitude of 1% at 25 °C for P4 gels with different amounts of oil with weight fraction of 0.65 (diamond), 0.75 (triangle), and 0.85 (square).

Figure 3. Dynamic storage modulus, G', (filled symbols) and loss modulus, G'', (open symbols) presented as a function of oscillatory frequency (ω) at a strain amplitude of 1% strain for P4 gels with weight fraction of 0.85 at temperature of 25 °C (square), 80 °C (triangle), and 100 °C (diamond).

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dynamic storage (G') and loss moduli (G'') of TPE gels with weight fraction of 0.85 for different types of hydrocarbon oil taken at 25 °C are given. From the figure, we can deduce that the type of hydrocarbon oil used for dissolving the midblock of the TPE has significant effect on the rheological properties of gel. The G' and G'' moduli decrease monotonically depending on the amount of paraffinic content and molecular weight of hydrocarbon oil. This behavior suggests that the midblock of the copolymer was dissolved in the low molecular weight hydrocarbon oil and large fraction of oil penetrates the polystyrene domains resulting in higher stretching of the physical network, which has very weak cross-links in the chain. Another possible explanation is due to partial mixing of polystyrene endblock and ethylene-butylene midblocks.[23] This phenomenon was observed by Soenen and *et al.*,[16] wherein the glass transition lowers due to the presence of oil in the polystyrene domains. All gels may seem to behave as physical gels as indicated by their moduli behavior showing G' exceeding G'' over the entire range of frequency as about an order of magnitude. However, the behavior of G' and G'' as a function of frequency depend on the type of oil. In the case of P3 and P4 TPE gels, G' is virtually independent of frequency at 1% strain, which is consistent with the dynamic mechanical behavior of a physical gel. The G'' of P3 and P4 TPE gels slightly decreases and then increases with increasing frequency. Both (G' and G'') moduli of P1 and P2 gels are dependent on frequency but tend to a constant value at high frequency. On the other hand G' decreases more sharply as the frequency becomes lower and G'' tends to decrease with increasing frequency. This behavior suggests that the junctions are not strong enough and under a weak stress they will eventually split and, therefore, the long-time behavior of P1 and P2 TPE gels will be liquidlike. Similar
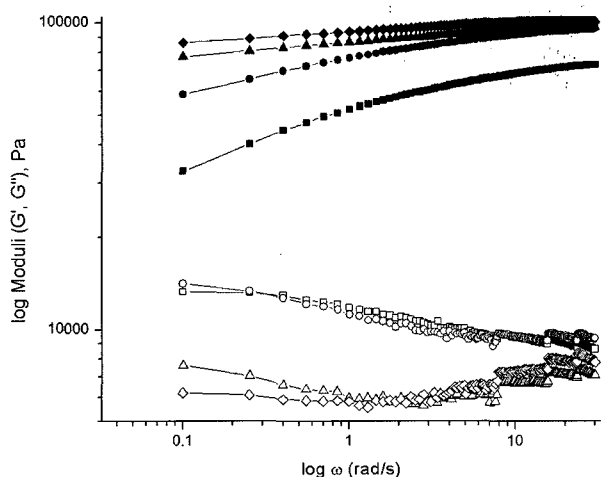

Figure 4. The frequency (ω) spectra of G' (filled symbols) and G'' (open symbols) are displayed for 0.85 weight fraction of TPE gels with varying types of hydrocarbon oil, P1 (square), P2 (circle), P3 (triangle), and P4 (diamond).

results were obtained by Quintana[17] for different molecular weight of SEBS.

Effect of Temperature. The storage modulus, G' was also determined as a function of temperature as shown in Figure 5(a), 5(b), 5(c), and elastic modulus, G'' in Figure 5(d). The figure shows that the TPE gels P1 and P2 TPE gels exhibited similar G' and G'' behavior, whereas P3 and P4 TPE gels have similar trends. Since the P1 and P2 TPE gels containing oil with weight fraction of 0.85 are in semi-liquid state at ambient temperature, G' and G'' moduli decrease monotonically as the temperature increases (see Figure 5(a)). This characteristic reflects reduction in the elastic copolymer network which can be attributed to the penetration of a small fraction of oil in the polystyrene phase. On the contrary, gels containing P3 and P4 behave as elastic solid-like at a typical application of 30 °C. Above 60 °C, they start to decrease thereby indicating a softening of the gel structure. On decreasing the hydrocarbon oil content in P1 and P2 TPE gels, G' and G'' moduli relatively change their behavior. At 0.65 weight fraction of oil, the G' and G'' curves have shown similar behavior as in 0.85 of P3 and P4 gels. The values of G' and G'' linearly decrease with increasing oil concentration for all types of hydrocarbon oils. At temperature between 25 and 30 °C, the TPE gels have the property of elastic moduli, G' nearly independent of frequency and G'' is much longer than G' as can be seen in Figure 2. This indicates that at ambient temperature a physical network is present. This is in accordance with observations made by many scientists.[15,17,18,21,24] The P3 and P4 TPE gels where the oil contains relatively higher paraffinic hydrocarbon than P1 and P2 TPE gels result in higher moduli in their solid state. Decrease in the molecular weight and with certain amount of aromaticity of oil in gels gives very low moduli at ambient temperature. Thus, it can be concluded from the rheological data that the elastic behavior of the gels are associate to the formation of midblock bridges, dangling ends and midblock loops in which different hydrocarbon oils contribute to such characteristics.

Gelation Melting Temperature. The influence of different types of hydrocarbon oil and copolymer concentration on the gelation melting temperature is shown in Figure 6, where the gelation melting temperature, T_{GM} is plotted as a function of hydrocarbon oil contents. T_{GM} was measured by two different methods. In the first method, a test tube containing the gel was tilted from it vertical to slightly horizontal position and the temperature at which the solution no longer flows was taken as the gelation melting temperature, T_{GM}. Although, the test seems to be simple, it was found to be giving accurate results as observed by Quintana.[17] The second method is based on the observations from the dynamic rheometer. On heating the as-prepared samples in dynamic rheometer, the storage modulus G' and loss modulus G'' will cross at temperatures above the glass transition at which point the system will lose its elasticity and

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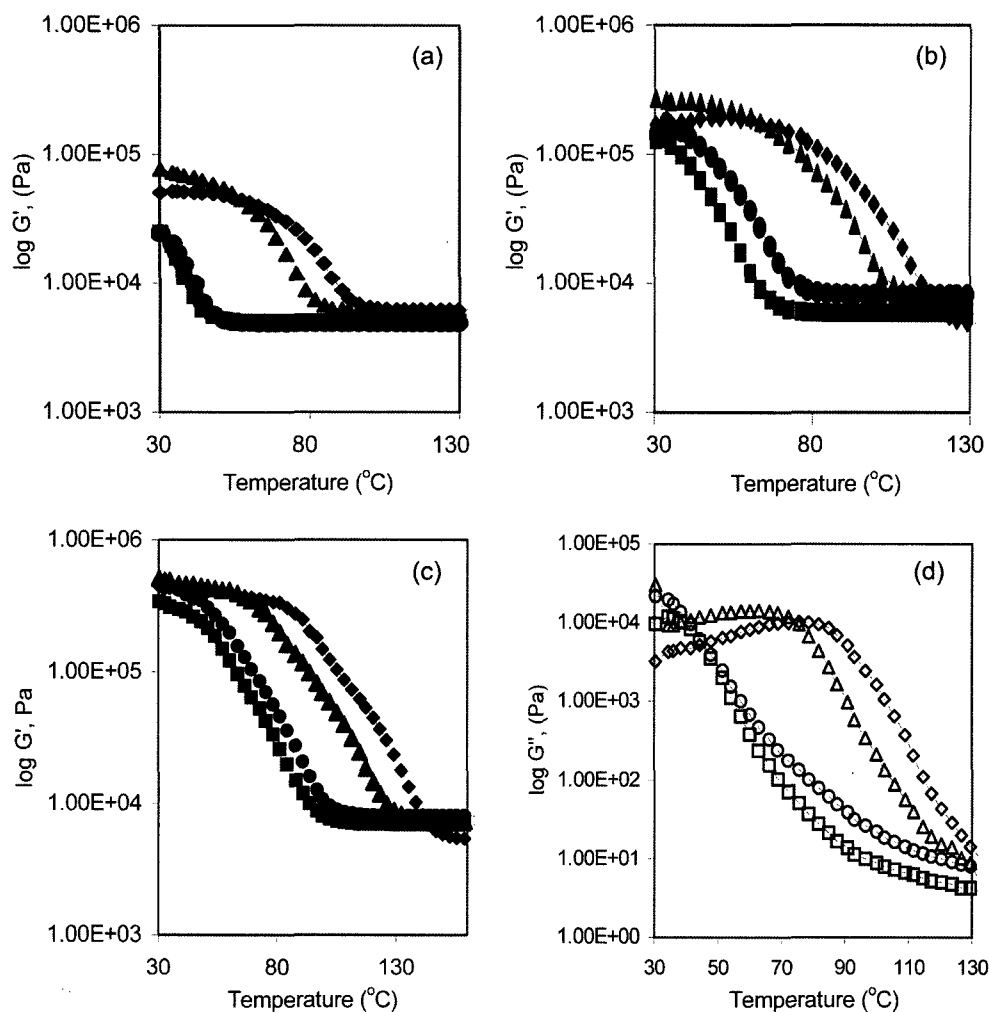
Figure 5. Storage modulus, (G') (filled symbols) of TPE gels with different types of oil (a) 0.85, (b) 0.75, (c) 0.65 weight fraction concentration, and (d) G'' for 0.85 weight fraction (open symbols), P1 (square), P2 (circle), P3 (triangle), and P4 (diamond).
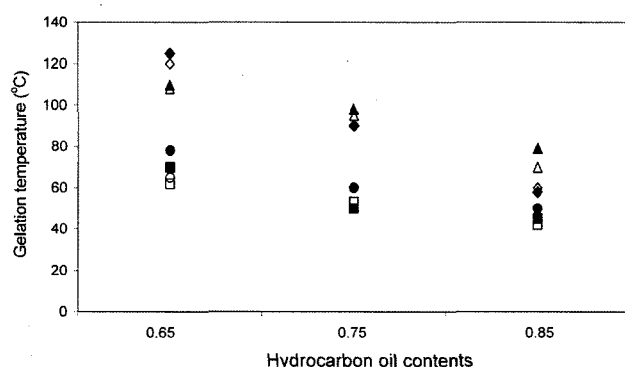

Figure 6. Dependence of gelation melting temperatures of TPE gels on the different types and concentrations of hydrocarbon oils measured by dynamic rheometer (filled symbols) and tilting (open symbols). P1 (square), P2 (circle), P3 (triangle), and P4 (diamond).

becomes a viscous fluid.[17,23] At temperatures below the gel

point, the elastic properties dominated by G' rather than G'' and the logarithmic curves shows a slight curvature where the melting took place. This is taken as the gelation melting temperature. The results from tilting method are somewhat lower but in some cases, it nearly the same. The gelation melting temperature decreases as the hydrocarbon oil increases for all types of oils. It means that the higher the copolymer concentration in the gel, the higher the temperature will be at which the minimum number of physical junction necessary to form the gel.[18] Above the gel transition, the midblock aggregates dissociate to give viscoelastic behavior that result in a freely flowing liquid similar to a viscous polymer solution. When the temperature is decreased below the gel temperature, the rubbery PS domains become glassy at ambient temperature (25-30 °C). The gelation melting temperature of the gels also increases when the paraffinic content of the hydrocarbon oil increase as in P4 TPE gel. However, as the paraffinic content of

hydrocarbon oil decreases in the case of P2 and P3 TPE gels, the gelation melting temperature drastically drop. An enormous drop of gelation melting temperature can be observed when there is aromatic hydrocarbon present in the oil as in P1 TPE gel. It was mentioned earlier in the viscoelastic behavior that some fraction of the oil penetrates the PS phase of the SEBS triblock copolymer. This can be discerned in the swelling experiment (Figure 7). The results denote the strong gelation temperature dependence of the triblock copolymer/type of oil interactions. Similar results have also been obtained for the SEBS triblock copolymer with different molar mass dissolved in an extender oil and n-octane.[17,18] It should be noted that although the polystyrene block is responsible for the gel junctions and the length of copolymer block and thereby determining the ease of gelation and thermal stability of the gels formed, however this study proved that the molecular weight and paraffinic hydrocarbon contents have also contributed to the stability of micelles and the incompatibility of hydrocarbon oil in triblock copolymer. Small amount of aromatic content in hydrocarbon oil decreases the thermal stability of micelle formation of the gel and increases the compatibility of the solvent with the triblock copolymer. This indicates that lower molecular weight of hydrocarbon oil resulted in an increase in chain diffusion during micellization. This explanation is supported by the changes in rheological properties, SAXS and swelling ratio induced by varying the types and concentration of hydrocarbon oil.

**Swelling Measurements.** The swelling kinetics for all
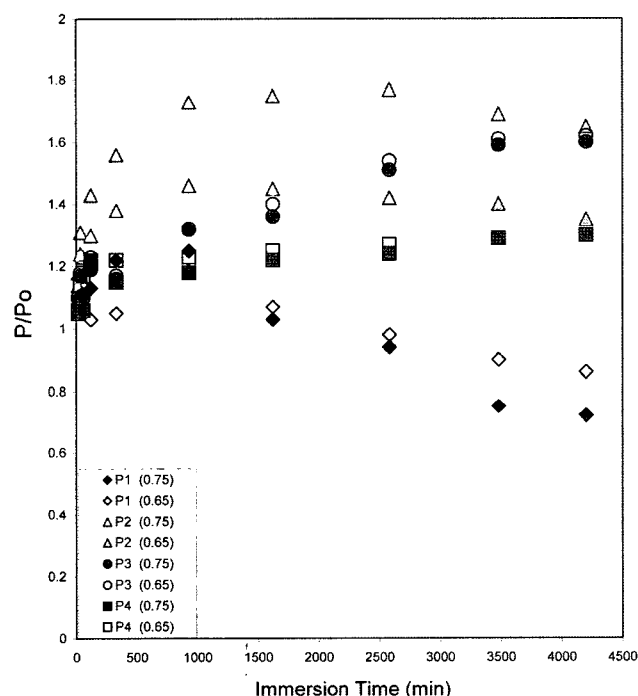
Figure 7. Swelling ratio versus immersion time for four gels P1, P2, P3, and P4 with weight fraction of 0.75 and 0.65 hydrocarbon oil.

gels with weight fraction of 0.75 and 0.65 for all types of oil contents is shown in Figure 7. At the initial immersion time, the swelling behaviors of all gels are similar. However after 1,000 min in excess oil, the P1 TPE gel with different concentrations start to dissolve. Surprisingly, weight fraction of oil 0.65 P2 gel swells more than others gels, but after longer immersion, both concentrations show deswelling and dissolve at a certain degree. Similarly, the swelling behavior of P3 and P4 TPE gels in all these concentrations are the same. The P1 and P2 TPE gels containing oil with weight fraction of 0.85 were not measured due to their semi-liquid state at ambient temperature.

SAXS Experiments. To understand the effect of oil in the gel systems, SAXS measurement of neat SEBS was first obtained at 25 °C, as shown in Figure 8(a). SAXS was employed for studying structural features of soft materials and macromolecular systems.[25,26] The scattering curve exhibits two low angles: maximum peak at lower angle and small broad peak at higher angle. The strong maximum as attributed to the interdomain interference of midblock segment while the maximum peak at higher angle was attributed to the form factor of the phase separated PS domains. These PS domains are packed in a two dimensional hexagonal arrangement.[16,27] After the addition of oil in the system, the maximum interdomain interference shifts to higher angle while small shoulder peak at lower angle appears which is likewise dependent on the composition and type of hydrocarbon oil. This behavior is also shown in the SAXS frames (Figure 9(a) and 9(b)), showing the disappearance of tail. Similarly, the small peak at higher angle disappears with the addition of hydrocarbon oil, as shown in Figure 8(b) and 8(c). The shift to the higher angle with the addition of oil is probably due to more compact arrangement of PS domains. The scattering curves of gels formed using P4 oil show small shoulder at the maximum peak, which is dependent on composition (Figure 8(b)). With decrease in the amount of oil, the shoulder started to disappear. This maybe attributed to increasing the size of PS domain. However, if the oil contains aromatic hydrocarbon, then only one peak was observed as shown in Figure 8(c), especially at higher amount of oil. Small-angle scattering methods provide accurate rate measurements of the interdomain spacing (D) and the mean micellar radius (r) through analysis of the intensity peaks that arise from both interdomain and intradomain scattering. Since the population of bridged and looped midblocks are expected to be sensitive to the quality of the midblock-compatible solvent,[20] variation of D with composition for TPE gels under isothermal conditions should offer insight into the fraction of midblock bridging and the degree of midblock entanglement. Systems with higher values of D should, for instance, possess a higher fraction of midblock loops than bridges. Table II shows the intensities taken from SAXS scattering curves for all sample gels. In all types of oils, increasing the amount of oil in
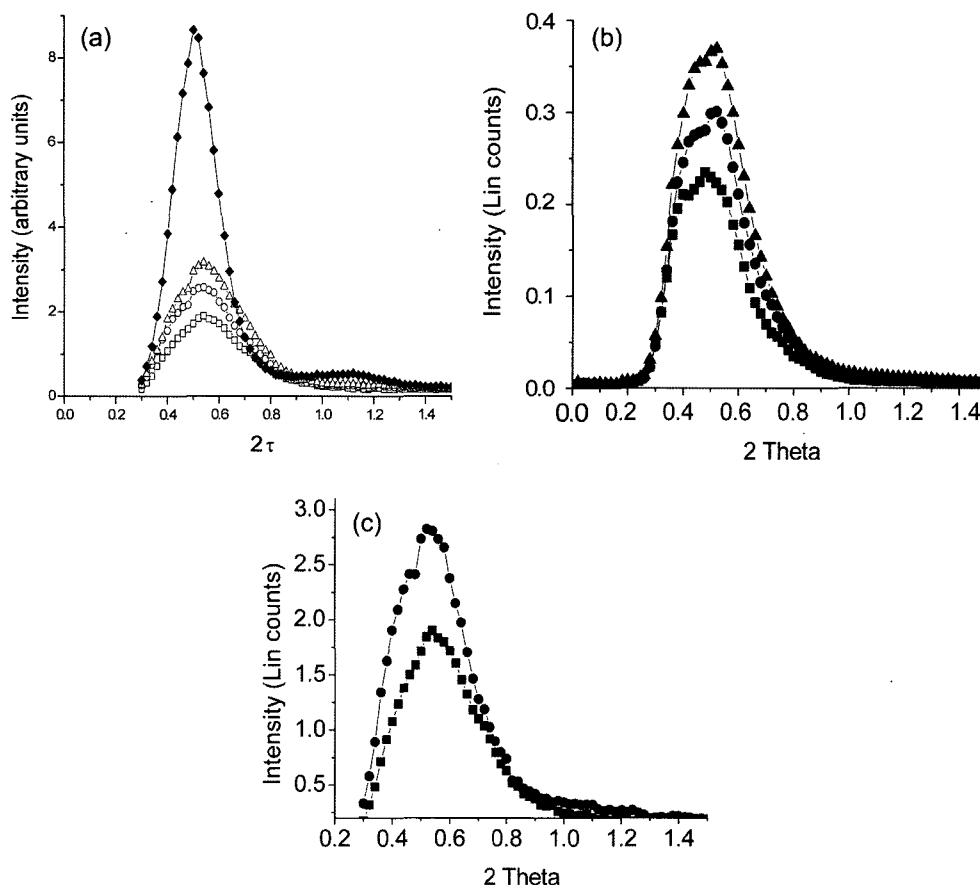
Figure 8. SAXS scattering curves for: (a) neat SEBS (filled symbol) and open symbols for sample gels with weight fraction of 0.75 of different types of oil P1 (square), P2 (circle), P3 (triangle), (b) P4 gels containing w_{oil} 0.65 (triangle), 0.75 (circle), 0.85 (square), and (c) P1 gels containing w_{oil} 0.65 (circle), 0.75 (square).
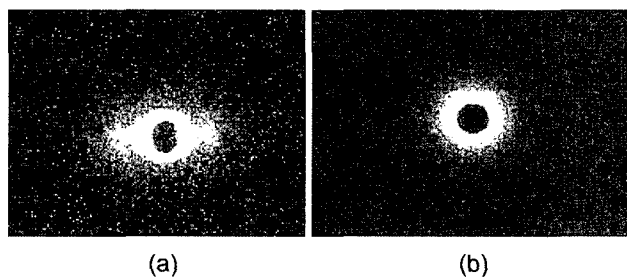
Figure 9. SAXS frames for (a) neat SEBS and (b) P4 gel containing 0.85 weight fraction of oil.

Table II. SAXS Intensities in Lin (counts) for All Sample Gels

Oil Weight Fraction \ Type of Oil Code	P1	P2	P3	P4
0.65	2.8	3.5	3.9	4.0
0.75	1.8	2.5	3.2	3.5
0.85	*	*	1.9	2.3

*The sample gels were not able to measure due to very soft characteristics. The gels flow during the measurements.

the gels decreases the intensity of the strong peak and the second peak at low angle become more pronounced and broader. The type of oil in the gels has significant effect on the intensity. But, P1 and P2 TPE gels with oil weight fraction of 0.85 are not suitable to conduct the study owing to the very soft characteristics of the materials which tend to flow at this temperature. The oil with higher content of paraffinic hydrocarbon resulted in higher intensity compared with less amount of paraffin, and the intensity is much lower when the oil used to form gel contains small amount of aromatic hydrocarbon, as can be seen in Table II. The caused was explained in swelling experiment.

Conclusions

The results of the study has proved that poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) thermoplastic elastomer forms thermoreversible gels in hydrocarbon oils by self-assembly of interdomain and intradomain molecular

association due to its PS component. Thermoreversible gelation of TPE in hydrocarbon oil essentially depends on polymer concentration and types of hydrocarbon oil. It was also proved that the molecular weight and paraffinic hydrocarbon contents in oil have also contributed to the stability of micelles and the incompatibility of hydrocarbon oil in SEBS. The gels formed by low molecular weight hydrocarbon oil and with small amount of aromacity are less stable at room temperature. The gels are fragile at high hydrocarbon oil content and found to be stronger at higher polymer concentration.

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