

Swelling Characteristics of Block Order Networks Prepared by Styrene–Ethylene/Butylene ABA Triblock Copolymer and Styrene Homopolymer Binary Blends

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SYNOPSIS

Mixed networks based on polystyrene (PS) and styrene–ethylene/butylene triblock copolymer (SEBS) binary blends were synthesized via a postpolymerization Friedel–Crafts-type reaction employing styrene units and a bis-chloromethylated crosslinking agent. The swelling behavior of the produced gels was studied in relation to network density, SEBS/PS mass ratio, and solubility parameter of the swelling media, in a range of aliphatic, chlorinated, and aromatic solvents. Swelling characteristics of the mixed macronets were found to differ markedly from those of pure homopolymer gels. Selective swelling was observed in three different regions in respect to the solvent solubility parameter, in contrast to pure PS networks where adsorption was favored in a single region of solvents. This phenomenon was found to depend primarily on the SEBS/PS constitution of gels, while the solvent holding capacity depended directly on the crosslinking density. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Block copolymers and blends with the corresponding homopolymers are a category of materials with increasing scientific interest. Physical, rheological, and thermodynamic properties of styrene–ethylene/butylene and other ABA triblock copolymers have been noted to be the subject of several recent investigations.

It has been experimentally proved¹ that the mid-block's chemical structure and the incompatibility between the mid- and the end block have a strong effect on physical and rheological properties of styrene–ethylene/butylene copolymer (SEBS). Microphase separation transition (MST) of diblock copolymers, diblock copolymer–homopolymer mixtures, and triblock copolymers has been both theoretically and experimentally viewed.^{2–5} As a result, styrenic block copolymers like SEBS have been

shown to exist in a two-phase order, i.e., polystyrene (PS) domains dispersed in a rubbery phase, which is converted to a homogeneous one at elevated temperatures.

Weiss et al.^{6,7} introduced chemical modifications on SEBS by partially sulfonating the PS end blocks. The prepared ionomers were found to exhibit a three-phase structure, owing to polar associations of the composed ionic groups, while viscoelastic and mechanical properties were also studied.

Mixing of block copolymers with the corresponding homopolymers has been reported^{8–12} to lead to materials having improved and desired mechanical properties. In the present work, mixed networks composed of PS and SEBS were prepared through a Friedel–Crafts postpolymerization reaction.

Grassie and Gilks¹³ and Davankov et al.¹⁴ reported crosslinking of PS with the use of a Friedel–Crafts-type reaction which employed chloromethylated aromatic compounds as crosslinkers. 1,4-Dichloromethyl-2,5-dimethylbenzene (DCMDMB) has been proved to be a desirable Friedel–Crafts crosslinking agent by the work of Peppas and Valkanas.¹⁵

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It has been successfully used for PS modification¹⁶⁻¹⁸ under the influence of protonic and Lewis acid catalysts and has been found to undergo very limited polycondensation under these reaction conditions. Block order networks based on SEBS have been synthesized by members of our group¹⁹ via a similar-type reaction between DCMDMB and PS end blocks, under TiCl_4 catalysis. According to this method, irreversible networks were formulated with their crosslinks located exclusively in the PS domains while the mid-block remained intact.

In the present communication, synthesis of macronets based on SEBS/PS blends was accomplished. Such products can be considered as binary blends where the two components are chemically bound, a fact that makes them insoluble and infusible. Macronets having different SEBS/PS ratios and network density were prepared, while swelling characteristics were studied in a range of aliphatic, chlorinated, and aromatic hydrocarbons in order to reveal the specific swelling behavior of such products. The described process suggests that a new class of materials having predicted block structure, desired swelling characteristics, and regulative mechanical properties can be achieved.

EXPERIMENTAL

Preparation of DCMDMB

DCMDMB was synthesized according to the technique proposed by Peppas et al.²⁰ The reaction mixture was composed of 106 g of *p*-xylene (Fluka, analytical grade), 180 g of 36% formalin (Mallinckrodt, analytical grade), and 1000 mL of 37% hydrochloric acid, corresponding to a molar ratio of 1 : 6 : 12. The reaction took place in a three-necked flask for 5 h at $95 \pm 1^\circ\text{C}$ under a vertical condenser and with rapid stirring. The precipitated product was isolated after filtration and washed with deionized water for the removal of the oily monochloromethylated derivative of *p*-xylene. After repeated recrystallization from ethanol and washing with cool diethylether, DCMDMB was obtained in the form of a white crystalline solid (mp 133°C).

Synthesis of Networks

The preparation of block order networks was based on PS and SEBS as starting materials. PS ($M_w = 260,000$, $M_n = 118,000$) was supplied by Dow Chemical Co. and was purified by dissolving in carbon tetrachloride (Merck, analytical grade), pre-

cipitation after the addition of methanol, and finally drying in vacuum. SEBS (Aldrich Chemical Co., $M_w = 105,000$, $M_n = 85,000$) containing 28 wt % styrene was purified by the same procedure. Fresh bottles of TiCl_4 (Merck, analytical grade) were used in order to avoid hydrolysis phenomena.

Actually, 2 g of polymer were dissolved in 10 mL of carbon tetrachloride. Afterward, the appropriate amount of the crosslinker (DCMDMB) and 500 μL of catalyst (TiCl_4) were added. All reactions were carried out at $60 \pm 1^\circ\text{C}$ for 24 h in a 50 mL flat-bottomed flask under vigorous agitation and dry nitrogen atmosphere. The products were shaped to small particles and washed with 1,2-dichloroethane and pure methanol. Subsequently, the networks were kept in deionized water for 2 days, which resulted in the conversion of TiCl_4 to TiO_2 . The oxide formed was removed by repeated washings with a 12N HCl solution followed by drying of the products at 100°C for 24 h.

Swelling Experiments

The swelling ability of block order networks was estimated as follows: Prewashed dry gels remained in a solvent bath at 25°C for 24 h, a time period adequate in order to achieve equilibrium swelling, as indicated from preliminary experiments. Finally, the swollen materials were filtered and reweighed. Swelling behavior was studied in 15 aliphatic, chlorinated, and aromatic solvents.

Scanning Electron Micrographs

The morphology of the produced macronets was defined by scanning electron microscopy. Analysis was carried out with a JEOL JSM-35 electron microscope. Micrographs were depicted for polymer fractions having diameter less than 1 mm following critical point drying. Specimens were sputtered with gold and carbon dioxide was used as filling material before drying.

RESULTS AND DISCUSSION

Crosslinking Reaction

Preparation of mixed block order networks was based on five starting materials with different SEBS/PS mass ratios as shown in Table I. Every starting material was modified with the appropriate amounts of DCMDMB in order to achieve networks having average number of polymer repeating units

Table I Starting Materials Used for the Preparation of Block Order Networks

Starting Polymer	PS Content (Wt %)	SEBS Content (Wt %)	PEB/PS Weight Ratio
N1	0	100	2.57
N2	25	75	1.17
N3	50	50	0.56
N4	75	25	0.21
N5	100	0	0

between the crosslinks (x_c) which varied from 25 to 450. The corresponding crosslinking ratio X (mol DCMDMB/mol repeating unit) can be calculated by using the following equations:

$$M_{c,t} = 2M_0/X \quad (1)$$

$$\text{but } x_{c,t} = M_{c,t}/M_0 \quad (2)$$

$$\text{and further } X = 2/x_{c,t} \quad (3)$$

where M_0 is the molecular weight of polymer repeating unit, and $M_{c,t}$, the number-average molecular weight between the crosslinks.

Thus, the appropriate DCMDMB/polymer mass ratio (Y) for each crosslinking reaction can be estimated by the equation

$$Y = XM_0/M \quad (4)$$

where M is the molecular weight of DCMDMB (MW = 203). M_0 can be estimated as follows:

$$M_0 = aM_1 + bM_2 \quad (5)$$

where a and b are the styrene and ethylene/butylene weight fractions in the starting material, respectively; M_1 , the molecular weight of the styrene unit (MW = 104); and M_2 , the molecular weight of the hydrogenated butadiene unit (MW = 56). Hydrogenated butadiene was considered to be the repeating unit of poly(ethylene/butylene) (PEB) segments because SEBS is normally prepared by hydrogenation of the butadiene mid-block of a styrene-butadiene triblock copolymer.

Reactions were carried out in solution as mentioned earlier and 25 different products were fabricated. It has to be noticed that pure PS and pure SEBS solutions were transparent, in contrast to those of PS/SEBS mixtures that appeared to be opaque, a fact which is attributed to the presence of styrene-rich macrophases.⁴ All reactions proceeded under rapid stirring in order to ensure statistical

distribution of PEB and PS phases in the reaction mixture. Gel points were achieved at reaction times ranging between 5 min to 3 h owing to varying crosslinking agent and PS concentrations. The red-brown-colored, insoluble, and infusible products were found to have increasing brittleness as the PS weight fraction increased, a fact which is in agreement with reported observations⁸⁻¹² for block copolymer/homopolymer blends. The reaction proceeds between DCMDMB and PS domains, while the ethylene/butylene mid-block remains unaffected as proved in a previous work.¹⁹ A more detailed analysis of the reaction mechanism as well as characterization of block order networks based on SEBS have been reported in the same publication.

Properties of Products

A scanning electron micrograph of product having a ratio of SEBS/PS = 3 is shown in Figure 1. Line

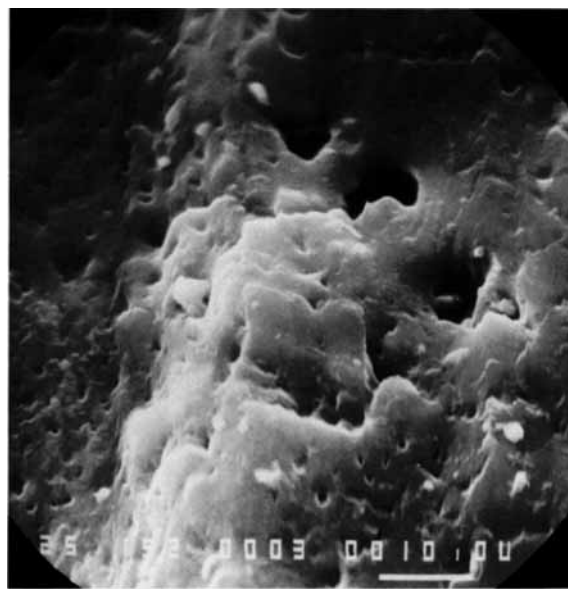


Figure 1 Scanning electron micrograph of network containing 75 wt % SEBS and 25 wt % PS with $x_c = 300$. Line indicates 10 μm .

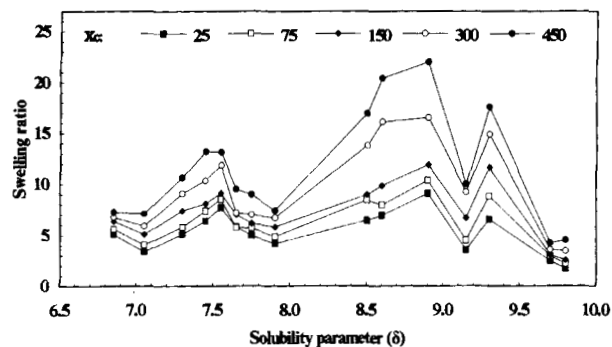


Figure 2 Swelling ratio of SEBS networks as a function of solvent solubility parameter.

indicates a 10 μm distance. A micrograph was depicted for dry particle having a diameter less than 1 mm. The products obtained by solution crosslinking have morphology which depends on the technique applied for the decreasing of materials size after preparation. Although some pores appear in the photographs, the formed networks can be classified as of gel type. The pore appearance can be attributed to factors such as the bubble formation caused by the vigorous agitation of the reaction mixture and the evolution of hydrogen chloride which is produced during the reaction.

Swelling experiments were performed in 15 aliphatic, chlorinated, and aromatic solvents in order to demonstrate the swelling behavior of the produced mixed gels. Each experimental value presented in Figures 2–6 was generated by the average of three repetitions.

The swelling ratio (q_s) can be calculated by using the equation

$$q_s = Q + 1 \quad (6)$$

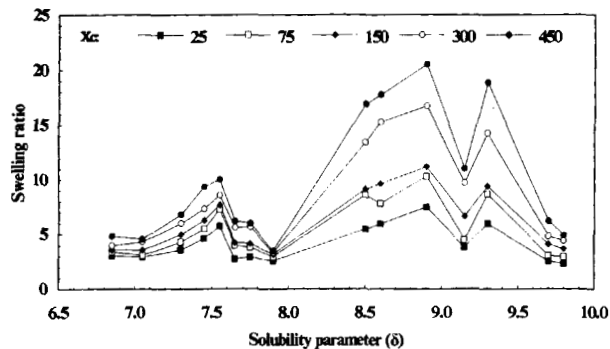


Figure 3 Swelling ratio of networks containing 75 wt % SEBS and 25 wt % PS as a function of solvent solubility parameter.

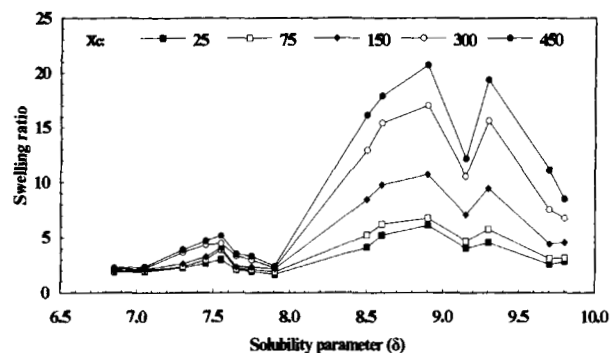


Figure 4 Swelling ratio of networks containing 50 wt % SEBS and 50 wt % PS as a function of solvent solubility parameter.

where the term Q is derived from the equation

$$Q = (W - W_p)d_p/W_p d \quad (7)$$

where d and d_p are the densities of solvent and network, respectively; W , the weight of the swollen network, and, finally, W_p , the weight of the dry network.

Densities of the produced macronets were experimentally determined and they varied between 0.95 g/cm^3 for pure SEBS to 1.03 g/cm^3 for pure PS gels. From Figures 2–6 where the swelling ratio as a function of the solvent solubility parameter²¹ ($\text{cal}^{1/2} \text{cm}^{-3/2}$) and the average number of polymer repeating units between the crosslinks (x_c) is illustrated, it is noticed that for all the synthesized macronets maximum swelling ratio occurs in toluene. It is clearly demonstrated that the swelling ratio increases by the increase of x_c , which is in agreement with Flory's theory²² about crosslinked polymers. An obvious characteristic is the influence of SEBS/PS mass ratio in the network's swelling ability. As

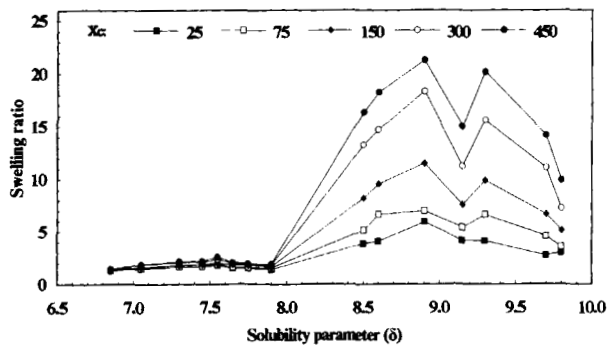


Figure 5 Swelling ratio of networks containing 25 wt % SEBS and 75 wt % PS as a function of solvent solubility parameter.

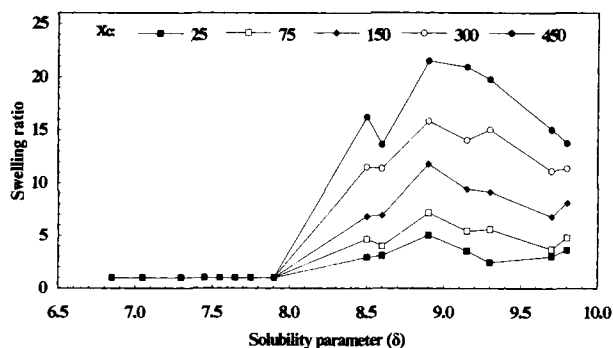


Figure 6 Swelling ratio of PS networks as a function of solvent solubility parameter.

shown in the same figures, the SEBS/PS ratio affects considerably the adsorption of most of the occupied solvents, with the exception of swelling in chloroform ($\delta = 9.3$), toluene ($\delta = 8.9$), carbon tetrachloride ($\delta = 8.6$), and 1,1,1-trichloroethane ($\delta = 8.5$), where the network composition has a less pronounced effect. By increasing the PS weight fraction, swelling increases in 1,2-dichloroethane ($\delta = 9.8$), dichloromethane ($\delta = 9.7$), and benzene ($\delta = 9.15$), while it decreases in isooctane ($\delta = 6.85$), *n*-pentane ($\delta = 7.05$), *n*-hexane ($\delta = 7.3$), *n*-heptane ($\delta = 7.45$), *n*-octane ($\delta = 7.55$), *n*-nonane ($\delta = 7.65$), *n*-decane ($\delta = 7.75$), and *n*-dodecane ($\delta = 7.9$). It is obvious that the presence of the ethylene/butylene sequence is the determinative factor for the adsorption of aliphatic hydrocarbons. Decrease of the PEB weight fraction leads to decreasing holding capacity of these solvents, which finally becomes equal to zero in the case of pure PS networks. Therefore, even in the absence of crosslinks in it, the PEB sequence can be responsible for swelling in solvents due to its physical crosslinking, the extent of which depends on the network density of the PS segments.

As it can be seen from Figure 6, the pure PS gels present an expected behavior. The observed curve shows that maximum q_s is achieved in solvents (toluene $\delta = 8.9$, benzene $\delta = 9.15$) having solubility parameters close to this of PS ($\delta = 9.1$). Thus, for PS networks, a single "selective" in respect to the swelling ability region of solvents, between 1,1,1-trichloroethane ($\delta = 8.5$) to 1,2-dichloroethane ($\delta = 9.8$) is observed. In contrast, mixed networks containing an ethylene/butylene sequence ($\delta = 8.3$)¹ exhibit a more complicated behavior (Figs. 2–5). This behavior is demonstrated by the existence of three different areas in which swelling is favored. The first of these solvent regions is between isooctane ($\delta = 6.85$) and *n*-dodecane ($\delta = 7.9$), where

the maximum swelling ratio appears in *n*-octane ($\delta = 7.55$). A second selective region is located between *n*-dodecane ($\delta = 7.9$) and benzene ($\delta = 9.15$), with maximum adsorption achieved in toluene ($\delta = 8.9$). Swelling is also favored in a third area which is limited by benzene ($\delta = 9.15$) and 1,2-dichloroethane ($\delta = 9.8$), while sorption in this region is maximized in the case of chloroform ($\delta = 9.3$).

The described behavior in the case of aliphatic hydrocarbons can be simply attributed to the presence of large PEB segments in the produced macronets, as was mentioned earlier. In the case of the two selective swelling regions in the range of chlorinated and aromatic hydrocarbons, this can be attributed to the fact that for swelling in these solvents both PS and PEB domains are responsible. The difference in tendencies for swelling of PEB and PS can be considered as the decisive factor for this specific behavior. It must be emphasized that the intensity of this performance is strongly affected by the SEBS/PS or PEB/PS ratio but it is not significantly influenced by the crosslinking density (x_c).

Conclusively, by following the described postpolymerization procedure, selectively crosslinked block order networks with large uncrosslinked segments which lead to specific swelling behavior can be formulated. Regulation of swelling behavior and mechanical properties by simply altering both the proportion of the rubbery and the glassy phase and the density of crosslinking indicates the possible use of such materials in several applications. It is also obvious that by using the same technique crosslinking of styrenic diblock copolymers or blends with either PS homopolymer or other styrenic copolymers can take place, thus leading to a new class of polymeric networks.

CONCLUSIONS

Mixed block order networks having different SEBS/PS mass ratios were prepared via a postpolymerization reaction. The Friedel–Crafts-type reaction leads to macronets having large unreacted PEB segments between the crosslinked PS domains and high swelling ability. Swelling behavior of the PEB containing gels was shown to deviate from the normal one which characterizes homopolymer networks like this of crosslinked PS. Selective adsorption of nonpolar solvents belonging to different regions in respect to their solubility parameter was observed, in contrast to homopolymer networks where swelling is favored in solvents having δ close to the homo-

polymer's one only. The SEBS-containing networks appeared to demonstrate selective swelling in the region of aliphatic solvents and in two regions in the area of chlorinated and aromatic hydrocarbons. The swelling ratio in these regions was found to be maximized in *n*-octane, toluene, and chloroform, respectively, while pure PS macronets appeared a single region of selective adsorption with maximum swelling ratio in the case of toluene. This behavior was noticed to depend directly on the rubbery/glassy phase constitution of products, a fact which indicates that formation of crosslinked structures with regulative and desired swelling characteristics is possible by following the above described route.

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