

# Low Molecular Weight Block Copolymers as Plasticizers for Polystyrene

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**ABSTRACT:** Polystyrene-*b*-alkyl, polystyrene-*b*-polybutadiene-*b*-polystyrene, and polystyrene-*b*-poly(propylene glycol)monotridecyl ether were synthesized using macro initiators and atom transfer radical polymerization or by esterifications of homopolymers. The aim was a maximum molecular weight of 4 kg/mol and minimum polystyrene content of 50 w/w %, which by us is predicted as the limits for solubility of polystyrene-*b*-alkyl in polystyrene. DSC showed polystyrene was plasticized, as seen by a reduction in glass transition temperature, by block copolymers consisting of a polystyrene block with molecular weight of approximately 1 kg/mol and an alkyl block with a molecular weight of approximately of 0.3 kg/mol. The efficiency of the block copolymers as plasticizers increases with decreasing molecular weight and polystyrene content. In addition, polystyrene-*b*-alkyl is found to be an efficient plasticizer also

for polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) block copolymers. The end use properties of SIS plasticized with polystyrene-*b*-alkyl, measured as tensile strength, is higher than for SIS plasticized with dioctyl adipate. The polystyrene-*b*-polybutadiene-*b*-polystyrene and polystyrene-*b*-poly(propylene glycol)monotridecyl ether series were only partially soluble in polystyrene and insoluble in the polystyrene phase of SIS. For the lowest molecular weight samples, this leads to measurable plasticization of polystyrene but no plasticization of SIS. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 981–991, 2005

**Key words:** diblock copolymers; triblock copolymers; synthesis; atom transfer radical polymerization (ATRP); glass transition; miscibility

## INTRODUCTION

Plasticizers are used throughout the plastics industry to control processing and end use properties. Plasticizers for amorphous polymers are most often low molecular weight (LMW) compounds that lower the glass transition temperature ( $T_g$ ), thereby making the polymers softer and increasing their ability to flow. High molecular weight plasticizers have a number of attractive properties, including low vapor pressure, low toxicity, and low diffusion.<sup>1</sup> Despite these attractions polymeric plasticizers are rare due to the inherent incompatibility of polymers.

Three decades ago Kanig<sup>2</sup> discussed a number of requirements for a good plasticizer. The plasticizer should have low interaction energy with the polymer and have both low cohesive energy and LMW. This is, of course, in conflict with high solubility of the plasticizer in the polymer, and an LMW has its drawbacks. One way to combine the contradicting demands of a

good plasticizer is to look for the behavior of a surfactant. Thus, one part should solubilize the plasticizer and another part should perform the plasticization. In addition, compromises regarding the molecular weight must be made.<sup>2</sup> A block copolymer can be seen as a surfactant like high molecular weight plasticizer. One block gives the surfactant good solubility while the other block lowers the  $T_g$ .

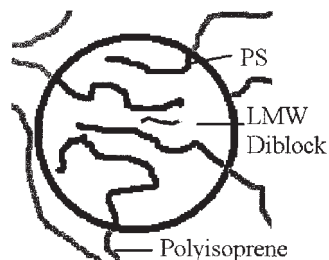
The solubility of LMW homopolymers in block copolymers has been thoroughly investigated.<sup>3</sup> In contrast, the solubility of LMW block copolymers in high molecular weight homopolymers has to our best knowledge not been investigated.

If the polymer to be plasticized is a block copolymer, an additional constraint is added. The plasticizer needs to be preferably soluble in the phase that is to be plasticized.

LMW block copolymers with a high ratio of A block have been found to be partly soluble in the A domain of a larger block copolymer if there is a large difference in molecular weight between the low and the high molecular weight block copolymers<sup>4,5</sup> (see Fig. 1).

The  $T_g$  of such mixtures has to our knowledge not been investigated, but it can be expected to follow the Fox equation<sup>6</sup> (see equation 1).

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**Figure 1** An LMW diblock copolymer incorporated in the PS domain of SIS.

$$\frac{1}{T_{g\text{ mix}}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

The Fox equation expresses the  $T_g$  of a mixture comprising weight fraction  $w_1$  of component 1 with  $T_{g1}$  and  $w_2$  of component 2 with  $T_{g2}$ .

In the case where the AB LMW diblock copolymer is soluble in the A phase of either a block copolymer or a homopolymer, the  $T_g$  of the mixture is expected to be affected according to eq. 1. From this it can be deduced that the LMW block copolymer acts as a plasticizer in the case that it has a lower  $T_g$  than the A phase; and it is clear that if one wants to lower the  $T_g$ , the aim is to have as much with as low  $T_g$  component as possible dissolved in the original polymer. The  $T_g$  of the block copolymer is likewise expected to follow the Fox equation. A low  $T_g$  of the block copolymer can be achieved by having a  $T_g$  lowering part with a low  $T_g$  and/or by a high ratio of the  $T_g$  lowering part. The chemical nature of the  $T_g$  lowering end and solubility increasing end and the ratio between these will affect the solubility.

Thus, a semiquantitative model for solubility of LMW block copolymers consisting of polystyrene (PS) block and an alkyl block in PS has been used to predict the solubility limits. With these limits in mind, PS containing block copolymers with varying molecular weight and  $T_g$  lowering segments (alkyl, polybutadiene, and poly(propylene glycol)monotridecyl ether) were synthesized using both anionic polymerization and atom transfer radical polymerization (ATRP).

Their plasticizing efficiency for PS was evaluated using differential scanning calorimetry (DSC). In addition, their effectiveness as plasticizers for PS in polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) was evaluated by dynamic mechanical analysis (DMA). For selected samples, changes in maximum elongation and stress were evaluated by tensile elongation.

## EXPERIMENTAL

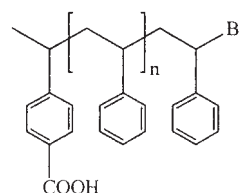
### Materials

Xylene, tetrahydrofuran, dichloromethane, and triethylamine were chromatography grades and dried by

distillation over calcium hydride under nitrogen. The inhibitor in styrene was removed on an aluminum oxide column. Prior to use, styrene was distilled over calcium hydride under reduced pressure. Copper(I) bromide, 2,2'-bipyridine, 2-bromoisobutyryl bromide, 4-methylaminopyridine (DMAP), and *N,N'*-dicyclohexylcarbodiimide (DCC) were purchased from Aldrich (Vallensbaek, Denmark) and used without further purification. Mono hydroxyl terminated polybutadiene (PB)  $M_n = 1$  kg/mol and polystyrene  $M_n = 16$  kg/mol, PDI = 1.6 and  $T_g = 102^\circ\text{C}$  were purchased from Polymer Source Inc. (Quebec, Canada) and used as described in sample preparation. Poly(propylene glycol)monotridecyl ether (PPG)  $M_n = 0.45$  kg/mol and  $M_n = 0.8$  kg/mol were samples from Clariant (Burgkirchen, Germany) and dried with molecular sieves 4Å. Hydroxyl terminated polybutadiene (2.4–2.6 hydroxyl groups pr chain)  $M_n = 1.2$  kg/mol was a sample from Sartomer (Exton, PA, USA) and dried with molecular sieves 4Å. SIS (Kraton D1163)  $M_n$  187 kg/mol, 15 w/w % polystyrene and with a content of 38 w/w % diblock copolymer was purchased from Kraton Polymers (Hoogvliet, The Netherlands) and used without further purification. Dioctyl Adipate (DOA) was purchased from Cognis Performance Chemicals Ltd (Düsseldorf, Germany) and used without further purification. 4-(Dimethylamino)pyridinium 4-Toluensulfonate (DPTS) was prepared according to Moore and Stupp.<sup>7</sup> m. p.: 174°C.

### Instrumentation

$^1\text{H-NMR}$  was recorded at 300 K on 250 MHz Bruker, using  $\text{CDCl}_3$  as solvent and tetramethylsilane as internal standard. Size-exclusion chromatography (SEC) was carried out on Shimadzu SIL-10AD, two PLgel 5  $\mu\text{m}$  MIXED D columns, and a Viscotek Model 200 Refractive Index detector. THF as eluent and polystyrene standards were used. Glass transition temperatures and melting points were measured with a differential scanning calorimeter (DSC) Q1000 from TA Instruments at second heating. The heating and cooling rates were 10°C/min and sample size 5–15 mg. Tensile properties were measured using an Instron 5564 tensile tester equipped with a 100N load cell. The strain rate was 100 mm/min, and 3–4 specimens of



**Scheme 1**

TABLE I  
ATRP of Styrene with 4-(1-bromoethyl)benzoic Acid as the Initiator

Amount of the initiator, mmol	Reaction time, h	Yield, %	$M_n^{\text{Theor. a}}$ , kg/mol	$M_n$ by SEC, kg/mol	$M_w/M_n$	$M_n$ by $^1\text{H NMR}$ , kg/mol
5.31	17	33	0.6	2.8	1.36	2.2
2.39	17	74	1.9	3.4	1.23	3.3
1.14	17	70	3.6	5.7	1.25	6.1
5.31	18	80	1.1	1.6	1.16	1.7
2.39	18	78	2.0	2.2	1.14	3.7
7.04	11	42	0.6	1.6	1.21	2.2
7.04	11	36	0.5	1.6	1.21	2.2

<sup>a</sup> Calculated from:  $M_n^{\text{Theor.}} = ([\text{Styrene}]/[\text{I}]) M_{\text{Styrene}} \text{Yield} + M_{\text{Initiator}}$ .

each sample were tested. DMA was performed between 20 and 160°C on a RheoStress RS600 from Haake. The heating rate was 2°C/min, deformation rate 1 Hz, and a 1% deformation.

**4-(1-Bromoethyl)benzoic acid** was prepared according to Malz et al.<sup>8</sup> m. p.: 145°C.  $^1\text{H-NMR}$  250 MHz ( $\text{CDCl}_3$ ):  $\delta$  2.1 (d,  $J = 7$  Hz, 3H,  $-\text{CH}_3$ ), 5.2 (q, 1H,  $-\text{CHBr}$ ), 7.6 (d, 2H, *ortho* ArH), 8.1 (d, 2H, *meta* ArH).

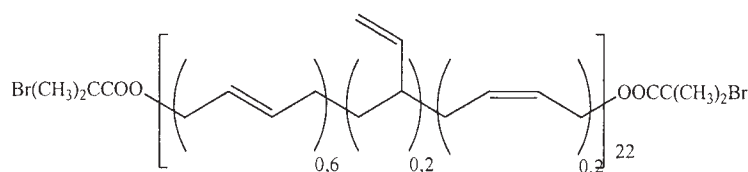
**Carboxylic acid terminated polystyrenes (PS-COOH)** were prepared according to Matyjaszewski et al.<sup>9,10</sup> A Schlenk tube was charged with 4-(1-bromoethyl)benzoic acid, Cu(I)Br, and 2,2'-bipyridine (1 : 1 : 2). The amounts are shown in Table I. 12 mL of xylene and 6 mL (52.1 mmol) of styrene were added, and the system was degassed three times by the freeze-pump-thaw method and then heated at 110°C under nitrogen. After the reaction times listed in Table I, the reaction mixture was cooled down, filtered, and precipitated in a large excess of methanol. The polymers were dried in vacuum at room temperature.  $^1\text{H-NMR}$  250 MHz ( $\text{CDCl}_3$ ):  $\delta$  0.7–1.7 (broad,  $\text{CH}_3$  from the initiator and  $\text{CH}_2$  from PS), 1.7–2.7 (broad, CH from PS), 4.3–4.6 (broad, CH-Br), 6.2–6.9 (broad, *meta* ArH), 6.9–7.4 (broad, *ortho* and *para* ArH), 7.7–8.2 (2H, broad, Ar  $-\text{CH}-\text{C}(\text{COOH})-$ ).

**Polybutadiene macroinitiator (PB-Br)** was prepared according to Jankova et al.<sup>11</sup> 0.535 g (4.34 mmol) of DMAP in 10 mL of THF were mixed with 4.5 mL (32.5 mmol) of freshly distilled triethylamine. After cooling to 0°C, 5.4 mL (32.4 mmol) of 2-bromoisobutyl bromide in 30 mL of THF was added under nitrogen. Subsequently, 10.0 g (21.7 mmol hydroxyl

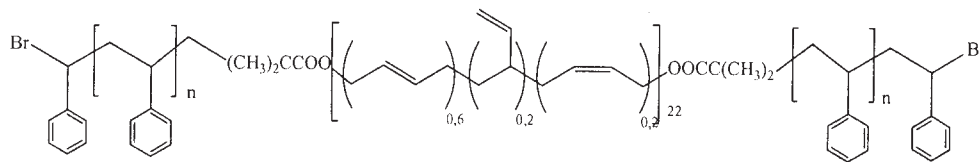
functionality) of hydroxyl terminated polybutadiene in 40 mL THF was added dropwise during 1 h. Thereupon, the temperature was allowed to rise to room temperature, and the reaction was continued for 42 h. The reaction mixture was filtered and then concentrated. Toluene was added, and the mixture was filtered while precipitating PB-Br in a large excess of methanol. After two additional precipitations from toluene/methanol, PB-Br was dried in vacuum at room temperature. PB-Br was obtained as a light yellow viscous liquid in 6.53 g (49%) yield.  $^1\text{H-NMR}$  300 MHz ( $\text{CDCl}_3$ ):  $\delta$  1.1–1.6 (9H, broad,  $-\text{CH}_2-\text{CH}-$ ), 1.9 (15H,  $-\text{CH}_3$ ), 2.0–2.2 (75H, broad,  $-\text{CH}_2-\text{CH} = \text{CH}-$ ), 4.8–5.2 (9H, broad,  $\text{CH}_2 = \text{CH}-$ ), 5.2–6.0 (40H, broad,  $-\text{CH}_2-\text{CH} =$ ).

**Polystyrene-*b*-polybutadiene-*b*-polystyrenes (PS-*b*-PB-*b*-PS)** were synthesized according to Jankova et al.<sup>11,12</sup> A Schlenk tube was charged with PB-Br, Cu(I)Br, and 2,2'-bipyridine (1 : 1 : 2). Styrene was added (see Table II), and the system was degassed three times and then heated to 110°C under nitrogen. The reaction mixture was cooled down, filtered, and precipitated in a large excess of methanol. The polymers were dried in vacuum at room temperature.  $^1\text{H-NMR}$  250 MHz ( $\text{CDCl}_3$ ):  $\delta$  0.7–2.5 (broad,  $\text{CH}_2$  and CH from PS and  $-\text{CH}_2-\text{CH}-$ ,  $-\text{CH}_3$  and  $-\text{CH}_2-\text{CH} = \text{CH}-$  from PB-Br), 4.7–5.1 (9H, broad,  $\text{CH}_2 = \text{CH}-$  from PB-Br), 5.2–5.8 (40H, broad,  $-\text{CH}_2-\text{CH} =$  from PB-Br), 6.2–7.5 (broad, ArH from PS).

**Polystyrene-*b*-poly(propylene glycol)monotridecyl ether (PS-*b*-PPG).** *In situ* preparation of the acid chloride (PS-COCl) and the following esterifications



Scheme 2



Scheme 3

were done according to Busson et al.<sup>13</sup> Poly(propylene glycol)monotridecyl ether (PPG) (1.74 eq.–2 eq.), DMAP (0.87 eq.), and triethylamine (2.61 eq.) in 10 mL of THF were mixed at 0°C. PS-COCl (2 eq.), diluted in a small amount of THF, was added dropwise under nitrogen. After the reaction mixture was stirred at 0°C for 1 h, it was allowed to reach ambient temperature and stirred for a minimum of 20 h. The solvent was evaporated under vacuum, and the residue was dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was first washed three times with saturated NaHCO<sub>3</sub>, then three times with 2M HCl, and finally three times with brine. The organic phase was dried over MgSO<sub>4</sub>, filtered, and evaporated under vacuum. A CH<sub>2</sub>Cl<sub>2</sub> solution of the crude product was precipitated into a large excess of methanol. The precipitated product was filtered off and dried under vacuum. The product was purified by flash chromatography on silica gel, eluting with 4 : 1 hexane/ethyl acetate. See Table III for further specifications. <sup>1</sup>H-NMR 250 MHz (CDCl<sub>3</sub>): δ 0.7–2.5 (broad, CH<sub>3</sub> from the initiator, CH<sub>2</sub>, and CH from PS and CH<sub>3</sub>-(CH<sub>2</sub>)<sub>11</sub>-CH<sub>2</sub>-, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>11</sub>-CH<sub>2</sub>- and CH<sub>3</sub>-CH- from PPG), 3.2–3.8 (broad, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>11</sub>-CH<sub>2</sub>-, -O-CH<sub>2</sub>-CH-, and -O-CH<sub>2</sub>-CH- from PPG), 6.2–7.5 (broad, ArH from PS), 7.8–8.1 (2H, broad, Ar -CH-C(COO)-).

**PS-*b*-Octyl** was prepared in accordance with Ihre et al.<sup>14</sup> 1.01 g (0.63 mmol) of PS-COOH (*M<sub>n</sub>* = 1.6 kg/mol) and 0.07 g (0.23 mmol) of DPTS were added to a 100 mL three-neck round-bottom flask equipped with a condenser, a gas inlet/outlet, and a magnetic stirring bar. After the reaction flask was flushed with nitrogen, 90 μL (0.57 mmol) of 1-octanol and 10 mL of CH<sub>2</sub>Cl<sub>2</sub>

were added. Subsequently, 0.30 g (1.46 mmol) of DCC dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was added. The system was heated to reflux, and the reaction mixture was stirred for 18 h under nitrogen. Once the reaction was complete, the DCC-urea was filtered off in a glass filter and washed with a small volume of CH<sub>2</sub>Cl<sub>2</sub>. The excess of PS-COOH was removed by flash chromatography on silica gel eluting with 4 : 1 hexane/ethyl acetate. To remove DCC, the crude product was dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was washed three times with a concentrated aqueous citric acid solution and three times with saturated NaHCO<sub>3</sub>. The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. Finally, the product was dissolved in hexane and separated from DCC-urea by filtration. The hexane was evaporated to give a light yellow sticky product: 0.69 g (71%). <sup>1</sup>H-NMR 250 MHz (CDCl<sub>3</sub>): δ 0.5–2.9 (broad, CH<sub>3</sub> from the initiator, CH<sub>2</sub> and CH from PS and CH<sub>3</sub>, and CH<sub>2</sub> from octyl), 4.2–4.7 (2H, -CH<sub>2</sub>-OOC-PS), 6.2–7.4 (broad, ArH from PS), 7.7–8.1 (2H, broad, Ar -CH-C(COO)-).

#### PS-*b*-Octadecyl

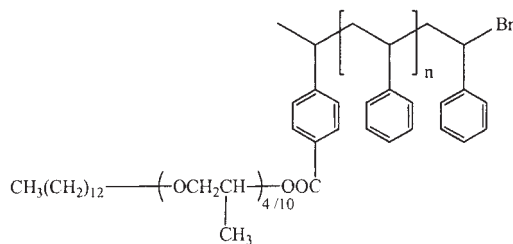
Method 1: PS-*b*-Octadecyl was prepared by DCC-coupling like PS-*b*-Octyl with minor modifications. The washing procedure was performed before the flash chromatography eluting with 5 : 1 hexane/ethyl acetate. Furthermore, hexane and ethyl acetate were evaporated to give 0.54 g (51%) of PS-*b*-Octadecyl as a light yellow sticky material. <sup>1</sup>H-NMR 250 MHz (CDCl<sub>3</sub>): δ 0.6–2.7 (broad, CH<sub>3</sub> from the initiator, CH<sub>2</sub> and CH from PS, and CH<sub>3</sub> and CH<sub>2</sub> from octadecyl), 4.1–4.6 (2H, -CH<sub>2</sub>-OOC-PS), 6.2–7.4 (broad, ArH from PS), 7.7–8.1 (2H, broad, Ar -CH-C(COO)-).

TABLE II  
ATRP of Styrene with Polybutadiene as Macroinitiator

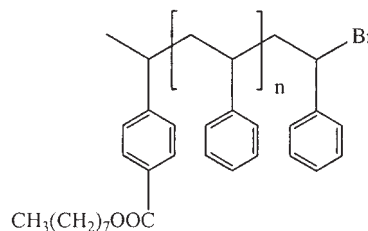
PS- <i>b</i> -PB- <i>b</i> -PS	Amount of styrene, ml	Amount of PB-Br, mmol	Reaction time, h	<i>M<sub>n</sub></i> <sup>Theor.,max a</sup> , kg/mol	<i>M<sub>n</sub></i> by SEC, kg/mol	<i>M<sub>n</sub></i> by <sup>1</sup> H NMR, kg/mol	Conversion calc. from <i>M<sub>n</sub></i> ( <sup>1</sup> H NMR), %
1	5.0	0.32	4	7.0	5.5	2.8	40
2	20.0	0.32	4	23.0	29.6	19.0	83
3	20.0	0.34	4	22.0	8.8	7.0	32
4	13.4	0.33	4	16.0	12.3	11.0	69
5	12.0	0.64	3	18.4	19.1	12.0	65
6	12.0	0.64	0.5	18.4	7.5	4.7	26

<sup>a</sup> Calculated from: *M<sub>n</sub>*<sup>Theor.,max</sup> = ([Styrene]/[I]) *M<sub>n</sub>*<sub>Styrene</sub> + *M<sub>n</sub>*<sub>Initiator</sub>





Scheme 4



Scheme 5

Method 2: Hydroxyl terminated polystyrene was prepared by anionic polymerization.<sup>15</sup> The esterification step from the preparation of PS-*b*-PPG was also used to synthesize PS-*b*-Octadecyl. An excess of octadecanoyl chloride was used in all cases (see Table IV). Flash chromatography was not necessary to purify the product. PS-*b*-Octadecyl was obtained as a white powder. <sup>1</sup>H-NMR 250 MHz (CDCl<sub>3</sub>): δ 0.5–2.5 (broad, CH<sub>3</sub> from the initiator, CH<sub>2</sub> and CH from PS, and CH<sub>3</sub> and CH<sub>2</sub> from octadecyl), 3.5–3.9 (2H, PS-CH<sub>2</sub>-OOC), 6.3–7.3 (broad, ArH from PS).

**Preparation of samples.** Mixtures were made from 25 w/w % toluene solutions. Solvent was evaporated at room temperature for 2 days. All samples were dried for two days at 90°C under vacuum. Samples for DMA were pressed to 1 mm thickness, while samples for elongation were pressed to 0.5 mm thickness. Microdumbbell samples with gauge length of 16 mm, width of 4 mm, and thickness of 0.5 mm were used for tensile measurements.

## RESULTS AND DISCUSSION

### Prediction of solubility window

A qualitative approach was used to estimate molecular weights and compositions for which a block copolymer would be soluble in PS. Thus, the following assumptions were made using meanfield approximation applicable to disordered systems: The block co-

polymer can be seen as a random copolymer and there are no polar interactions.

The upper miscibility limit of one polymer in another polymer may be expressed by the limiting interaction parameter  $\chi_{crit}$ <sup>16</sup> which is a function of the degrees of polymerization of the polymers ( $N_A$ ,  $N_B$ ) as seen in eq. 2:

$$\chi_{crit} = \frac{1}{2} \left( \frac{1}{N_A^{0.5}} + \frac{1}{N_B^{0.5}} \right)^2 \quad (2)$$

If  $\chi$  is not known, it can be estimated from the Hildebrand solubility parameters ( $\delta_A$ ,  $\delta_B$ ) and the molar volume ( $V_r$ )<sup>16</sup> and be expressed as in eq. 3.

$$\chi = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (3)$$

The above-mentioned solubility parameters can be estimated for block copolymers by approximating the block copolymer as a random copolymer. The solubility parameter of a random copolymer with the volume fraction  $\alpha_i$  of component *i* with the solubility parameter  $\delta_i$  becomes:

$$\delta_{random} = \alpha_A \delta_A + (1 - \alpha_A) \delta_B \quad (4)$$

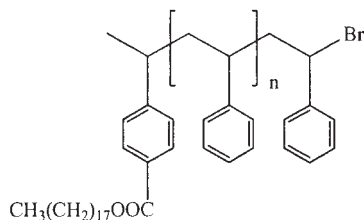
A suitable model block copolymer consists of: PS as the solubility increasing end and an alkyl chain as the

TABLE III  
Preparation of PS-*b*-PPG by Esterification

PS- <i>b</i> -PPG	$M_n$ by SEC (PS-COOH), kg/mol	$M_n$ from Clariant (PPG), kg/mol	Amount of PS-COCl, mmol	Amount of PPG, mmol	Amount of solvent: THF, ml	Reaction time, h	Yield, %
1	1.6	0.8	0.62	0.54	19	45	74
2	1.7	0.5	0.58 <sup>a</sup>	0.58	15	72	33 <sup>b</sup>
3	2.2	0.5	0.44 <sup>a</sup>	0.44	15	69	26 <sup>b</sup>
4	2.2	0.8	0.46	0.40	21	46	76
5	3.4	0.8	0.26 <sup>a</sup>	0.26	15	70	40 <sup>b</sup>

<sup>a</sup>The solution of PPG, DMAP, and triethylamine in THF was added to PS-COCl.

<sup>b</sup>These products were purified by flash chromatography on silica gel eluting with chloroform.



Scheme 6

$T_g$  lowering end. After inserting  $\delta_{PS} = 9.5$  ( $\text{cal cm}^{-3}$ ) $^{1/2}$ ,  $\delta_{Alkyl} = 7$  ( $\text{cal cm}^{-3}$ ) $^{1/2}$ ,  $V_r = 100$  ( $\text{cm}^3\text{mol}^{-1}$ ) $^{1/2}$  from Coleman,<sup>17</sup> and  $N_{PS} = 200$  in eqs. 2 and 3, it is possible to plot the critical difference in solubility parameter ( $(\delta_{PS}-\delta_{block})_{crit}$ ) between PS and the model block copolymer as a function of the molecular weight of the model block copolymer (see Fig. 2).

A conservative estimate of the properties for a high molecular weight plasticizer for PS can be made in the following way: By inspection of Figure 2, it is seen that the critical difference in solubility parameters becomes very molecular weight dependent for molecular weights below 4 kg/mol where the value is approximately 1.3 ( $\text{cal cm}^{-3}$ ) $^{1/2}$ . By use of eq. 4 and ignoring differences in density, the difference in solubility parameters between PS and a PS-*b*-alkyl copolymer with 50 w/w % alkyl is calculated to 1.25 ( $\text{cal cm}^{-3}$ ) $^{1/2}$ . The educated guess is, therefore, that the molecular weight should be below 4 kg/mol and the alkyl content should be below 50%. If polybutadiene or poly(propylene glycol)monotridecyl ether is used instead of alkyl as the  $T_g$  lowering part, the molecular weight limit is expected to be slightly higher. The argument is that they both have a solubility parameter that is closer to PS than alkyl does.

If the aim is to plasticize the PS phase in, for example, a SIS block copolymer, there is an additional constraint not included in this approach. An LMW block copolymer consisting of a PS block with either an alkyl, polybutadiene, or poly(propylene glycol)monotridecyl ether block should be asymmetric and rich in PS in order for the block copolymer to be soluble in the PS phase and not in the polyisoprene or interphase.<sup>4,5</sup> Consequently, we estimate that the candidate should have a PS content of 75% or above.

### Synthesized block copolymers and properties

The plasticizing efficiency of an LMW block copolymer is expected to depend on molecular weight, ratio between blocks, and the nature of the blocks. Block copolymers with PS as one block and PPG, PB, and alkyl as the other have been synthesized with varying molecular weights and ratios between blocks.

Table V lists the molecular weights, compositions, and glass transition temperatures of the PS-*b*-PPG block copolymers synthesized. The negative  $\Delta T_g$  values can be explained in the following way: The end of the block that is connected to PPG has lower mobility than a free end. The contribution to free volume from the linked chain end is, therefore, lower than for a free end. To compensate for this, some authors<sup>19,20</sup> have divided the  $K$  in the Fox-Flory equation for a PS homopolymer with 2. To our knowledge the limits to this approach have not been investigated, and the question is if it is applicable to all block copolymers independent of molecular weight and structure. For the low molecular weights used in the PS-*b*-alkyl and the low  $T_g$  of the block attached to the chain end, both chain ends must be expected to have some mobility and therefore add to the free volume. We, therefore, use the constant for 2 free ends knowing that we overestimate the  $T_g$  in PS domain for the highest molecular weight block copolymers, which can explain the negative  $\Delta T_g$  values.

The PS-*b*-PB-*b*-PS samples fall outside the predicted solubility limits, either due to the molecular weight or due to the composition (Table VI). (PS-*b*-PB-*b*-PS)<sub>2800</sub> and (PS-*b*-PB-*b*-PS)<sub>4700</sub> were found to crosslink, observed as large inhomogeneities, which prevented the measurements in SIS.

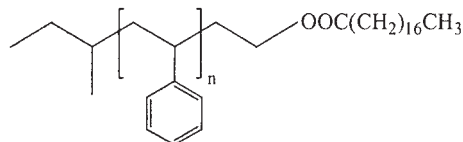
All the PS-*b*-alkyl samples fall within the predicted solubility limits and have low  $T_g$ s (Table VII) and therefore look to be good candidates for a plasticizer for PS.

### Plasticization of polystyrene

PS was mixed with the synthesized LMW block copolymers in a 1 : 1 ratio. The LMW block copolymers' efficiency as plasticizers was evaluated by DSC as listed in Table VIII.

All the mixtures of PS with PS-*b*-PB-*b*-PS have two  $T_g$ s indicating phase separation. The highest plasticization is seen for the two samples with the lowest molecular weight. The plasticization indicates that the block copolymers have some solubility in PS despite the fact that the samples are phase separated.

PS<sub>1600</sub>-*b*-PPG<sub>800</sub> acts as a plasticizer for PS but is not fully compatible, as seen by two  $T_g$ s (Table IX). The remaining PS-*b*-PPG LMW block copolymers show



Scheme 7

TABLE IV  
PS-*b*-Octadecyl Prepared from PS-OH and Octadecanoyl Chloride

PS- <i>b</i> -Octadecyl	M <sub>n</sub> PS-OH by SEC, kg/mol	Amount of PS-OH, mmol	Amount of octadecanoyl chloride, mmol	Amount of solvent: THF, ml	Reaction time, h	Yield, %
1	2.5	1.61	2.05	40	48	94
2	1.4	0.71	1.02	35	48	76
3	1.2	2.83	3.28	50	48	80
4	0.9	3.68	4.24	50	48	79

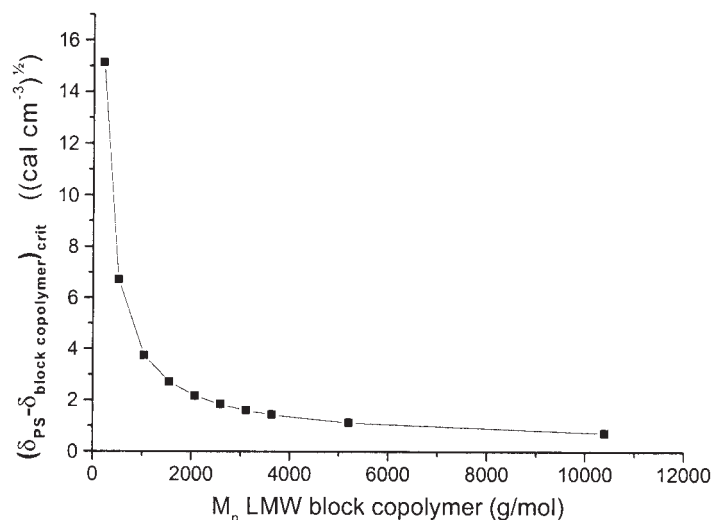


Figure 2 The critical difference in solubility parameter between PS ( $M_n = 20,000$ ) and model block copolymer as a function of the molecular weight of the model block copolymer.

TABLE V  
Properties of PS-*b*-PPG Block Copolymers

Products	M <sub>n</sub> by SEC (PS-COOH), kg/mol	M <sub>n</sub> <sup>a</sup> (PPG), kg/mol	M (Total), kg/mol	PS, wt%	T <sub>g</sub> <sup>c</sup> , °C	T <sub>g</sub> PS block calc. <sup>b</sup> , °C	Δ T <sub>g</sub> PS <sup>c</sup> , °C
PS <sub>1600</sub> - <i>b</i> -PPG <sub>800</sub>	1.6	0.8	2.4	67	46	59	13
PS <sub>1700</sub> - <i>b</i> -PPG <sub>450</sub>	1.7	0.5	2.2	77	88 <sup>d</sup>	62	-26
PS <sub>2200</sub> - <i>b</i> -PPG <sub>450</sub>	2.2	0.5	2.7	81	92 <sup>d</sup>	70	-22
PS <sub>2200</sub> - <i>b</i> -PPG <sub>800</sub>	2.2	0.8	3.0	73	92 <sup>d</sup>	70	-22
PS <sub>3400</sub> - <i>b</i> -PPG <sub>800</sub>	3.4	0.8	4.2	81	95 <sup>d</sup>	81	-14

<sup>a</sup> From manufacturer (Clariant).

<sup>b</sup> These are calculated using Fox-Flory:  $T_g = 100 - 65050/M_n$  (block)<sup>18</sup>.

<sup>c</sup> T<sub>g</sub> PS block calculated - T<sub>g</sub> PS domain measured.

<sup>d</sup> A small unquantifiable transition at low temperature was seen.

very little plasticizing effect on PS despite their compositions being within the predicted limits.

All PS-*b*-alkyl mixtures are homogeneous as indicated by only one T<sub>g</sub> in Table X. The plasticizing effect increases with lower molecular weight. Addition of 50% PS<sub>900</sub>-*b*-octadecyl lowers the T<sub>g</sub> of the PS by 67°C. Using the Fox equation (see eq. 1) on T<sub>g</sub>s of the pure components and the mixture, a content of 52% PS<sub>900</sub>-*b*-octadecyl can be calculated, close to the composition of the mixture. A DSC of a mixture with PS initiated with *sec*-butyl lithium and molecular weight 1.4 kg/

mol has been included in the series to understand how much of the T<sub>g</sub> depression originated from the low molecular weight PS end and how much originates from the additional alkyl chain. The octadecyl chain gives rise to an additional lowering of 15°C, as seen by the comparison with PS<sub>1400</sub>-*b*-octadecyl.

The most efficient plasticizers are those that lead to homogenous mixtures indicated by only one T<sub>g</sub> on the DSC scans, as illustrated in Figure 3. Some lowering of glass transition temperatures is seen for inhomogeneous mixtures. This is attributed to partial miscibil-

TABLE VI  
Properties of PS-*b*-PB-*b*-PS Block Copolymers

Products	M <sub>n</sub> by <sup>1</sup> H NMR (PS), kg/mol	M <sub>n</sub> (PB-Br) <sup>a</sup> , kg/mol	M (Total), kg/mol	(PS), wt%	T <sub>g</sub> <sup>c</sup> , °C	T <sub>g</sub> PS block calc. <sup>b</sup> , °C	Δ T <sub>g</sub> PS <sup>c</sup> , °C
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>2800</sub>	1.2	1.6	2.8	43	-43 <sup>d</sup>	-36	7
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>19000</sub>	17.7	1.6	19.3	93	85 <sup>d</sup>	91	6
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>7000</sub>	5.4	1.6	7.0	77	49 <sup>d</sup>	70	21
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>11000</sub>	8.9	1.6	11.0	81	62 <sup>d</sup>	83	21
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>12000</sub>	10.1	1.6	11.7	84	67 <sup>d</sup>	84	17
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>4700</sub>	3.1	1.6	4.7	66	11	48	37

<sup>a</sup> M<sub>n</sub> of the macroinitiator is calculated from the information of PB-OH from Sartomer and Scheme 2.

<sup>b</sup> These are calculated using Fox-Flory: T<sub>g</sub> = 100 - 65050/M<sub>n</sub> (block)<sup>18</sup>.

<sup>c</sup> T<sub>g</sub> PS block calculated - T<sub>g</sub> PS domain measured.

<sup>d</sup> A small unquantifiable transition at low temperature was seen.

TABLE VII  
Properties of PS-*b*-alkyl Block Copolymers

Products	M (PS), kg/mol	M (alkyl) <sup>c</sup> , kg/mol	M (Total), kg/mol	(PS), wt%	T <sub>g</sub> <sup>c</sup> , °C	T <sub>g</sub> PS block calc. <sup>d</sup> , °C	Δ T <sub>g</sub> PS <sup>e</sup> , °C
PS <sub>1600</sub> - <i>b</i> -octyl <sup>a</sup>	1.6	0.2	1.8	89	36	57	21
PS <sub>1600</sub> - <i>b</i> -octadecyl <sup>a</sup>	1.6	0.3	1.9	84	19	57	38
PS <sub>2500</sub> - <i>b</i> -octadecyl	2.5	0.4	2.9	86	37 <sup>f</sup>	71	34
PS <sub>1400</sub> - <i>b</i> -octadecyl	1.4	0.4	1.8	78	17 <sup>f</sup>	49	32
PS <sub>1200</sub> - <i>b</i> -octadecyl	1.2	0.4	1.6	75	4	45	41
PS <sub>900</sub> - <i>b</i> -octadecyl	0.9	0.4	1.3	69	-9	28	37
PS <sub>1400</sub> <sup>b</sup>	1.3	0.05	1.4	97	51		

<sup>a</sup> Prepared by DCC coupling.

<sup>b</sup> PS homopolymer made by anionic polymerization using *sec*-butyl lithium as initiator.

<sup>c</sup> M (alkyl) is calculated from Scheme 7, where PS is defined as the part within the brackets.

<sup>d</sup> These are calculated using Fox-Flory: T<sub>g</sub> = 100 - 65050/M<sub>n</sub> (block)<sup>18</sup>.

<sup>e</sup> T<sub>g</sub> PS block calculated - T<sub>g</sub> PS domain measured.

<sup>f</sup> A small unquantifiable transition at low temperature was seen.

TABLE VIII  
T<sub>g</sub> of Mixtures of PS with Molecular Weight 16 kg/mol and PS-*b*-PB-*b*-PS

Products	Ratio PS- <i>b</i> -PB- <i>b</i> -PS : PS	T <sub>g</sub> low, °C <sup>b</sup>	T <sub>g</sub> PS domain, °C	Δ T <sub>g</sub> PS, °C <sup>a</sup>
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>2800</sub>	1 : 1	-70	73	29
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>19000</sub>	1 : 1	-71	95	7
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>7000</sub>	1 : 1	-69	82	20
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>11000</sub>	1 : 1	-70	83	19
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>12000</sub>	1 : 1	-50	84	18
(PS- <i>b</i> -PB- <i>b</i> -PS) <sub>4700</sub>	1 : 1	-46	67	35

<sup>a</sup> Calculated: T<sub>g</sub> PS<sub>16000</sub> (102 °C) - T<sub>g</sub> mixture.

<sup>b</sup> Transition very weak and difficult to quantify.

ity, which could be due to the molecular weight distributions or the fact that the sample is right on the limit of solubility. The addition of PS-*b*-alkyl leads to homogeneous mixtures and to large depressions in the T<sub>g</sub> of the PS homopolymer. Furthermore, the plasticization efficiency is increased for lower molecular weight and PS content of the PS-*b*-alkyl.

#### Plasticization of SIS block copolymer

SIS block copolymer was mixed with 13% of the synthesized LMW block copolymers. Their efficiency as plasticizers was evaluated by DMA. Due to the low styrene content, no maximum in tan δ arising from the PS domain was observed. Instead, the temperature for



**TABLE IX**  
T<sub>g</sub> of Mixtures of PS with Molecular Weight 16 kg/mol and PS-*b*-PPG

Products	Ratio PS- <i>b</i> -PPG : PS,	T <sub>g</sub> low, °C <sup>b</sup>	T <sub>g</sub> PS domain, °C	Δ T <sub>g</sub> PS, °C <sup>a</sup>
PS <sub>1600</sub> - <i>b</i> -PPG <sub>800</sub>	1 : 1	-46	67	35
PS <sub>1700</sub> - <i>b</i> -PPG <sub>450</sub>	1 : 1	-52	95	7
PS <sub>2200</sub> - <i>b</i> -PPG <sub>450</sub>	1 : 1	-50	97	5
PS <sub>2200</sub> - <i>b</i> -PPG <sub>800</sub>	1 : 1	-53	97	5
PS <sub>3400</sub> - <i>b</i> -PPG <sub>800</sub>	1 : 1	-49	99	3

<sup>a</sup> Calculated: T<sub>g</sub> PS<sub>16000</sub> (102 °C) - T<sub>g</sub> mixture.

<sup>b</sup> Transition very weak and difficult to quantify.

which  $\tan \delta = 1$  was compared to that of the nonplasticized block copolymer. The difference was used as a measure for the plasticizing effect.

Neither PS-*b*-PB-*b*-PS nor PS-*b*-PPG block copolymers plasticize SIS significantly, as seen in Figure 4. In a number of cases, antiplasticization is seen. The samples are opaque, which indicates phase separation. For the PS-*b*-PB-*b*-PS series, the two most promising samples were not soluble in toluene. An explanation could be that the two samples had crosslinked prior to testing in SIS. The LMW samples in the PS-*b*-alkyl series plasticize SIS more than the high molecular weight samples. Increasing alkyl content increases the plasticizing efficiency on SIS. This becomes evident when the sample with 97% PS, having a ΔT<sub>g</sub> of 8°C, is compared to one with the same PS block molecular weight but higher alkyl content and a ΔT<sub>g</sub> of 15°C. The most efficient plasticizer is PS<sub>900</sub>-*b*-octadecyl, which lowers the temperature for which  $\tan \delta = 1 \times 22^\circ\text{C}$ . Using the Fox equation, it can be calculated that 10% of the added PS<sub>900</sub>-C<sub>18</sub> is dissolved in the PS phase.

By use of  $\tan \delta$  as a function of temperature in the range 5–150°C as a measure for plasticizing efficiency

**TABLE X**  
T<sub>g</sub> of Mixtures of PS with Molecular Weight 16 kg/mol and PS-*b*-alkyl Block Copolymers

Products	Ratio PS- <i>b</i> -alkyl : PS	T <sub>g</sub> PS domain, °C	Δ T <sub>g</sub> PS <sup>c</sup> , °C
PS <sub>1600</sub> - <i>b</i> -octyl <sup>a</sup>	1 : 1	64	38
PS <sub>1600</sub> - <i>b</i> -octadecyl <sup>a</sup>	1 : 1	53	49
PS <sub>2500</sub> - <i>b</i> -octadecyl	1 : 1	62	40
PS <sub>1400</sub> - <i>b</i> -octadecyl	1 : 1	54	48
PS <sub>1200</sub> - <i>b</i> -octadecyl	1 : 1	44	58
PS <sub>900</sub> - <i>b</i> -octadecyl	1 : 1	35	67
PS <sub>1400</sub> <sup>b</sup>	1 : 1	69	33

<sup>a</sup> Prepared by DCC coupling.

<sup>b</sup> PS homopolymer made by anionic polymerization using *sec*-butyl lithium as initiator.

<sup>c</sup> Calculated: T<sub>g</sub> PS<sub>16000</sub> (102 °C) - T<sub>g</sub> mixture.

**TABLE XI**  
Tensile Strength and Maximum Elongation for Plasticized SIS Using LMW Block Copolymers Compared to DOA Plasticized SIS

SIS mixed with	Maximum stress, MPa	Maximum elongation, %
0% DOA	10.0 ± 0.7	2150 ± 61
4% DOA	4.7 ± 0.3	2180 ± 60
8% DOA	3.1 ± 0.2	1880 ± 49
13% PS <sub>1400</sub> -C <sub>18</sub>	7.6 ± 0.2	2080 ± 71
13% PS <sub>1200</sub> -C <sub>18</sub>	7.0 ± 0.1	2000 ± 138
13% PS <sub>900</sub> -C <sub>18</sub>	6.9 ± 0.6	2340 ± 76

(as illustrated in Fig. 5), one can conclude that the most effective LMW block copolymer plasticizer is PS<sub>900</sub>-C<sub>18</sub>. It can be added that 13 w/w % PS<sub>900</sub>-C<sub>18</sub> is as effective as 8 w/w % dioctyl adipate (DOA) (data not shown for clarity).

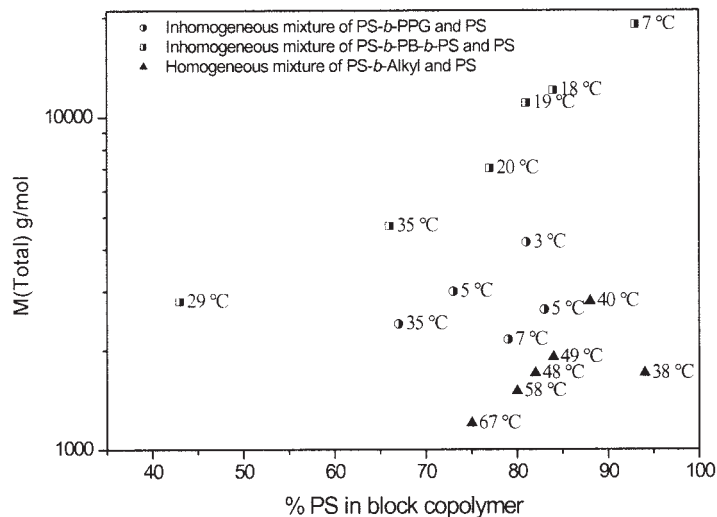
The tensile strength of SIS falls dramatically when DOA is added, as illustrated in Table XI. Mixtures of SIS with the three most effective LMW diblock plasticizers have higher tensile strength than the DOA plasticized SIS mixtures.

## CONCLUSION

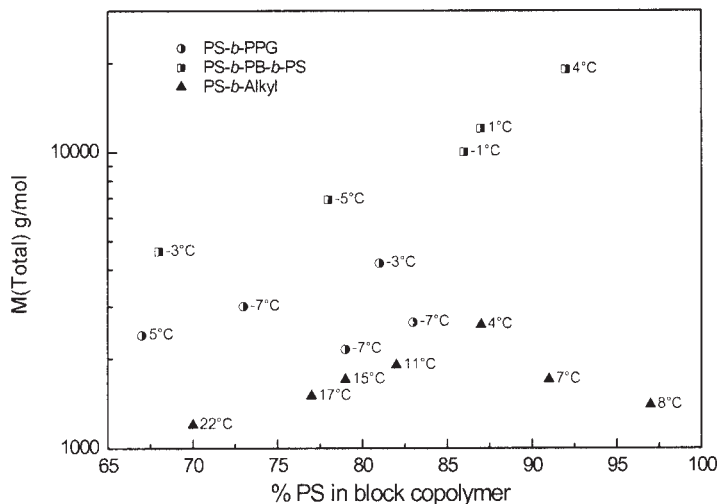
It is predicted that a minimum styrene content of 50% and a maximum molecular weight of 4 kg/mol is required for block copolymers of the type PS-*b*-alkyl to be soluble in PS.

Block copolymers consisting of a PS block with molecular weights of approximately 1 kg/mol and an alkyl block with a molecular weight of approximately 0.3 kg/mol are soluble in and plasticize PS. The T<sub>g</sub> lowering effect of the LMW block copolymers increases with decreasing molecular weight and PS content; it is noted that no PS-*b*-alkyl samples outside the predicted solubility limits were tested. In addition, PS-*b*-alkyl is found to be an efficient plasticizer also for SIS block copolymers. The end use properties, measured as tensile strength, of SIS plasticized with PS-*b*-alkyl is higher than SIS plasticized with DOA.

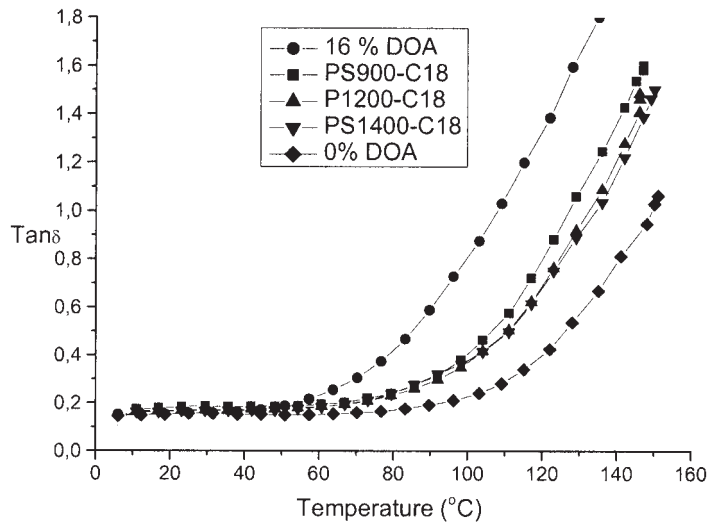
PS-*b*-PB-*b*-PS block copolymers with compositions near the proposed limits of solubility have a moderate plasticizing effect on PS and have low solubility in PS. It should be noted that the majority of PS-*b*-PB-*b*-PS samples have molecular weights that are higher than the predicted solubility limit. In the PS-*b*-PPG series, the majority of the samples have very little plasticizing effect on PS and low solubility in PS. This is despite the samples having molecular weights and composition well within the predicted solubility limits. The only PS-*b*-PPG sample that plasticized PS was the sample with the lowest molecular weight. None of the



**Figure 3**  $\Delta T_g$  (°C) of PS (Mn 16 kg/mol) blend with 50 w/w % LMW block copolymers. Higher values at markers indicate better plasticizers. Half symbols indicate opaque samples.



**Figure 4**  $\Delta T_g$  (°C) for the PS phase in SIS by addition of 13% LMW block copolymers. Higher values next to markers indicate better plasticizers. Half symbols indicate opaque samples.



**Figure 5**  $\tan \delta$  as function of temperature for mixtures of SIS with 13% PS<sub>900</sub>-C<sub>18</sub>, PS<sub>1200</sub>-C<sub>18</sub>, PS<sub>1400</sub>-C<sub>18</sub>, compared to samples with pure SIS (0% DOA) and SIS with 16% DOA.

tested PS-*b*-PB-*b*-PS or PS-*b*-PPG samples plasticized SIS to any practical extent.

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