

Enhancement of the High-Temperature Utility of a Polystyrene-*b*-Poly(ethylene-*co*-butylene)-*b*-Polystyrene Block Copolymer by Friedel–Crafts Naphthoylation

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ABSTRACT: A procedure was developed for the Friedel–Crafts naphthoylation of the polystyrene segments of a polystyrene-*b*-poly(ethylene-*co*-butene)-*b*-polystyrene (SEBS) triblock copolymer. It was possible to obtain up to 72% 1-naphthoylation or 100% 2-naphthoylation of the polystyrene segments in the copolymer. Naphthoylation could also be accomplished using trifluoromethanesulfonic acid as a catalyst. The naphthoylated products were characterized by ¹H-NMR spectroscopy, size-exclusion chromatography, and dynamic

mechanical thermal analysis. The mechanical properties of the original and naphthoylated polymers were measured from 25 to 125°C. The results obtained indicate that naphthoylation enhances the tensile properties of the polymers at elevated temperatures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1289–1295, 2003

Key words: block copolymers; modification; mechanical properties; NMR; thermal properties

INTRODUCTION

Triblock copolymers containing polystyrene end segments and hydrogenated polybutadiene, that is, poly(ethylene-*co*-butene) [poly(E-*co*-B)], segments are useful thermoplastic elastomers that are good candidates for chemical modification. Except for a few residual unsaturated units, the internal elastomeric segment is quite inert, but the polystyrene end segments can be modified by electrophilic substitution reactions. This provides a convenient means to introduce reactive or polar groups on the end segments or to increase their softening points and make the copolymers more useful at elevated temperatures. Weiss and coworkers,^{1–3} for example, sulfonated polystyrene-*b*-poly(ethylene-*co*-butene)-*b*-polystyrene (SEBS) block copolymers (Kraton G[®]) to obtain block copolymer ionomers that have significantly better tensile moduli, elongations, and ultimate strengths at 70–200°C than those of the parent copolymer. However, polyionomers are hygroscopic and sometimes difficult to process, and for some applications, it is worthwhile to pursue other methods of modifying the end segments of SEBS copolymers. Udding⁴ treated Kraton G[®], with 3-azido-sulfonylbenzoic acid to attach *m*-carboxybenzenesul-

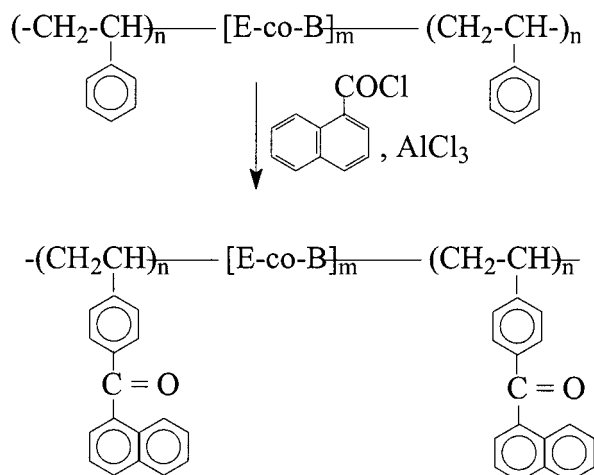
fonamide groups to the styrene units and thereby obtain a polymer with improved tensile strength. Hayashi⁵ alkylated the styrene units of Kraton G[®] using benzyl chloride or benzhydryl chloride as reagents in the presence of AlCl₃ and obtained products with higher moduli than those of the parent polymer but did not report *T*_g or tensile data. Similar work was reported by Matsumoto and Oshima.⁶ Liu and Jiang acetylated the styrene units in specially modified SEBS and then converted the resulting acetyl groups to carboxylic acid and alcohol groups, the degrees of substitution being 2–36%.⁷ Previously, we reported that benzoylation of the polystyrene segments in Kraton G[®] increased their glass temperature and that the resulting polymers had tensile properties that were superior to those of the original SEBS block copolymer, particularly so at elevated temperatures.⁸ In the present article, we report the results of studies on the naphthoylation of Kraton G[®] 1652 using 1- or 2-naphthoyl chloride and either aluminum chloride or trifluoromethanesulfonic acid as catalysts. The effect of naphthoylation on the tensile properties of the polymers at elevated temperatures is also reported.

Previously, polystyrene was naphthoylated to about 70% using naphthoyl chloride, carbon disulfide, and aluminum chloride. A pyrolysis-mass spectrometric examination of the polymer indicated that only monosubstitution of the styrene units occurred. The polymers were investigated as photoactive polymers.^{9,10} Except for our patents,^{11,12} there are no reports on the naphthoylation of Kraton G.:

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EXPERIMENTAL

Kraton G[®], a thermoplastic elastomer that is obtained by hydrogenating a polystyrene–polybutadiene–polystyrene block copolymer, was obtained from the Shell Chemical Co. (Houston, TX). The polymer is a triblock copolymer containing polystyrene end segments and a central ethylene/butene copolymer segment. The studies were done using Kraton G[®] 1652, which is reported by the manufacturer to have a molecular weight of 50,000 and to contain 30 wt % styrene units.

AlCl_3 -catalyzed naphthoylation of Kraton G[®] 1652

Kraton G[®] 1652 was 1- or 2-naphthoylated in various solvents and at various temperatures using aluminum chloride as the catalyst. In a typical reaction, a solution of Kraton G[®] 1652 (15 g, 0.043 mol styrene repeating units) in 420 mL carbon disulfide was prepared and mixed with 1-naphthoyl chloride (19.1 g, 0.100 mol). Aluminum chloride (14.0 g, 0.105 mol) was then added and the yellow solution that resulted was stirred at room temperature and bubbled with nitrogen to remove HCl. After 7 h, the solution formed a gel. Tetrahydrofuran was added to dissolve the gel and precipitate inorganic by-products. The solution was filtered and added dropwise into rapidly stirred methanol to precipitate the crude polymer product. This was purified by twofold reprecipitation from the THF solution into methanol and dried *in vacuo* at 45°C for 24 h. NMR analysis indicated that 19% of the styrene units in the polymer had been naphthoylated. GPC analysis indicated an M_w/M_n ratio of 1.26, which is slightly broader than that of the starting polymer (1.13). By doubling the amount of solvent and carrying out the reaction at 40°C, gelation of the reaction mixture could be avoided and a product ($M_w/M_n = 1.52$) with 64% of the styrene units naphthoylated was obtained in 5 h.

Naphthoylation could also be conducted using chlorobenzene or *o*-dichlorobenzene as solvents at 20 or

40°C. The reaction mixtures did not gel when the Kraton G[®] concentration was as high as 35.7 g/L and high extents of naphthoylation could be achieved. In fact, nearly complete 2-naphthoylation could be obtained in 10 h using *o*-dichlorobenzene at room temperature. Physical testing was done on polymers prepared using CS_2 as the solvent.

Trifluoromethanesulfonic acid-catalyzed naphthoylation of Kraton G[®] 1652

Trifluoromethanesulfonic acid was also used as a catalyst for naphthoylating Kraton G[®] 1652. It had the advantages of being liquid at ambient temperature, effective in small amounts (1–3 mol %), and soluble in appropriate solvents. The best results were obtained using 1,1,2-trichloroethane as the solvent but the degree of substitution of the styrene units was less than 35% for 1-naphthoylation or 50% for 2-naphthoylation. In a typical preparation, a solution of Kraton G[®] 1652 (8.0 g, 0.023 mol styrene repeating units) in 1,1,2-trichloroethane (100 mL) was prepared, mixed with 1-naphthoyl chloride (4.40 g, 0.023 mol), and heated to reflux temperature (111°C). Trifluoromethanesulfonic acid (0.10 g, 0.7 mmol) was added and the mixture was refluxed for 12 h. The reaction mixture was dropped slowly into rapidly stirred methanol to precipitate the polymer, which was collected and purified by twofold reprecipitation from the THF solution into methanol. It was then dried in a vacuum oven at 40°C for 24 h. NMR analysis indicated that 21% of the styrene units in the polymer had been 1-naphthoylated. GPC analysis indicated an M_w/M_n ratio of 1.30 for this material.

NMR analysis

¹H-NMR spectra of the polymers in the CDCl_3 solution (5%) were recorded at ambient temperatures using a Varian Gemini 200 NMR spectrometer. Figures 1 and 2 compare the spectra of Kraton G[®] 1652 and partially naphthoylated derivatives and provide assignments for the aromatic proton resonances observed. The degrees of naphthoylation of the styrene units were calculated from the ratios, R , of the resonance areas attributed to *ortho* protons (6.7–6.9 ppm) and other aromatic protons (6.9–8.3 ppm) using the following equation, where x is the fraction of styrene units naphthoylated and R is the observed ratio:

$$x = \frac{2 - 3R}{6R}$$

Size-exclusion chromatography

Molecular weight distributions were measured using a Viscotek instrument equipped with Waters Styra-

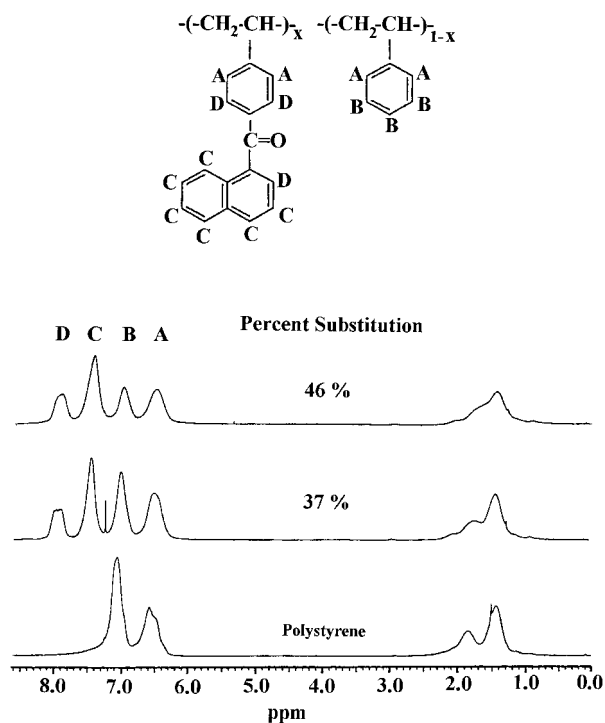


Figure 1 $^1\text{H-NMR}$ spectra, 200 MHz, of Kraton G[®] 1652 and 1-naphthoylated derivatives.

gel[®] HR1, 4E, and 5E (7.8 V 300 mm) columns and with a Waters 410 differential refractometer, a Viscotek Model 100 differential viscometer, and a Wyatt DAWN[®] EOS multiangle light-scattering detector. THF was the eluting solvent (1 mL/min) and measurements were made at 35°. Viscotek TriSEC triple-detection software was used to calculate molecular weights.

Dynamic mechanical thermal analysis

The T_g 's of Kraton G[®] 1652 and naphthoylated derivatives were determined using a Polymer Laboratories Model 9122 differential mechanical thermal analyzer equipped with a Hewlett-Packard data analyzer. The T_g 's of poly(E-co-B) segments were measured using a single-cantilever mode at a heating rate of 4°C per minute and a frequency of 1 Hz. The T_g 's of the polystyrene and modified polystyrene segments were measured in the shear mode at a heating rate of 2°C per minute and a frequency of 1 Hz.

Mechanical property measurements

Microdumbbell specimens approximately 1 mm in thickness and 2.5 mm in width were cut from sheets of the polymers that were prepared by compression molding. Parallel markings separated by 3 cm were placed on the specimens for use in making elongation and permanent set measurements.

Stress-strain measurements were made at various temperatures using an Instron mechanical tester equipped with an environmental box. The specimens were stretched at a rate of 5 cm/min after being equilibrated for 15 min at the desired temperature. Tensile stress was calculated by dividing the sample load by the initial cross-section area. The value at break is reported as the tensile strength of the sample.

Permanent set after 200% elongation was determined by stretching microdumbbell samples at a rate of 5 cm/min after an equilibration time of 15 min at the desired temperature until 200% elongation was obtained. The samples were maintained at this elongation for 2 min and then allowed to relax. The distances between the parallel marks on the samples were measured immediately after unloading and then 3 min later. Permanent set was calculated as $100(d - d_0)/d_0$, where d is the distance between the marks after 3 min and d_0 is the original distance between them.

RESULTS AND DISCUSSION

Naphthoylation reaction

The naphthoylation of Kraton G[®] 1652 with 1- or 2-naphthoyl chloride using either aluminum chloride or trifluoromethanesulfonic acid as catalysts was investigated. In general, 2-naphthoylation occurred eas-

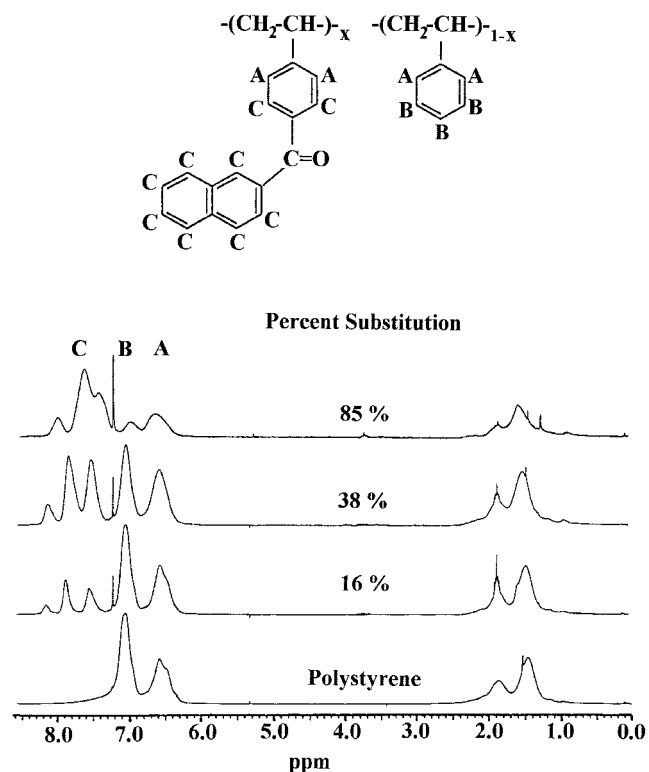


Figure 2 $^1\text{H-NMR}$ spectra, 200 MHz, of Kraton G[®] 1652 and 2-naphthoylated derivatives.

TABLE I
Variation of Percent Substitution, Molecular Weight, and Molecular Weight Distribution for Reactions of Kraton G[®] 1652 with 1-Naphthoyl Chloride in the Presence of AlCl₃

Solvent	Temperature (°C)	Reaction time (hf)	Percent substitution	Calculated M_n (K)	Observed M_n (K)	M_w/M_n
—	—	0	0	50	51	1.07
CS ₂	40	1	15	53	59	1.09
CS ₂	40	2	24	55	60	1.28
CS ₂	40	2.5	35	58	53	1.63
CS ₂	40	5	68	65	77	1.69
CS ₂	20	6	19	54	—	—
C ₆ H ₅ Cl	40	3	40	59	55	2.99
<i>o</i> -C ₆ H ₄ Cl ₂	20 ^a	1	39	58	52	2.08
<i>o</i> -C ₆ H ₄ Cl ₂	20	5	73	—	—	—

^a 2-Naphthoylation.

ier than did 1-naphthoylation but 1-naphthoyl groups had a larger effect on the glass transition temperatures of the products. Using AlCl₃ as the catalyst and *o*-dichlorobenzene as the solvent, 100% 2-naphthoylation or 72% 1-naphthoylation could be achieved. Some molecular weight distribution broadening occurred using carbon disulfide as the solvent. Some results obtained in the studies on the naphthoylation reactions are provided in Table I.

Refluxing 1,1,2-trichloroethylene proved to be a good solvent for 1-naphthoylations conducted using trifluoromethanesulfonic acid as the catalyst, but it did not prove possible to achieve more than 35% 1-naphthoylation or 50% 2-naphthoylation with it. Table II provides some typical results. In these reactions, it is possible that naphthoylation of naphthoyl groups in the partially naphthoylated polymers might compete with naphthoylation of styrene units at high extents of naphthoylation. Thus, Lancaster et al. reported previously that 2-naphthoyl chloride could be induced to condense with itself under Friedel-Crafts conditions to form an oligomer having a DP of approximately 6.¹³ Also, it has been reported that 1,5-dibenzoylnaphthalene is the major product obtained when benzoylnaphthalene is benzoylated with benzoyl chloride in the presence of aluminum chloride.¹⁴ To investigate whether naphthoyl groups in the polymers could be further naphthoylated, a sample of 72% 1-naphthoylated Kraton G[®] 1652 was submitted to further naph-

thoylation and the ¹³C-NMR and ultraviolet spectra of the resulting product were examined. The ¹³C-NMR spectrum contained only a single carbonyl carbon resonance and the ultraviolet spectra of the starting and renaphthoylated copolymers were essentially the same. We therefore believe that only styrene units are naphthoylated under the reaction conditions employed.

Dynamic properties of the copolymers

Dynamic mechanical thermal analysis was used to measure the dynamic properties of Kraton G[®] 1652 and its naphthoylated derivatives as a function of temperature. Figure 3 shows storage and loss moduli and tan δ data for the Kraton G[®] 1652 sample that was 30% naphthoylated, and Figure 4 shows tan δ data for Kraton G[®] 1652 and copolymers that were 30 and 64% naphthoylated. The temperatures at which maxima in the tan δ curve were observed were taken as measures of the glass transition temperatures of phases present in the samples. No explanation is available for the apparent maximum at about 165°C in the tan δ curve

TABLE II
Variation of Percent Substitution with Reaction Time for Reactions of Kraton G[®] 1652 with 1-Naphthoyl Chloride in the Presence of ~2% CF₃SO₃H

Solvent	Temperature (°C)	Reaction time (h)	Percent substitution
1,1,2-C ₂ H ₃ Cl ₃	114	4	14
1,1,2-C ₂ H ₃ Cl ₃	114	6	15
1,1,2-C ₂ H ₃ Cl ₃	114	12	22
1,1,2-C ₂ H ₃ Cl ₃	114	16	28
C ₆ H ₅ Cl	130	41	29

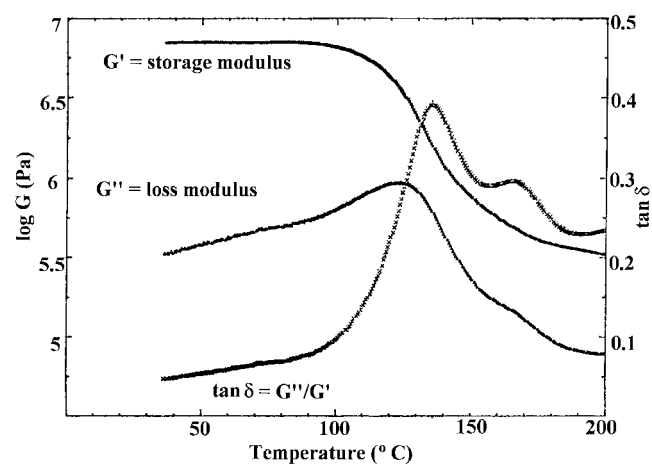


Figure 3 Tan δ , storage modulus, and loss modulus versus temperature for 30% 1-naphthoylated Kraton G[®] 1652.

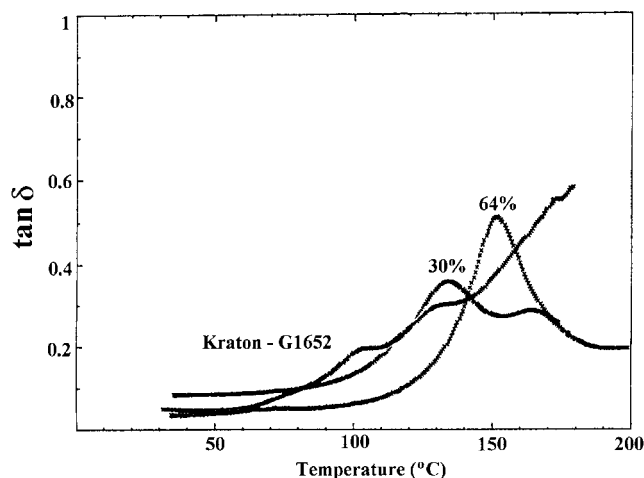


Figure 4 Tan δ curves for Kraton G[®] 1652 and 1-naphthoylated derivatives.

for the 30% naphthoylated sample. Table III lists the glass transition temperatures observed for the poly(E-co-B) and styrenic blocks present in samples that were naphthoylated to various extents. It can be seen that the T_g of the poly(E-co-B) phase occurs about -33°C in all the samples but that the T_g 's of the naphthoylated polystyrene segments steadily increase with the extent of naphthoylation. By considering the naphthoylated polystyrene segments to be copolymers containing styrene and naphthoylated styrene units, their glass transition temperatures, $T_g(\text{COP})$, can be related to the weight fraction of naphthoylated styrene units present, w , and the glass transition temperatures of polystyrene, $T_g(\text{PS})$, and completely naphthoylated polystyrene, $T_g(\text{PNS})$, as follows¹⁵:

$$\frac{1}{T_g(\text{COP})} = \frac{(1-w)}{T_g(\text{PS})} + \frac{w}{T_g(\text{PNS})}$$

Accordingly, a plot of $1/T_g(\text{COP})$ versus w should be linear. Figure 5 shows such a plot based on glass transition data obtained for Kraton G[®] 1652 and polystyrene samples that were substituted with either 1- or 2-naphthoyl groups. It can be seen that 1-naphthoylation has a larger effect on the T_g than does 2-naph-

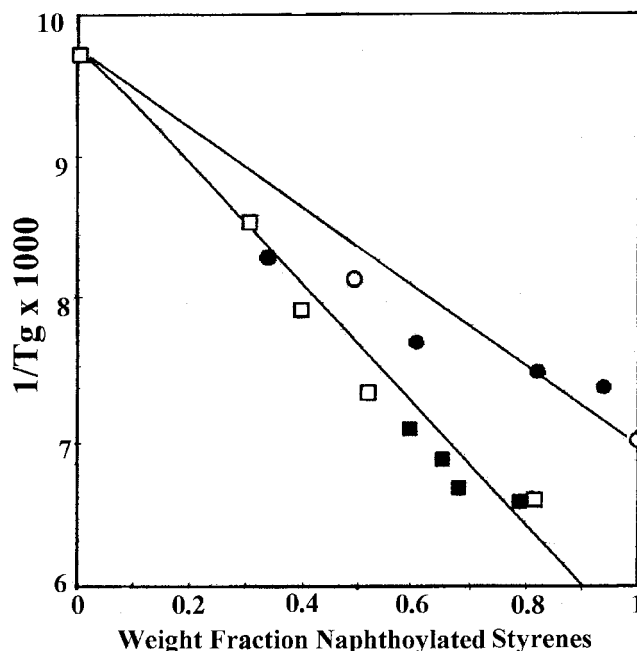


Figure 5 Plots of $1/T_g$ versus the weight fraction of naphthoylated styrene units in naphthoylated polystyrene and naphthoylated Kraton G[®] 1652. The solid line is a least-squares fit ($r = 0.986$) of the data for the 1-naphthoylated polymers. The dotted line connects $1/T_g$ values for the unmodified and completely 2-naphthoylated Kraton G[®] samples: (□) 1-naphthoylated Kraton; (■) 1-naphthoylated polystyrene; (○) 2-naphthoylated Kraton; (●) 2-naphthoylated polystyrene.

thoylation and that the glass transition temperatures of the naphthoylated polystyrene segments in Kraton G[®] 1652 are the same as those of the corresponding naphthoylated polystyrenes. Extrapolation of the plots to $w = 1.0$ indicates that the glass transition temperatures of the completely 1-naphthoylated and 2-naphthoylated polystyrene segments should be approximately 175 and 145°C , respectively.

Mechanical property studies

Films of Kraton G[®] 1652 and 1-naphthoylated derivatives were prepared by compression molding and evaluated for tensile properties at various tempera-

TABLE III
Glass Transition Temperatures of Segments in Kraton G[®] 1652 and Naphthoylated Derivatives

1-Naphthoylated			2-Naphthoylated		
Percent substitution	T_g (E-co-B)	T_g (styrene)	Percent substitution	T_g (E-co-B)	T_g (styrene)
0	-33	103	0	-33	103
15	—	117	28	—	123
21	-31	126	100	-30	141
30	—	136			
64	-33	151			

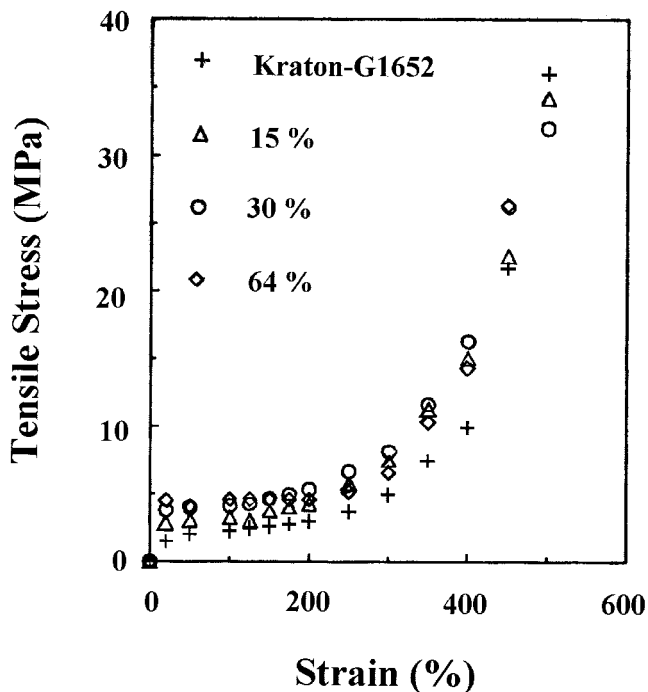


Figure 6 Stress-strain curves for Kraton G[®] 1652 and 1-naphthoylated derivatives at 25°C.

tures. Figure 6 shows tensile stress-strain curves for the various samples at 25°C. They are fairly similar except that the naphthoylated samples exhibit higher initial moduli than those of the parent polymer and exhibit yield points at about 25% elongation. This is attributed to strain softening due to the presence of connected naphthoylated polystyrene segment domains.

The effect of naphthoylation is dramatically illustrated by the stress-strain curves measured at 105°C, which are shown in Figure 7. The parent polymer has almost no strength at 105°C but the initial moduli, yield strengths, ultimate elongations, and tensile strengths all increase with the extent of naphthoylation.

The stress-strain curves for 30% 1-naphthoylated Kraton G[®] 1652 at various temperatures are shown in Figure 8. The tensile stress decreases as the testing temperature increases, but even at 90°C, the polymer retains part of its elasticity with a tensile strength of 6 MPa and a tensile strain of 600%. The curves measured at 25 and 63°C have similar shapes in that strain-hardening occurs above a 400–500% strain. This indicates that, at temperatures below 63°C, the polymer behaves elastomerically; the end segments of the functionalized polystyrene segments act as polyfunctional crosslinking points which oppose viscous flow.

As is evident in Figures 6 and 7, the 100% modulus increases with the extent of naphthoylation. This probably reflects the increase in the volume fraction of the glassy segments with increased naphthoylation. It is

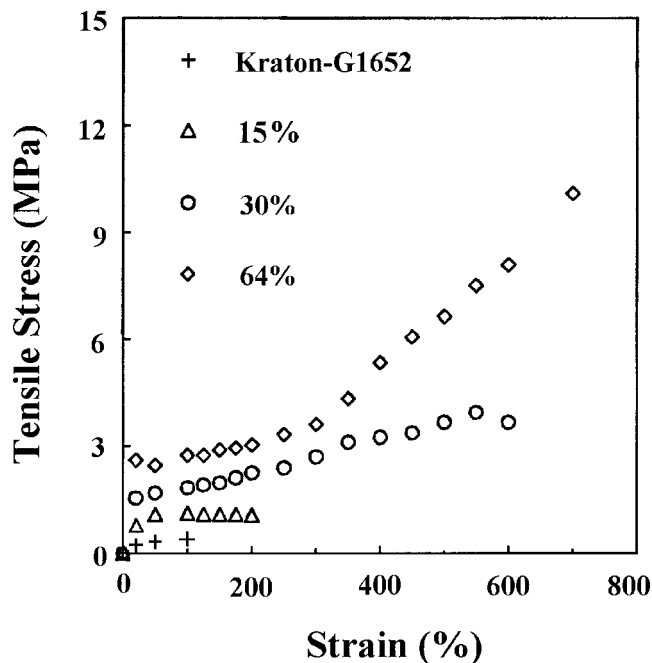


Figure 7 Stress-strain curves for Kraton G[®] 1652 and 1-naphthoylated derivatives at 105°C.

known from studies on SBS block copolymers that the modulus increases when the polystyrene content of a block copolymer is increased.¹⁶ The increase is thought to be due to the formation of a semicontinuous phase of substituted polystyrene segments.

Permanent (tensile) set measurements of Kraton G[®] 1652 and naphthoylated derivatives were made at various temperatures. As can be seen in Figure 9, permanent sets for the naphthoylated derivatives are *higher* than that for Kraton G[®] 1652 at 25°C. This is attributed

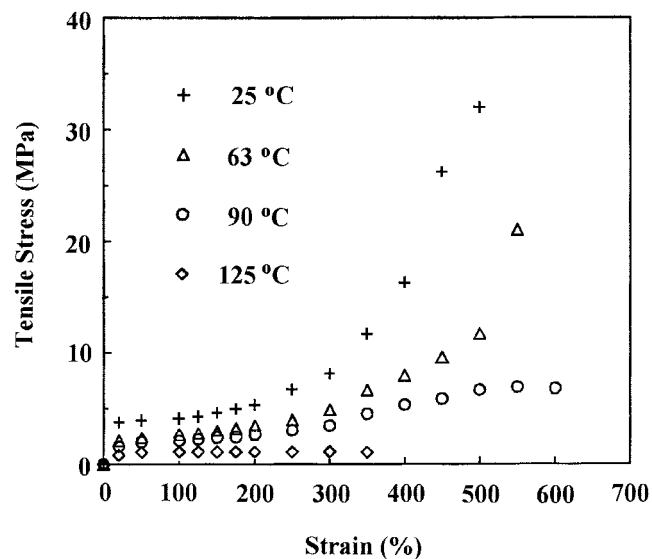


Figure 8 Stress-strain curves for 30% 1-naphthoylated Kraton G[®] 1652.

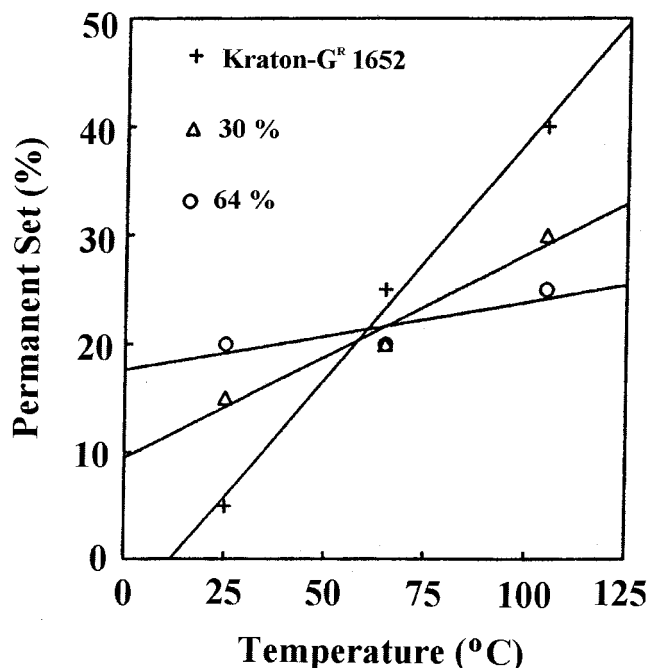


Figure 9 Permanent set versus temperature for Kraton G® 1652 and 1-naphthoylated derivatives.

to irreversible extension (yielding) of the hard end segments in the polymers, which are present as a semicontinuous phase. This yielding will be largest in the case of the more highly naphthoylated polymers because they contain a larger volume fraction of end segments and because higher stress is required to elongate them 200%. On the other hand, the permanent sets of the naphthoylated polymers at 105°C are considerably *less* than that of Kraton G®. This is attributed to the slippage of the physical crosslinks connecting the elastomeric segments being more significant for Kraton G® than for the naphthoylated products. The rate of such slippage will depend on the difference between the test temperature and the glass transition temperature of the hard segments present. This is effectively 0°C in the case of Kraton G® and 33 or 50°C, respectively, for the 30 and 64% naphthoylated polymers. At 100°C, the polystyrene end segments in Kraton G® 1652 will not be able to prevent flow of the elastomer segments while flow will be restricted and elastic recovery will be observed with the naphthoylated polymers.

CONCLUSIONS

The polystyrene segments in Kraton G® 1652 can be naphthoylated to high extents using aluminum chloride or trifluoromethanesulfonic acid as catalysts. The glass transition temperatures of the hard segments in the polymers were increased by naphthoylation and the resulting polymers had improved tensile properties at elevated temperatures. Naphthoylation increased the volume fraction of the hard segments in the polymers and this resulted in yielding phenomena and increased initial moduli. Naphthoylation improves the properties of Kratons more than does benzoylation but the increased volume fraction of end segments that it causes is a deterring factor.

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