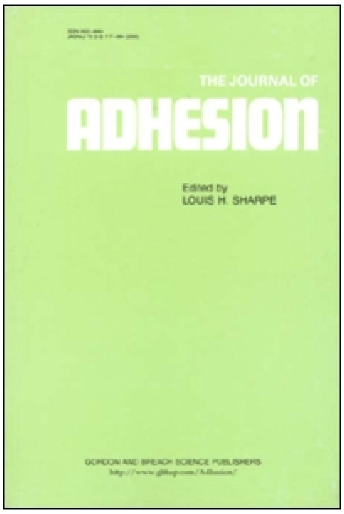

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Structural Effects on the Adhesive Properties of Butadiene/Styrene Radial Teleblock Copolymers[†]

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The effects of butadiene/styrene ratio, monomer distribution, and molecular weight distribution and branching on the pressure sensitive adhesive properties of butadiene/styrene radial teleblock copolymers are reported. Styrene content of polymers with varying structures shows a close relation with tack response, and styrene content and structure affect solution viscosity and shear adhesion. When part of the styrene is incorporated into the polybutadiene segment to yield a block progressively enriched in styrene (tapered block), solution viscosity and shear adhesion are reduced. When the butadiene segment is replaced by a block of randomly copolymerized butadiene and styrene, the polymers provide lower solution viscosities and shear adhesion but unchanged tack.

The molecular weight distribution of the radial teleblock polymers can vary from broad, highly branched compositions to narrow molecular weight distributions of almost linear polymers. The latter have relatively high solution viscosity and low shear adhesion, whereas the former polymers produce moderate solution viscosity but high shear adhesion. Tack is generally unaffected.

INTRODUCTION

The copolymerization of styrene, butadiene, as well as other monomers, with organometallic initiators in inert solvents provides considerable latitude in the preparation of copolymers.[1] For example, styrene and butadiene can be copolymerized so that strictly random copolymers, blocks of random copolymer and homopolymer, or blocks of strictly homopolymer are produced. Since the polymerization is conducted in the absence of chain terminating

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agents, the growing polymer chains are reactive and therefore can be branched[1,2] with any of a variety of reagents. For a butadiene/styrene copolymer, if the styrene is polymerized first, followed by the butadiene polymerization and then the branching step, the product will be a multichain polymer terminated with polystyrene blocks linked together through polybutadiene segments. A polystyrene-polybutadiene-X-polybutadiene-polystyrene (X is difunctional) structure is termed a teleblock polymer. If the number of branch chains is three or more, a radial teleblock polymer results.

The general characteristics of these polystyrene-terminated teleblock and radial teleblock polymers are well known. The incompatibility of the blocks causes the raw polymer to exhibit a distinct glass transition temperature for each segment.[3] The polystyrene segments associate with one another to form microdomains which effectively cross-links the molecules into a network structure. Depending on molecular weight and styrene content, these polymers exhibit relatively high tensile strengths.[3]

The block structure and the non-permanence of the network structure afford unique solubility characteristics. The copolymers are soluble in solvents in which the homopolymers are not normally soluble. Thus, these polymers are soluble in hexane plus a small quantity of toluene and similar solvents commonly employed in adhesives. The high bulk strength and unusual solubility of these polymers make up a balance of properties especially suited for pressure sensitive adhesive applications.

Pressure sensitive adhesive properties of radial teleblock polymers have been compared briefly with other polymers prepared in the solution process.[4] At comparable compositions and molecular weights (based on inherent viscosities) the radial teleblock-based adhesives showed moderate tack but high shear resistance. The present work examines the effect of composition and branching, molecular weight, and block structure on formulation viscosity, tack, peel strength, and shear resistance.

EXPERIMENTAL

The polymers were prepared by solution polymerization techniques described by Zelinski.[2] Copolymerizations in the presence of ethers and alkoxides were conducted according to described methods.[2,7,8] Molecular weights and molecular weight distributions were obtained by gel permeation chromatography and inherent viscosities were determined in toluene. The branching factor G is defined as the ratio

$$G = [\eta]_b/[\eta]_l$$

where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosities of the corresponding branched and linear molecules, the comparison being made at constant molecular weight. It is computed from the gel permeation chromatogram and $[\eta]$ of the whole polymer by means of a GPC calibration in terms of hydrodynamic volume, on the assumption that branching is uniform over the molecular weight distribution. When this assumption is not fulfilled, such as in mixtures of linear and coupled polymers, the value of G will be an average and there will be some error introduced into the computed molecular weight averages.[5] Tensile strength was obtained from compression molded slabs of the polymer obtained by pressing 20-mil thick films at 121°C for 5 minutes and cooling in the press. Dumbell samples were tested at room temperature on an Instron Tester at 20 inches/minute crosshead speed. Mooney viscosity was determined according to ASTM D927-57T. The properties of the polymers are given in the tables.

The pressure sensitive adhesive formulations consisted of equal parts of polymer and a commercial hydrogenated rosin ester in a 90/10 mixture of precipitation grade naphtha and toluene. Brookfield viscosities were determined on the solutions at 24°C. Tack was measured at 25°C on dry films of the adhesives on a Mylar backing with a Polyken Probe Tack Tester at 100 g/cm^2 contact pressure, for 1 second contact time, and at a separation rate of 1 cm/sec. Peel strength was conducted according to ASTM D1000. Shear adhesion was determined at 90°C by measuring the time required for 0.159 cm of slippage of a 6.46 cm^2 sample bonded vertically to stainless steel to which was attached a 908 gram weight.

RESULTS AND DISCUSSION

Table I shows the effects of the butadiene/styrene ratio (butadiene and styrene exist strictly as blocks) on the adhesive properties. The polymers were

TABLE I
Effect of butadiene/styrene ratio at equal molecular weights

	Polymer Properties			Adhesive Properties			
Butadiene/ Styrene	Inherent Viscosity[a]	Mooney Viscosity, MS-4, 138°C	Tensile Strength, PSI	Formulation Viscosity, Cps	Tack, Grams	Peel Strength, PIW[b]	Shear Adhesion, Hours to Failure
85/15	1.27	21	1700	650	510	2.1	0.03
80/20	1.38	66	4000	1630	660	2.9	1.0
75/25	1.14	68	4300	1260	660	3.1	1.1
70/30	1.07	71	4300	2960	830	4.1	2.5
65/35	1.05	83	4800	13,800	760	4.1	4.0
60/40	1.01	94	4900	> 60,000	690	4.6	4.5

[a] In toluene
[b] Pounds/inch width

prepared from the same quantity of initiator and have the same degree of branching. With compositions of 80/20 butadiene/styrene, significant shear adhesion develops which increases. Also nearly ultimate tensile strength is reached for these types of polymers when the butadiene/styrene ratio is 80/20 respectively. Correspondingly, the solution viscosity increases with increasing styrene content whereas tack appears to go through a maximum at 70/30 butadiene/styrene. The low tack response of the 85/15 butadiene/styrene polymer is probably a consequence of low cohesive strength (note shear adhesion and tensile strength of the bulk polymer), whereas high styrene causes a real reduction in tack. The solution viscosities and solubilities of the copolymers at low styrene contents (i.e., 85/15 butadiene/styrene, are similar to those of polybutadiene, both being highly soluble in the 90/10 naphtha/toluene mixture. Polymers containing higher levels of styrene (i.e., 60/40 butadiene/styrene, are not effectively dissolved in this solvent mixture and can form elastic solvent-swollen gels from interaction of the polystyrene blocks. For a particular formulation, as the percentage of toluene is increased, the polystyrene segments become more soluble yielding much lower viscosities with a minimum occurring, typically, for these polymers near 50:50 mixtures of naphtha and toluene (Figure 1). Apparently, as the toluene concentration increases, aggregates of the associated polystyrene segments are disrupted, followed by complete uncoiling and solution of the polystyrene segments.[6]

From the results of Table I, adhesive properties are not a direct function of the bulk properties of the polymer. High tensile strength does not necessarily impart high shear resistance. For example, the 75/25 and 70/30 butadiene/styrene copolymers exhibit the same tensile strength but different shear adhesion values. Nor do the inherent viscosity and Mooney viscosity vary directly with adhesive performance.

The polymers discussed in Table I were of constant degree of radiality or branching. The degree of branching does, however, affect adhesive properties. From a series of polymers of equal composition (70/30 butadiene/styrene) and initiator charge, significant differences in solution viscosity and shear adhesion are observed (Table II).

When a single parent polymer precursor with a given molecular weight is employed, polymers with low degrees of branching (Branching Index, $G = 0.95$–0.91) have higher solution viscosity and lower shear adhesion than the more highly branched polymers. The lower shear response exhibited at the highest degree of branching ($G = 0.71$) is most likely caused by the presence of free, uncoupled styrene-butadiene block polymer. The optimum situation is illustrated by the polymer in Table II in which there is considerable branching ($G = 0.80$) as well as nearly complete coupling (Gel Permeation Chromatograms, Figure 2). The uncoupled polymer appears as a

FIGURE 1. Solution viscosities of radial teleblock polymer/tackifier blends in naphtha/toluene mixtures

TABLE II
Effect of degree of branching

	Polymer Properties		Adhesive Properties			
Branching Index, G	Inherent Viscosity	Tensile Strength, PSI	Formulation Viscosity, Cps	Tack, Grams	Peel Strength, PIW	Shear Adhesion, Hours to Failure
0.95	0.99	2800	4390	900	4.4	1.0
0.91	1.01	4300	5940	880	4.4	2.5
0.80	1.07	4300	2960	830	4.1	2.5
0.71	1.12	3600	2620	740	2.7	1.1
0.77	0.91	1600	1070	480	3.7	0.2

shoulder on the higher-count side of the gel permeation chromatogram. Polymer A contains a large quantity of uncoupled polymer, approximately bimodal in composition, and Polymer *B* has less but a significant amount of uncoupled polymer. This polymer has, however, the highest calculated degree of branching. The optimum polymer in this study, *C*, and *D* and *E* exhibit shoulders indicative of uncoupled polymer. The presence of large amounts of parent polymer result in final products of low cohesive strength which also have low tack response. For other polymers tack is generally independent of degree of branching.

The effect of molecular weight for a series of polymers of equal composition (70/30 butadiene/styrene) and branching is shown in Table III. As molecular weight increases both formulation viscosity and shear adhesion increase.

If, however, the molecular weights of a highly branched polymer and lower branched polymer are adjusted so that approximately equal shear adhesion is observed, the effect of degree of branching can be seen (Table IV). In adhesive performance, the highly branched polymer affords lower solution viscosities. Higher cohesive strength is observed in the bulk polymer.

The results and discussion of the effect of butadiene/styrene ratio, degree of branching, and molecular weight, have been applied to radial teleblock polymers in which the polymerized styrene and butadiene exist as pure blocks. The monomer distribution can be changed, however, by alteration of the polymerization process. When 10 per cent of the styrene of a 60/40 butadiene/styrene copolymer is incorporated into the butadiene segment in the absence of randomizer (to be discussed below) the styrene copolymerizes in increasing concentration along the block with a small portion appearing as the additional and terminal segment. These are termed tapered block copolymers. The adhesive properties of this type of polymer are shown in Table V. Reduction of the major styrene block size from 40 weight per cent to 30 per cent does effect a lowering of the formulation viscosity. Also, the cohesive strength of the polymer is reduced making it comparable to a 70/30 butadiene/styrene polymer. Compared to the latter polymer, polymers with styrene in the polybutadiene segment have reduced solubility. Also, modification of the monomer distribution does not affect the tack response.

When 10 weight per cent of the styrene is copolymerized with the butadiene but in the presence of ether and alkoxide randomizers,[2,7,8] further reductions in formulation viscosity, shear adhesion, and bulk strength are observed (Table VI). Although the total styrene composition is 40 weight per cent, these polymers are lower in bulk strength than the 70/30 butadiene/styrene radial teleblock copolymer. Correspondingly, the shear adhesion of the 70/30 butadiene/styrene polymer is higher. The randomizers effect more randomization of styrene in the butadiene during polymerization and thereby reduce total block styrene content. However, randomizers are also known to alter the cis, trans, and vinyl content of the polybutadiene segment.[9]

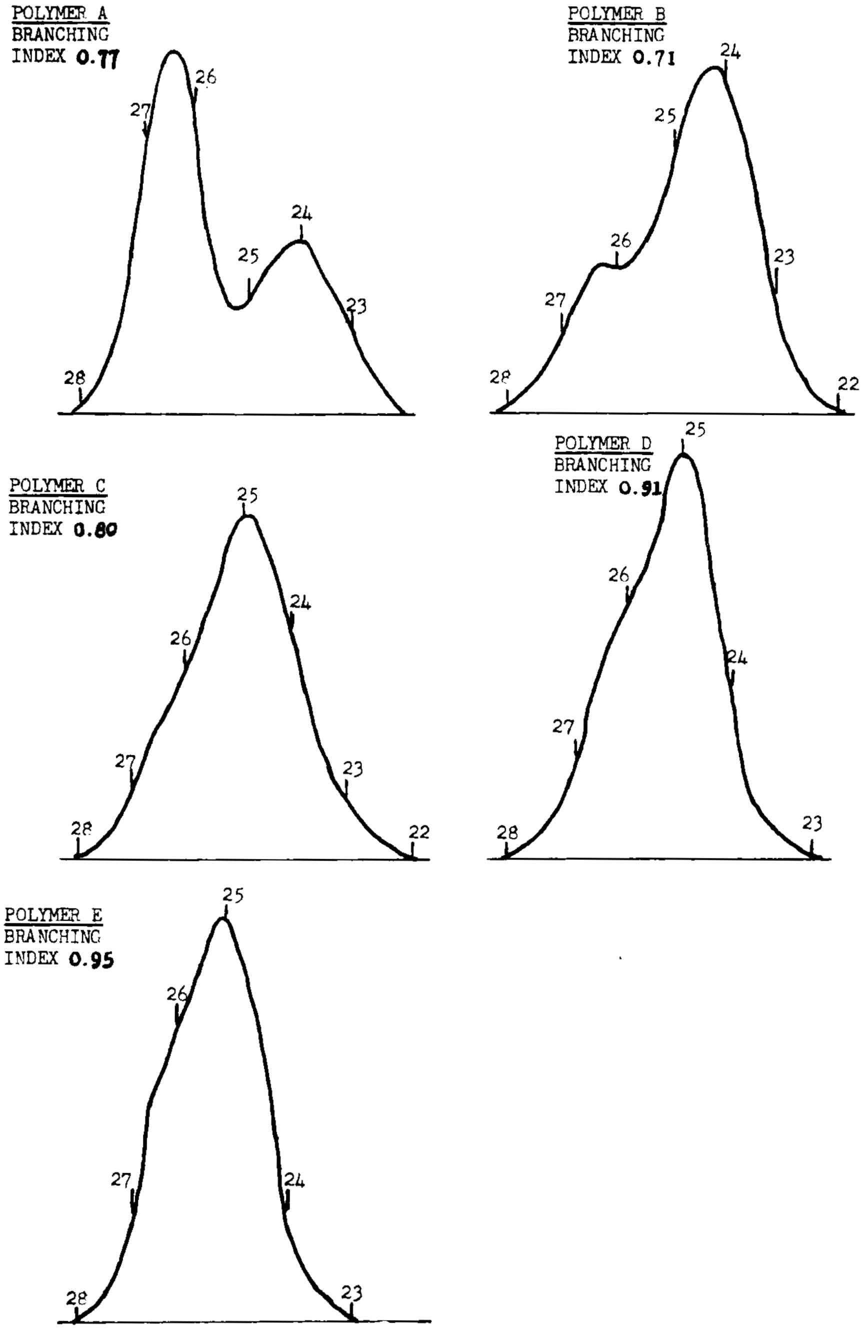

FIGURE 2. Gel permeation chromatograms of butadiene/styrene radial teleblock polymers of different degrees of branching

TABLE III
Effect of molecular weight at equal branching

	Polymer Properties[a]		Adhesive Properties			
MW × 10^{-3}	Inherent Viscosity	Tensile Strength, PSI	Formulation Viscosity, Cps	Tack, Grams	Peel Strength, PIW	Shear Adhesion, Hours to Failure
158	0.97	4500	770	590	3.4	0.4
173	1.04	4200	2350	763	3.4	1.6
192	1.22	4200	58,800	780	4.1	4.7

[a] Butadiene/styrene, 70/30.

TABLE IV
Effect of branching

	Polymer Properties		Adhesive Properties			
Branching Index, G	Inherent Viscosity	Tensile Strength, PSI	Formulation Viscosity, Cps	Tack, Grams	Peel Strength, PIW	Shear Adhesion, Hours to Failure
0.73	1.04	4200	2352	760	2.4	1.6
1.0	1.00	3000	3850	810	3.8	1.5

TABLE V
Influence of monomer distribution in tapered block copolymer

	Polymer Properties		Adhesive Properties			
Composition Bd/S-S	Inherent Viscosity	Tensile Strength, PSI	Formulation Viscosity, Cps	Tack, Grams	Peel Strength, PIW	Shear Adhesion, Hours to Failure
60/0-40	1.01	4900	60,000	690	4.6	4.5
60/10-30	1.10	4200	10,400	560	4.3	5.0
70/0-30	1.15	4100	6,400	820	3.5	4.7

TABLE VI
Properties of randomized butadiene/styrene radial teleblock copolymers

		Polymer Properties		Adhesive Properties			
Composition Bd/S-S	Randomizer	Inherent Viscosity	Tensile Strength, PSI	Formulation Viscosity, Cps	Tack, Grams	Peel Strength, PIW	Shear Adhesion, Hours to Failure
60/0-40	none	1.01	4900	> 60,000	690	4.6	4.5
60/10-30	none	1.1	4200	10,400	560	4.3	5.0
60/10-30	Ether	0.94	3600	1,560	530	4.9	0.9
60/10-30	Alkoxide	0.94	3200	1,080	650	5.3	0.7
70/0-30	none	1.15	4100	6,400	820	3.5	4.7

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