Anionic Graft Copolymers. I. Vinylaromatic Grafts on Polydienes

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ABSTRACT

Lithiated polydienes were readily prepared by direct
metalation of the diene polymers with sec-butyllithium and
tetramethylethylenediamine in cyclohexane at room tempera-
ture. Reaction of the polylithiodienes with styrene or α-
methylstyrene formed graft copolymers. Poly-1,4-butadiene,
poly-1,2-butadiene, cis-poly-1,4-butadiene, and polyisoprene
were the substrates lithiated. The extent of metalation was
much greater than previously reported metalations with
n-butyllithium and tetramethylethylenediamine. The grafting
efficiencies, determined by acetone extraction and gel perme-
ation chromatography, were greater than 95%. The physical
properties of the graft copolymers are compared as a function
of molecular weight, graft site level, and composition. At
certain molecular weights, graft site level, and compositions,
elastomers are formed without vulcanization. Their properties
are comparable to SBS rubber and offer higher melt flow as an
advantage.

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INTRODUCTION

The literature contains many routes to anionic graft copolymers, including reaction of polymer anions with preformed polymers [1, 2], halogen-metal interconversion on polymeric backbones followed by anionic polymerization of added monomers [3, 4], production of radical anions on polymeric backbones with a subsequent additional reaction of monomers [5, 6], and introduction of dialkylaluminum sites onto polymeric substrates to give polymeric alkylaluminum initiators [7].

Direct introduction of alkali metal sites on polymers by trans-metalation has also been reported. Gosnell et al. [8] examined the reaction of chelated organolithiums with poly(2-vinylpyridine) and subsequent reactions of this polylithiated species with styrene and isoprene. Yampolskaya metalated polystyrene with n-butyllithium-tetramethylethylenediamine chelate [9], and Minoura and Harada [10, 11] similarly metalated poly-1,4-butadiene and poly-1,4-isoprene. The polylithiated diene was reacted with vinyl monomers such as styrene to give graft copolymers, usually with low graft efficiency. Many investigators have studied the metalation of polydienes and subsequent graft polymer formation [12-17], and virtually all indicated that graft copolymer formation occurred in moderate to low efficiencies.

Minoura and Harada, using n-butyllithium complexed with tetramethylethylenediamine, found that short metalation times of 1 to 2 hr at temperatures from 50 to 100°C, followed by graft polymer formation with styrene, produced from 30 to 70% graft efficiencies and severe degradation of the polydiene substrate as measured by decrease in solution viscosity. Tate et al. [17] subsequently confirmed that rapid degradation of polybutadiene and polyisoprene substrates occurred at 50°C, and that graft efficiencies of 65 to 97% could be realized only by carrying out the metalation for extended times, up to 23 hr at 50°C. None have reported high metalation and grafting efficiencies under conditions which leave the substrate essentially intact.

This paper describes the metalation of poly-1,4-butadiene, poly-1,2-butadiene, cis-poly-1,4-butadiene, poly-1,4-isoprene, and poly-3,4-isoprene with sec-butyllithium and tetramethylethylenediamine and subsequent grafting with styrene or α-methylstyrene. The grafting efficiencies, determined by acetone extraction, are far better than previously reported for the very mild reaction condition of room temperature and 2-hr reaction time. Graft efficiencies of >95% are achieved with negligible degradation of the polymer substrate. Thus more direct control of structure and composition in graft polymers is achieved than previously thought possible. It should be pointed out that quenched substrate polymers were deliberately used to avoid formation of end block copolymers. The product properties thus represent real correlations of structural effects in graft copolymers.

EXPERIMENTAL SECTION

Materials

sec-Butyllithium was purchased from the Foote Chemical Company. Tetramethylethylenediamine was obtained from the Eastman Kodak Company and was distilled prior to use. The butadiene was Phillips special purity and was distilled and passed over molecular sieves prior to use. Cyclohexane was passed through molecular sieves. Tetrahydrofuran was distilled from sodium metal and potassium hydroxide and used immediately. All reactions and reagent transfers were carried out under a dry nitrogen atmosphere using the typical capped bottle techniques of Hsieh [18]. Hypodermic syringes were used to transfer reagents and catalysts.

Polybutadiene [19]

Butadiene, 30.0 g (0.556 moles), was dissolved in 650 ml of nitrogen degassed cyclohexane. The polymerization was initiated with 0.3 mmole of sec-butyllithium to give a 100,000 MW polymer. After 16 hr at 50°C the living polymer was quenched with 0.3 mmole of isopropanol. IR analysis showed the microstructure to contain 43% cis-1,4, 49% trans-1,4, and 8% 1,2 structure. The polymer was used immediately in grafting reactions.

Poly-1,2-butadiene was prepared in a similar manner with the addition of an amount of tetramethylethylenediamine equivalent to the sec-butyllithium initiator. The polymer contains 70% 1,2 and 30% cis- and trans-1,4 structures.

cis-Poly-1,4-butadiene

cis-Poly-1,4-butadiene was prepared according to the method of Gippin [20] using an alkylaluminum-cobalt chloride catalyst. The cis-1,4 content, determined from the IR spectrum, was 95% or greater. The polymer was extracted with dilute aqueous acid (5%) and water prior to grafting reactions to remove catalyst residues.

Polyisoprene

cis-Poly-1,4-isoprene was prepared in a manner similar to that of poly-1,4-butadiene. IR analysis showed the structure to be predominately cis-1,4.

Poly-3,4-isoprene was made by polymerizing isoprene with

sec-butyllithium and an equivalent amount of tetramethylethylene-diamine. The microstructure was predominately 3,4 as shown by IR analysis.

Polystyrene Graft Reactions on Poly-1,4-butadiene

In a typical example, 30.0 g of poly-1,4-butadiene, 100,000 MW, was dissolved in 650 ml of nitrogen degassed cyclohexane. sec-Butyllithium, 4.5 mmoles, and 4.5 mmoles of tetramethylethylenediamine were added, and the reaction mixture was stirred at room temperature for 2 hr. This amount was calculated to produce 15 graft sites per polymer chain. Freshly distilled styrene, 30.0 g (0.288 mole), was then added and the mixture was stirred at 50°C for 15 hr. The amber living polystyrene color was quenched with isopropanol. The polymer-solvent mixture was coagulated in isopropanol and dried at 60°C under vacuum. The graft copolymer was isolated in greater than 95% yield. Extraction in a Soxhlet apparatus of the graft copolymer with acetone, a polystyrene solvent, yielded no measurable polystyrene, indicating that greater than 95% of the polystyrene was grafted onto the poly-1,4-butadiene.

Poly-α-methylstyrene Graft Reactions on Poly-1,4-butadiene

Poly-1,4-butadiene, 13.5 g, 94,000 MW, dissolved in 400 ml of nitrogen degassed cyclohexane was prepared as previously described. sec-Butyllithium, 0.72 mmole, and 0.72 mmole of tetramethylethylene-diamine were added, and the reaction mixture was stirred at room temperature for 2 hr. This amount was calculated to produce five graft sites per polymer chain. A solution of 31.5 g (0.267 mole) of α-methylstyrene in tetrahydrofuran, which had been brought to a faint red color with sec-butyllithium, was added. The reaction mixture was immediately cooled to -40°C and stirred for 17 hr. The mixture was cooled to -78°C and kept at this temperature for 2 hr. The cold, living graft copolymer was quenched by addition of excess isopropanol. The polymer-solvent mixture was then coagulated in methanol and dried at 60°C under vacuum. The graft copolymer was isolated in greater than 95% yield. No suitable solvent system was found for the determination of graft efficiency by extraction. Gel permeation chromatography indicated a high graft efficiency.

RESULTS AND DISCUSSION

Metalation of the polydiene substrates was accomplished with a sec-butyllithium—tetramethylethylenediamine complex by reaction at room

temperature for 2 hr. The complex contained equivalent amounts of sec-butyllithium and tetramethylethylenediamine. The theoretical average number of lithiated sites on each molecule of the polylithiodiene was determined from the equation:

$$\text{number of graft sites per molecule} = (\text{moles of melating agent}) \Big/ \left(\dfrac{\text{grams of poly-1,4-butadiene}}{\text{poly-1,4-butadiene molecular weight}} \right)$$

Grafting was done by adding styrene to the lithiated polydiene, at the desired level, and running the graft polymerization reaction at 50°C for 15 hr. The amber color of the living polystyrene graft copolymer on poly-1,4-butadiene was titrated to colorless with a known amount of isopropanol. The polymer-solvent mixture was coagulated in isopropanol and dried at 60°C under vacuum. The graft copolymers reported in this paper were isolated in greater than 95% yield.

Extraction of the graft copolymers in a Soxhlet apparatus with acetone, a polystyrene solvent, gave graft efficiency data. The percent graft efficiency was determined from the equation:

$$\% \text{ graft efficiency} = \dfrac{\left(\begin{array}{c}\text{total wt of styrene}\\\text{polymerized}\end{array}\right) - \left(\begin{array}{c}\text{wt of polystyrene}\\\text{acetone extracted}\end{array}\right)}{(\text{total wt of styrene polymerized})} \times 100$$

The graft efficiencies of all of the graft copolymers of polystyrene on polybutadienes reported in this paper were greater than 95%. This represents a considerable improvement over other reported polydiene metalations, in particular the work of Tate et al. [17] and Minoura et al. [10]. Lower graft efficiencies were realized with very short reaction times, and at excessively high temperatures as well. A study of these aspects will be separately reported.

Graft Copolymers of Polystyrenes on Poly-1,4-Butadiene

The physical properties of graft copolymers of polystyrene on poly-1,4-butadiene are dependent on the molecular weight of the poly-1,4-butadiene substrate. At low molecular weights the graft copolymers mold into films which are weak and in most cases too weak to test. At high molecular weights the graft copolymers may be molded only with great difficulty. The most suitable viscosity-number average molecular weight range is between 90,000 and 150,000.

The choice of styrene level in graft copolymers of polystyrene on poly-1,4-butadiene has a marked effect on the physical properties at a

TABLE 1. Physical Properties of Graft Copolymers of Polystyrene on Poly-1,4-butadiene as a Function of Percent Polystyrene

Entry	% Styrene	Graft sites	PBD[a] (MW × 10^{-3})	Tensile strength		% Elongation
				Yield (psi)	Ultimate (psi)	
1	10	10	112	Too weak to test		
2	25	10	118	150	630	1300
3	34	10	123	300	1600	900
4	42	10	123	500	1800	750
5	50	10	112	110	1800	580
6	70	10	113	-	3500	4
7	10	3	112	<100	< 100	360
8	25	3	111	100	180	450
9	34	3	123	300	300	380
10	42	3	123	400	500	330
11	50	3	113	900	800	160
12	75	3	100	Too brittle to test		

[a]PBD = poly-1,4-butadiene.

constant graft site level and constant poly-1,4-butadiene molecular weight. Table 1 shows this effect. At 10 graft sites and poly-1,4-butadiene molecular weights of 110,000 to 120,000, a 10% polystyrene containing polymer molds into a film which is too weak to test, Entry 1. Increasing the polystyrene to 25, 34, 42, and 50%, Entries 2 to 5, gives rubbery materials with low tensile yields coupled with high ultimate tensile strengths and high elongation. The rubbery properties are achieved without vulcanization and are equal to the properties of a commercial polystyrene—poly-1,4-butadiene—polystyrene block copolymer, Shells Kraton 1101, with an ultimate tensile strength of 1,610 psi and an elongation of 580%, and Phillips polystyrene—poly-1,4-butadiene multiblock polymer Solprene 406C, which has an ultimate tensile strength of 3,000 psi and a 660% elongation. At 70% styrene, brittle materials result, Entry 6.

Graft copolymers of polystyrene on poly-1,4-butadiene at three sites are weak materials at styrene percentages of 10, 25, 34, 42, and 50, Entries 7 to 11, Table 1. Brittle materials result at 70% styrene, Entry 12.

Changes in graft level at a given styrene content produce remarkable shifts in physical properties, Table 2. With three graft sites at 42%

TABLE 2. Physical Properties of Graft Copolymers of Polystyrene on Poly-1,4-butadiene as a Function of Graft Level

Entry	Graft sites	% Styrene	PBD[a] (MW × 10^{-3})	Tensile strength Yield (psi)	Ultimate (psi)	% Elongation
1	3	42	123	400	500	330
2	7	42	120	400	1200	730
3	10	42	123	500	1800	750
4	20	42	123	460	2970	900
5	35	42	120	160	740	980
6	3	34	123	300	300	380
7	7	34	116	280	1080	840
8	10	34	123	300	1600	900
9	20	34	123	200	2500	1200
10	35	34	115	Too weak to test		

[a]PBD = poly-1,4-butadiene.

styrene and 120,000 molecular weight, a weak material is produced, Entry 1. At a constant molecular weight and styrene composition, as the graft site level is increased from 3 to 20, progressively stronger and then more rubbery materials are produced, Entires 2 through 4. The maximum strength occurs at 20 sites; the material is tough and rubbery with an ultimate tensile strength of 2970 psi coupled with a tensile yield of 460 psi and an elongation of 900% with good elastic recovery. At graft site levels much above 20, weak materials result, Entry 5.

Similar results are noted at a constant styrene composition of 34% and molecular weight of ~120,000, Entries 6 through 10. Tough, rubbery materials occur at 20 graft sites. At both higher and lower graft site levels weaker materials occur.

Graft Copolymers of Polystyrene on Poly-1,2-butadiene

The microstructure of the polybutadiene backbone has an effect on the physical properties of graft copolymers made thereon.

Polybutadiene containing 70% 1,2 structure and 30% 1,4 structure was made by initiating butadiene polymerization with sec-butyllithium and an equivalent amount of tetramethylethylenediamine. Lithiation

TABLE 3. Physical Properties of Graft Copolymers of Polystyrene on Poly-1,2-butadiene[a]

| Entry | % Styrene | Graft sites | Tensile strength | | % Elongation |
			Yield (psi)	Ultimate (psi)	
1	25	10	130	1170	790
2	34	3	160	210	100
3	34	10	310	1810	820
4	34	20	220	1290	650
5	42	10	160	2000	620
6	50	10	990	1600	330
7	70	10	-	4400	7

[a]110,000 molecular weight.

was accomplished by reaction with a sec-butyllithium—tetramethylethylenediamine complex. Addition of styrene gave, in greater than 95% yields, graft copolymers of polystyrene on poly-1,2-butadiene. Grafting efficiencies, as determined by acetone extraction, were greater than 95%.

The physical properties of these graft copolymers are reported as a function of polystyrene composition and graft site level, Table 3. Poly-1,2-butadiene, 110,000 MW, was the substrate lithiated. A comparison of these data with the data in Table 2 indicates that a high 1,2-diene structure results in decreased tensile yield and increased ultimate tensile with similar elongation. At 42% polystyrene and 10 graft sites a tough rubbery material results, Entry 5, with an ultimate tensile strength of 2000 psi, a tensile yield of 160 psi, and a 330% elongation. The comparable polystyrene graft on poly1,4-butadiene is shown in Table 2, Entry 3. The material has a 500-psi tensile yield, a 1800-psi ultimate tensile strength, and a 750% elongation. Increasing the polystyrene content to 70% gives a brittle material with an ultimate tensile strength of 4400 psi and an elongation of 7%.

Graft Copolymers of Polystyrene on cis-Poly-1,4-butadiene

Polybutadiene having a high cis-1,4 content was prepared by the procedure reported by Gippin [20]. An alkylaluminum-cobalt chloride catalyst modified by small amounts of water was used. The cis-1,4 content, determined from the IR spectrum, was 95% or greater.

cis-Poly-1,4-butadiene was extracted with dilute aqueous acid (5%) and water to remove catalyst residues. Use of this polybutadiene gives a third type of diene microstructure to be evaluated in graft polymer systems. cis-Poly-1,4-butadiene may be metalated only in the absence of catalyst residue. The metalation and polystyrene grafting reactions were identical to the metalation and polystyrene grafting on poly-1,4-butadiene. Polystyrene graft copolymers on cis-poly-1,4-butadiene were isolated in greater than 95% yields with graft efficiencies, determined by acetone extraction, in excess of 95%.

As is the case with anionic poly-1,4-butadiene and poly-1,2-butadiene, the physical properties of graft copolymers of polystyrene on cis-poly-1,4-butadiene are dependent on the molecular weight of the cis-poly-1,4-butadiene substrate. The molecular weight range for useful graft polymer preparations is quite narrow in contrast to the anionic poly-1,4-butadiene graft system. At low molecular weights the graft copolymers mold into films which are too weak to test. At higher molecular weights the graft copolymers cannot be molded. The optimum viscosity-number average molecular weight range appears to be between 50,000 and 70,000. The molecular weight distribution is broad compared to the narrow molecular weight distribution of anionic polybutadiene.

The physical properties of graft copolymers of polystyrene on cis-poly-1,4-butadiene are a function of the polystyrene composition, Table 4. The cis-poly-1,4-butadiene molecular weight is 57,000 and the graft site level is held constant at 10 sites.

TABLE 4. Physical Properties of Graft Copolymers of Polystyrene on cis-Poly-1,4-butadiene as a Function of Styrene Level[a,b]

| Entry | % Styrene | Tensile strength | | % Elongation |
		Yield (psi)	Ultimate (psi)	
1	20	Too weak to test		
2	34	100	700	620
3	50	800	2000	700
4	60	-	2210	< 5
5	70	Too brittle to test		
6	80	Too brittle to test		

[a] 57,000 molecular weight cis-poly-1,4-butadiene.
[b] Graft level, ten sites.

TABLE 5. Physical Properties of Graft Copolymers of Polystyrene on cis-Poly-1,4-butadiene as a Function of Graft Level[a,b]

Entry	Graft sites	Tensile strength		% Elongation
		Yield (psi)	Ultimate (psi)	
1	1	Too weak to test		
2	3	-	600	250
3	5	1050	1190	350
4	10	800	2000	700
5	15	910	1670	800
6	20	580	1370	960
7	25	370	820	840
8	50	Too weak to test		
9	75	Too weak to test		

[a]57,000 molecular weight cis-poly-1,4-butadiene.
[b]Styrene level, 59%.

Low levels of styrene result in weak materials, Entry 1. As the polystyrene composition is increased to 34, 50, and 60%, tougher materials result, Entries 2, 3, and 4. At 50% polystyrene a tough rubbery material is formed with an ultimate tensile strength of 2000 psi coupled with a 800-psi tensile yield and a 700% elongation. At polystyrene percentages greater than 50%, more brittle materials result.

As expected, the number of graft sites, at a constant polystyrene composition and molecular weight, greatly affect the physical properties of graft copolymers of polystyrene on cis-poly-1,4-butadiene, Table 5. At high (75) and low (1) graft site levels, weak materials result. At intermediate graft site levels tougher materials result with the optimum physical properties occurring at 10 graft sites, Entry 4. The material has an ultimate tensile strength of 2000 psi coupled with a tensile yield of 800 psi and an elongation of 700%.

The physical properties of graft copolymers of polystyrene on cis-poly-1,4-butadiene are similar to graft copolymers of polystyrene on anionic poly-1,4-butadiene and poly-1,2-butadiene. The physical properties of the rubbery materials are equal to or better than commercial polystyrene—poly-1,4-butadiene—polystyrene block and multiblock copolymers, Kraton and Solprene.

Graft Copolymers of Poly-α-methylstyrene on Poly-1,4-butadiene

Graft copolymers of poly-α-methylstyrene on poly-1,4-butadiene may be made by initiating α-methylstyrene polymerization with lithiated poly-1,4-butadiene. It was hoped that the presence of α-methylstyrene in the copolymer would give materials with increased heat distortion.

The graft polymerization technique used to prepare polystyrene grafts on poly-1,4-butadiene was modified somewhat to accomplish α-methylstyrene graft copolymerization. During the grafting reaction the reaction temperature was kept below the temperature at which poly-α-methylstyrene is in equilibrium with its monomer in an anionic system. Temperatures as low as -40°C must be used to achieve complete conversion of α-methylstyrene to polymer [21]. In our system, tetrahydrofuran was added to a solution of lithiated poly,1,4-butadiene in cyclohexane. This prevented solidification of the reaction mixture during low temperature polymerization. α-Methylstyrene monomer was added; the reaction mixture was cooled to -40°C and stirred at this temperature for 17 hr. The reaction mixture was then cooled to -78°C and kept at this temperature for 2 hr. Isopropanol was added and the reaction mixture was allowed to warm to room temperature. The graft copolymer was coagulated in methanol and isolated in greater than 95% yield. Although no suitable solvent system was found to separate grafted and nongrafted poly-α-methylstyrene, gel permeation chromatography indicated a high graft efficiency.

The physical properties of these graft copolymers were studied at several poly-α-methylstyrene compositions, several graft site levels, and at two poly-1,4-butadiene molecular weights. Although an increased heat distortion was noted compared to analogous polystyrene grafts, the physical properties of the materials were not good. At poly-α-methylstyrene compositions of less than 70%, weak materials were produced, and brittle materials resulted at greater than 70% poly-α-methylstyrene.

Graft Copolymers of Polystyrene on Polyisoprene

Substrates other than polybutadienes may be used in graft copolymer preparations. Poly-1,4-isoprene and poly-3,4-isoprene are two examples. The preparations of cis-poly-1,4-isoprene and poly-3,4-isoprene were identical to the preparations of poly-1,4-butadiene and poly-1,2-butadiene. IR analysis showed cis-poly-1,4-isoprene to contain predominately the cis-1,4 structure and the poly-3,4-isoprene to contain predominately the 3,4 structure. The metalation and

TABLE 6. Physical Properties of Graft Copolymers of Polystyrene on cis-Poly-1,4-isoprene[a] and on Poly-3,4-isoprene[b]

| Entry | % Styrene | Graft sites | Tensile strength | | % Elongation |
			Yield (psi)	Ultimate (psi)	
Grafts on cis-Poly-1,4-isoprene					
1	25	10	70	280	1280
2	34	10	280	1410	1080
3	42	10	490	2360	1000
4	50	10	1090	2300	740
5	42	15	480	1810	980
6	42	20	470	1380	890
Grafts on Poly-3,4-isoprene					
7	25	10	170	1240	490
8	34	10	510	1360	400
9	42	10	980	1690	300
10	50	10	1720	1870	190
11	42	15	1180	1370	200
12	42	20	1190	1230	220

[a]100,000 molecular weight cis-poly-1,4-isoprene.
[b]100,000 molecular weight poly-3,4-isoprene.

polystyrene grafting reactions were identical to the metalation and polystyrene grafting on poly-1,4-butadiene. Polystyrene graft co-polymers on the polyisoprenes were isolated in greater than 95% yield with graft efficiencies, determined by acetone extraction, in excess of 95%.

The physical properties of some graft copolymers of polystyrene on cis-poly-1,4-isoprene and poly-3,4-isoprene are listed in Table 6. The molecular weight was held constant at 100,000 and the graft site level and polystyrene composition varied. At low polystyrene contents, weak materials result with cis-poly-1,4-isoprene substrates. Increasing the polystyrene content leads to increased toughness. At 42% polystyrene, Entry 3, at 10 graft sites the material is tough and rubbery with a tensile yield of 490 psi, a tensile strength of 2360 psi, and an elongation of 1000%. Increasing the graft site level at this polystyrene composition, Entires 5 and 6, leads to decreased ultimate tensile strength with similar tensile yields and elongations. Poly-3,4-isoprene

based materials are slightly weaker than their poly-1,4-isoprene counterparts. Tough rubbery materials do occur at 42% polystyrene and 10 graft sites, Entry 9, with a tensile yield of 980 psi, an ultimate tensile strength of 1690 psi, and an elongation of 300%.

The best of the polyisoprene materials are similar in properties to the best materials based upon the rubbers: anionic poly-1,4-butadiene, anionic poly-1,2-butadiene, and cis-poly-1,4-butadiene.

Comparison of Block and Graft Copolymers

Polystyrene—poly-1,4-butadiene—polystyrene block polymers are isomeric with graft copolymers of the same composition. Block copolymers of styrene and butadiene are linear while graft copolymers possess, in the examples reported in this paper, a number of polystyrene arms radiating from a common poly-1,4-butadiene backbone.

TABLE 7. A Comparison of the Physical Properties of ABA Block Copolymers and Graft Copolymers

% Styrene	Graft sites·	MW × 10⁻³	Tensile strength		% Elongation
			Yield (psi)	Ultimate (psi)	
Block Polymers[a]					
25	-	135	200	500	600
34	-	150	300	1400	600
50	-	200	800	2300	700
Kraton 1101[b]				1610	580
Solprene 406C[b]				3000	660
Graft Polymers[c]					
34	20	123[d]	200	2500	1200
42	20	123[d]	460	2970	900
50	10	57[e]	800	2000	700
42	10	100[f]	490	2360	1000

[a]Polystyrene—poly-1,4-butadiene—polystyrene.

[b]Dissolved in chloroform and precipitated in methanol to remove stabilizers.

[c]Graft copolymers of polystyrene on poly-1,4-butadiene.

[d]Molecular weight of poly-1,4-butadiene.

[e]Molecular weight of cis-poly-1,4-isoprene.

[f]Molecular weight of cis-poly-1,4-isoprene.

A given styrene composition in the graft system can have a wide range of structures while in the block ABA copolymer there is only one polymer at any given styrene content.

Because of the similarities in composition and differences in structure, a comparison of block and graft copolymers is desirable. Table 7 presents a comparison of the physical properties of ABA block copolymers, polystyrene—poly-1,4-butadiene—polystyrene, with graft copolymers of polystyrene on poly-1,4-butadiene. Comparisons are made in the 25 to 50% polystyrene composition range and in the 100,000 to 200,000 MW range. The physical properties of the two types of copolymers are similar. They both are tough and rubbery with high ultimate tensile strengths coupled with low tensile yields and high elongations.

A rather striking difference exists between graft and block co-polymers in the melt flow characteristics. A comparison of polystyrene—poly-1,4-butadiene—polystyrene ABA block copolymers and graft copolymers of polystyrene on poly-1,4-butadiene is made in Table 8. The melt flow at 200°C is studied under 5.0 kg load. Similar

TABLE 8. A Comparison of the Melt Flow of ABA Block Copolymers and Graft Copolymers[a]

% Styrene	Graft sites	MW × 10^{-3}	Melt index (g/10 min)
		Block Polymers[b]	
25	-	135	0[c]
34	-	150	0[c]
34	-	65	0[c]
50	-	100	0[c]
70	-	250	0[c]
		Graft Polymers[d]	
34	10	66[e]	1.3
50	20	791[e]	9.2
80	10	57[e]	8.5
34	20	123[f]	1.2
34	7	56[f]	g

[a]Melt flow at 200°C under 5.0 kg load.
[b]Polystyrene—poly-1,4-butadiene—polystyrene.
[c]No measurable flow under these conditions.
[d]Graft copolymers of polystyrene on poly-1,4-butadiene.
[e]Molecular weight of cis-poly-1,4-butadiene.
[f]Molecular weight of anionic poly-1,4-butadiene.
[g]Flow too fast to measure.

molecular weight and polystyrene composition copolymers are compared. Under these conditions block copolymers of styrene and butadiene show no flow while similar graft polymers flow easily.

CONCLUSION

Lithiated polydienes are readily prepared by direct metalation of diene polymers with sec-butyllithium and tetramethylethylenediamine in cyclohexane at room temperature. The extent of metalation, greater than 95%, is considerably better than previously reported metalations with n-butyllithium and tetramethylethylenediamine. Graft copolymers are formed by reacting the metalated polydiene with styrene or α-methylstyrene. The physical properties of the graft copolymers are a function of molecular weight, graft site level, and composition. At certain molecular weights, graft site level, and compositions, rubbery materials result with physical properties equal to or better than commercial polystyrene—poly-1,4-butadiene—polystyrene block or multiblock copolymers, Kraton 1101 and Solprene 406C. The greater melt flow exhibited by graft polymers compared to block polymers enables easier processibility.

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