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Anionic Graft Copolymers. III. Hydrogenation of Polydienes Grafted with Vinylaromatics

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ABSTRACT

A new method is described to prepare graft copolymers of polystyrene and polyvinylcyclohexane on polyethylene and poly(ethylene, butene-1). Hydrogenation of the butadiene moieties of graft copolymers of polystyrene on poly-1,4-butadiene and high vinyl polybutadiene forms graft copolymers of polystyrene on polyethylene and on poly(ethylene, butene-1). Graft copolymers of polyvinylcyclohexane on polyethylene and on poly(ethylene, butene-1) are prepared by completely hydrogenating graft copolymers of polystyrene on poly-1,4-butadiene and on high vinyl polybutadiene. The physical properties of these polymer systems depend on composition and graft level, resulting in either tough polymers or elastomers.

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INTRODUCTION

Hydrogenation has been widely employed as a means of modifying polymer systems. Corordination catalysts derived from alkyl-aluminums and transition metal salts of 2-ethylhexanoic acid have been used to hydrogenate polybutadiene-polyisoprene-polybutadiene block copolymers [1-3] and 1,4-butadiene-1,2-butadiene block copolymers [4], giving uniquely structured olefin block copolymers containing combinations of ethylene, butene-1, isoprene, and propylene. Polystyrene-polybutadiene-polystyrene block copolymers can be hydrogenated only in the olefinic portion, or under more drastic conditions to be completely hydrogenated polyvinylcyclohexane-polyethylene-polyvinylcyclohexane block copolymers [5-7]. Numerous other investigators have studied the hydrogenation of vinyl aromatic-diene copolymers [8-14].

Graft copolymers of polystyrene on polybutadiene may be prepared free of cross-linked gel by recently reported [15] anionic graft copolymerization routes. These highly soluble structures may be readily hydrogenated to give unique styrene-ethylene and vinylcyclohexane-ethylene graft copolymers. The physical properties of these materials vary with structure, both of the grafts and of the backbone. The correlation of some of these structural effects, as well as reporting their syntheses, is the purpose of this paper.

RESULTS AND DISCUSSION

Graft Copolymers of Polystyrene on Polyethylene

Graft copolymers of polystyrene on polyethylene were prepared by the hydrogenation of graft copolymers of polystyrene on polybutadiene. The polymers, dissolved in cyclohexane, were hydrogenated at 50°C, 50 psi hydrogen, with a triethylaluminum-cobalt(II) 2-ethylhexanoate catalyst having an aluminum/cobalt ratio of 3/1. Hydrogenations were complete in less than 1 hr. The IR spectra showed no absorption resulting from polybutadiene unsaturation. After a dilute acid wash to remove catalyst residue, the graft copolymer was precipitated in 2-propanol and dried at 60°C under vacuum. The graft copolymers were isolated in quantitative yield. Higher temperatures and pressure are required to hydrogenate the aromatic unsaturation in polystyrene. A minimum hydrogen pressure of 4000 psi and a minimum temperature of 250°C are required to hydrogenate both the polystyrene and polybutadiene moieties of the graft copolymers. In this manner graft copolymers of polyvinylcyclohexane on polyethylene and on poly(ethylene, butene-1) are formed by hydrogenating graft

copolymers of polystyrene on poly-1,4-butadiene and high vinyl polybutadiene.

The requisite graft copolymers of polystyrene on polybutadiene were prepared according to the method of Schlott and Falk [15]. Polybutadiene, prepared by anionic polymerization initiated by *s*-butyllithium, has a microstructure, by IR analysis, containing 43% *cis*-1,4 49% *trans*-1,4, and 8% 1,2 structure. Hydrogenation gives a polyethylene containing 8% butene-1. Poly-1,2-butadiene was prepared in a similar manner with the addition of an amount of tetramethylethylenediamine equivalent to the *s*-butyllithium initiator. The polymer contains 70% 1,2 and 30% *cis*- and *trans*-1,4 structures by IR analysis. Hydrogenation gives poly(ethylene, butene-1) containing 70% butene-1. Other compositions of poly(ethylene, butene-1) may be prepared by varying the 1,2 and *cis*- and *trans*-1,4 structures in the substrate polybutadiene. This is accomplished by varying the ratio of tetramethylethylenediamine to initiator.

The physical properties of graft copolymers of polystyrene on polyethylene as a function of composition are described in Table 1.

These styrene-grafted polyethylenes give clear, flexible, tough films which vary little in ultimate tensile strength over a wide range of styrene content. The only changes noted up to 50% styrene content were an increase in tensile yield strength coupled with a small decrease in tensile elongation. Beyond that point, increases in styrene content result in more rigid and, finally, brittle materials.

Similarly, as shown in Table 2, increases in graft level at constant styrene content result in only very slight changes, reflected as small decreases in tensile properties.

These reported data were developed for copolymers with a constant backbone length of 115,000 viscosity-average molecular weight. The final copolymer molecular weight, then, varies with styrene content.

The composition and graft site levels affect the physical properties of graft copolymers of polystyrene on poly(ethylene, butene-1), Table 3. The composition was examined at two polystyrene levels, two graft site levels were studied, and the ethylene:butene-1 ratio in the poly(ethylene, butene-1) backbone was studied at two levels. This was done at a constant poly(ethylene, butene-1) molecular weight of 117,000.

The primary effect of changing the backbone microstructure by increasing the butene-1 component is to produce a sharp decrease in tensile yield strength, coupled with a high ultimate tensile strength and good elongation. The result is the development of elastomeric properties. Entry 1, with a 17% butene-1 component, is in fact a tough elastomer exhibiting good elastic recovery even though unvulcanized. Further increases in butene-1 content to 60% reduce the ultimate tensile strength as well. Compare Entries 1 with 3 and 2 with 4. All are elastomers, and careful selection of graft level, styrene content, and butene-1 content can produce a copolymer tailored to the desired balance of properties.

TABLE 1. Physical Properties of Graft Copolymers of Polystyrene on Polyethylene^a as a Function of Percent Polystyrene

Entry	% Styrene	Graft sites	Tensile strength		% Elongation
			Yield (psi)	Ultimate (psi)	
1	10	3	1300	3000	500
2	25	3	1600	2400	350
3	34	3	2000	2900	380
4	42	3	2300	3200	360
5	50	3	2500	3100	280
6	70	3	-	4200	7
7	10	10	1400	2600	430
8	25	7	1600	2800	380
9	34	10	2000	2200	260
10	42	10	2420	2920	300
11	50	10	2800	2700	90
12	70	10	Too brittle to test		

^a115,000 molecular weight polyethylene. Based upon a 110,000 molecular weight poly-1,4-butadiene substrate.

Hydrogenation of graft copolymers of polystyrene on *cis*-polybutadiene (>95% *cis*-1,4) is an alternate route to graft copolymers of polystyrene on polyethylene. At 35% polystyrene and 10 graft sites with a 73,000 MW polyethylene (derived from *cis*-polybutadiene), the graft copolymer has an ultimate tensile strength of 2350 psi coupled with a tensile yield of 2700 psi and an elongation of 40%. These copolymers are thus similar to those prepared from anionic polybutadiene, e.g., Table 2, Entry 3.

Polystyrene graft copolymers on poly(ethylene, propylene) may be prepared by hydrogenation of a graft copolymer of polystyrene on polyisoprene. If anionic polymerization in cyclohexane is used to prepare polyisoprene, the polymer will contain isoprene predominately in the *cis*-1,4 configuration (by IR), and hydrogenation gives predominately an alternating poly(ethylene, propylene) containing some

TABLE 2. Physical Properties of Graft Copolymers of Polystyrene on Polyethylene^a as a Function of Graft Level

Entry	Graft sites	% Styrene	Tensile strength		% Elongation
			Yield (psi)	Ultimate (psi)	
1	3	34	2000	2900	380
2	9	34	1900	2300	250
3	10	34	2000	2200	260
4	35	34	1720	1740	125
5	3	42	2300	3200	360
6	7	42	2300	2600	240
7	10	42	2420	2920	300
8	35	42	2130	2680	300

^a115,000 molecular weight polyethylene. Based upon a 110,000 molecular weight poly-1,4-butadiene substrate.

TABLE 3. Physical Properties of Graft Copolymers of Polystyrene on Poly(ethylene, butene-1)^a

Entry	% Styrene	Graft sites	Tensile strength		% Elongation
			Yield (psi)	Ultimate (psi)	
1 ^b	25	10	570	4020	510
2 ^b	34	10	980	2250	360
3 ^c	25	10	160	1380	640
4 ^c	34	10	280	1770	675
5 ^c	34	20	340	1760	740
6 ^c	42	10	560	1700	470

^a117,000 molecular weight polyethylene. Based upon 113,000 molecular weight polybutadiene substrate.

^b17% butene-1 in poly(ethylene, butene-1).

^c60% butene-1 in poly(ethylene, butene-1).

TABLE 4. Physical Properties of Graft Copolymers of Polyvinylcyclohexane on Polyethylene

Entry	% PVCHX ^a	Graft sites	Polyethylene ^b MW × 10 ⁻³	Tensile strength		% Elongation
				Yield (psi)	Ultimate (psi)	
1	10	7	113	1500	3000	420
2	25	7	105	2200	2900	380
3	50	3	60	-	2300	170
4	50	10	120	-	2900	36
5	65	10	70	-	2200	25
6	70	7	145	-	3900	7
7	34	7	60 ^c	740	2400	500

^aPVCHX = polyvinylcyclohexane.

^bBased upon the molecular weight of the polybutadiene substrate.

^c63% 1,2-polybutadiene.

butene-1 units. An anionic graft copolymer of styrene on poly(ethylene, propylene) containing 34% styrene at 10 graft sites (133,000 MW) is a weak rubbery material having an ultimate tensile strength of 950 psi with a 220-psi tensile yield and 1000% elongation.

Graft Copolymers of Polyvinylcyclohexane on Polyethylene

Complete hydrogenation of graft copolymers of polystyrene on poly-1,4-butadiene forms graft copolymers of polyvinylcyclohexane on polyethylene. Table 4 lists the physical properties of these graft copolymers as a function of polyvinylcyclohexane composition, graft site level, and polyethylene molecular weight.

The trends noted for styrene-ethylene graft copolymers appear to carry over into this system. At low levels of polyvinylcyclohexane, the copolymer films are clear, tough, and flexible. With increased polyvinylcyclohexane content, more rigid, lower elongation films result. A change in backbone microstructure from polyethylene to polyethylene-butene-1, made by hydrogenation a polystyrene-63% poly-1,2-butadiene graft copolymer, again gave a sharp reduction in tensile yield strength, to impart elastomeric properties.

Hydrogenation of polystyrene to polyvinylcyclohexane leads to a higher heat distortion material [14]. An increase of 60°C occurs. This same effect occurs in our system. A polyvinylcyclohexane (70%) graft copolymer on polyethylene, Table 4, Entry 6, has a 46°C higher heat distortion than the graft copolymer substrate, polystyrene on polyethylene, from which it was made. At lower polystyrene (polyvinylcyclohexane) concentrations the increase is less pronounced.

In summary, graft copolymers of polystyrene and polyvinylcyclohexane on polyethylene and poly(ethylene, butene-1) backbones are readily prepared by hydrogenation of the corresponding polystyrene-polybutadiene anionic graft copolymers. The physical properties of these materials depend largely on styrene content and backbone microstructure. Useful elastomeric properties result upon incorporation of butene-1 into the backbone structure, while intermediate levels of polyvinylcyclohexane or polystyrene grafted on polyethylene produce clear, flexible, tough films.

EXPERIMENTAL SECTION

Graft Polymer Preparation

Graft copolymers of polystyrene on poly-1,4-butadiene and on 1,2- and 1,4-butadiene copolymers were prepared according to the method described by Schlott and Falk [15].

Partial Hydrogenation of Graft Copolymers

In a typical example a graft copolymer of polystyrene on poly-1,4-butadiene, 20.0 g, was dissolved in 1500 ml of cyclohexane and placed with 0.3 mole % (based on the weight of polybutadiene in the graft copolymer) of triethylaluminum-cobalt(II) 2-ethylhexanoate catalyst having an aluminum-cobalt ratio of 3/1 in a 2-liter reactor thermostated at 50°C. Hydrogen was bubbled through the reactor at a constant hydrogen pressure of 50 psi throughout the hydrogenation. The reaction was carried out until the IR spectrum of an aliquot was free of absorption due to butadiene unsaturation, less than 1 hr reaction time. The polymer solvent mixture was washed with dilute aqueous acid to remove catalyst residue, then precipitated in 2-propanol and dried at 60°C under vacuum. The graft copolymer of polystyrene on polyethylene was isolated in quantitative yield.

Complete Hydrogenation of Graft Copolymers

Complete hydrogenation of graft copolymers of polystyrene on poly-1,4-butadiene was effected in a manner similar to the partial

hydrogenation of graft copolymers. A hydrogen pressure of 4000 psi and a temperature of 250°C was required to prepare graft copolymers of polyvinylcyclohexane on polyethylene quantitatively.

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