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### Functional Polymers. XVII. Radical Grafting of Methyl 5-Vinylsalicylate onto Polybutadienes

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## Functional Polymers. XVII. \* Radical Grafting of Methyl 5-Vinylsalicylate onto Polybutadienes

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### ABSTRACT

Methyl 5-vinylsalicylate was successfully grafted onto 1, 2- and cis-1,4-polybutadiene. When the grafting reaction was carried out in benzene at 60°C with azobisisobutyronitrile or benzoyl peroxide as the initiator, methyl 5-vinylsalicylate was transformed into grafted poly(methyl 5-vinylsalicylate) with a grafting efficiency of 5-22%. It was very important to carry out the grafting reaction under carefully controlled conditions and at relatively low concentration of polybutadienes, otherwise utilization of methyl 5-vinylsalicylate was low and cross-linking of polybutadiene occurred.

### INTRODUCTION

Grafting of vinyl monomers onto unsaturated polymers with radical initiators was accomplished many years ago and is now widely used [1-5]. Numerous publications are concerned with the grafting of monomers onto unsaturated polymers, like latex, in solution and

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in bulk. However, grafting of vinyl monomers with free phenolic hydroxyl groups, especially of methyl 5-vinylsalicylate (M5VS), a typical polymerizable ultraviolet absorber, onto unsaturated polymers has not yet been studied.

M5VS has been synthesized, polymerized, and copolymerized with a number of comonomers such as styrene, methyl methacrylate, and acrylic acid using azobisisobutyronitrile (AIBN) as the initiator [6]. Grafting of vinyl monomers onto unsaturated polymers had been carried out in the past with AIBN or with benzoyl peroxide (BPO) as the initiators. It is known that grafting on allylic groups can occur via addition of initiator radicals to the double bond, and these can come either from decomposition of BPO [7-14] or in some cases from AIBN as resonance stabilized radicals [10-12]. In general, radicals from BPO are superior to radicals from AIBN as grafting initiators [10-12]; in certain cases AIBN was actually ineffective [7-9, 13, 14].

It was the purpose of this work to investigate the grafting of M5VS onto polybutadiene (PBD) and to study the relative effectiveness of BPO and AIBN for grafting without cross-linking. The study of the compatibility of PBD and poly-M5VS, either with or without graft copolymers poly(BD-g-M5VS), was also the objective of this work.

## EXPERIMENTAL PART

### Materials

Methanol, butanone, petroleum ether, chloroform, and toluene (Fisher Scientific Co.) were distilled at atmospheric pressure.

Benzene (Fisher Scientific Co.) was washed with sulfuric acid, aqueous sodium hydroxide solution, and water, dried over phosphorous pentoxide, and distilled.

Azobisisobutyronitrile (AIBN) (Eastman Kodak Co.) and benzoyl peroxide (BPO) (Fisher Scientific Co.) were recrystallized twice from dry methanol and dry methanol/chloroform, respectively, and dried for 24 h at 0.05 mm at room temperature.

2,2'-Methylene bis (6-tert-butyl-p-cresol) (Pfaltz & Bauer) (MBC) and deuterated chloroform (Norell) were used as received.

1,2-Polybutadiene (RB-820) and cis-1,4-polybutadiene (BR-01) (Japan Synthetic Rubber Co.) had the following structure. RB-820: 1,2- (92%) and cis-1,4- (8%). BR-01: cis-1,4- (97.5%), trans-1,4- (1.2%), and 1,2- (1.3%). Both polybutadienes were purified by dissolving them in benzene, filtering the polymer solution, precipitating the polymer by pouring the solution into methanol, and drying the PBD's over phosphorous pentoxide.

Methyl 5-vinylsalicylate (M5VS) was synthesized in this laboratory [6].

### Measurements

Infrared spectra were recorded on Perkin-Elmer spectrometers, Model 727 or 283, in the form of films cast from chloroform solution.

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were obtained in 10 or 15% deuterated chloroform (Norell Co.) solutions at room temperature on a 60-MHz Varian T-60 and on a Varian CFT-20 spectrometer, respectively.

A Perkin-Elmer differential scanning calorimeter (DSC-2) was used for the determination of glass transition temperatures ( $T_g$ ) and the thermal behavior of the polymers. DSC scans were recorded at a temperature increase of  $20^\circ\text{C}/\text{min}$  with sample sizes of 5 to 15 mg. The temperature at which one-half of the  $\Delta C_p$  of transition was reached was recorded as the  $T_g$ .

### Procedures

#### Polymerization of M5VS with AIBN as the Initiator.

A 40-mL polymerization tube was charged with AIBN (2.8 mg, 0.017 mmol), M5VS (1.52 g, 8.5 mmol), and benzene (20 mL). The homogeneous mixture was degassed by three successive freeze-thaw cycles, sealed at 0.05 mm, and placed in a constant temperature bath at  $60^\circ\text{C}$ . After 3 d the tube was opened and the homogeneous contents poured into cold methanol (200 mL). The precipitated polymer was collected in a weighed sintered glass filter, washed, and dried at 0.1 mm to constant weight. Poly-M5VS was obtained in 41% yield (0.62 g).

The infrared spectrum showed a broad absorption at  $3200\text{ cm}^{-1}$  (OH stretching) and a sharp absorption at  $1685\text{ cm}^{-1}$  (C=O stretching).

#### Polymerization of M5VS with BPO as the Initiator.

A 40-mL polymerization tube was charged with BPO (3.9 mg, 0.016 mmol), M5VS (1.43 g, 8.0 mmol), and benzene (20 mL). The homogeneous mixture was degassed by three successive freeze-thaw cycles, sealed at 0.05 mm, and placed in a constant temperature bath at  $60^\circ\text{C}$ . After 3 d the tube was opened and the homogeneous solution was poured into cold methanol (200 mL). The precipitated polymer was collected on a sintered glass filter, washed, dried at 0.1 mm to constant weight, and gave poly-M5VS (0.27 g, 19%).

The infrared spectrum showed a broad absorption at  $3200\text{ cm}^{-1}$  (OH stretching) and a sharp absorption at  $1685\text{ cm}^{-1}$  (C=O stretching).

#### Grafting of M5VS onto 1,2-Polybutadiene (RB-820) with AIBN as the Grafting Initiator.

RB-820 (1.35 g, 25 mmol monomer) was dissolved in benzene (45 mL) under dry nitrogen in a 100-mL polymerization tube by shaking it in the dark for 1 d. M5VS (1.87 g, 10.5 mmol) and AIBN (3.4 mg, 0.021 mmol) were then added, followed by benzene (5 mL). The homogeneous mixture was degassed by three successive freeze-thaw cycles, sealed at 0.05 mm, and kept for 3 d at  $60^\circ\text{C}$ . The tube was opened and the solution poured

into cold methanol (500 mL). The precipitate was collected in a sintered glass filter, washed, and dried at 0.1 mm to constant weight. From the weight of total polymer and the initial weight of RB-820, the amount of polymerized M5VS was calculated to be 0.53 g (29% conversion).

Grafting of M5VS onto cis-1,4-Polybutadiene (BR-01) with AIBN as the Grafting Initiator. BR-01 (1.35 g, 25 mmol monomer) was dissolved in benzene (45 mL) under dry nitrogen in a 100-mL polymerization tube by shaking it in the dark for 1 d. M5VS (1.81 g, 10.2 mmole) and AIBN (3.3 mg, 0.020 mmol) were then added followed by benzene (5 mL). The homogeneous mixture was degassed, sealed at 0.05 mm, and kept at 60°C for 3 d. The tube was opened and the solution poured into cold methanol (500 mL). The polymer was collected, washed, and dried to constant weight at 0.1 mm. From the weight of total polymer and the initial weight of BR-01, the amount of polymerized M5VS was calculated to be 0.57 g (32% conversion).

Grafting of M5VS onto 1,2-Polybutadiene (RB-820) with BPO as the Grafting Initiator. RB-820 (1.35 g, 25 mmol monomer) was dissolved in benzene (45 mL) under dry nitrogen in a 100-mL polymerization tube as before. M5VS (3.64 g, 20.4 mmol) and BPO (10 mg, 0.041 mmol) were then added followed by benzene (5 mL), sealed at 0.05 mm, and heated to 60°C for 3 d. The tube was opened, the polymer solution poured into cold methanol (500 mL), the polymer collected by filtration, and dried at 0.1 mm to constant weight. The amount of M5VS converted to polymer was 0.31 g (8% conversion).

Grafting of M5VS onto cis-1,4-Polybutadiene (BR-01) with BPO as the Grafting Initiator. BR-01 (1.35 g, 25 mmol monomer) was dissolved in benzene (45 mL) under dry nitrogen in a 100-mL polymerization tube by shaking it for 1 d in the dark. M5VS (3.70 g, 20.8 mmol) and BPO (10 mg, 0.04 mmol) were then added, followed by benzene (5 mL). The tube was sealed at 0.05 mm and placed in a constant temperature bath at 60°C for 3 d. The polymer was isolated as before. M5VS had been converted to polymer in the amount of 0.87 g (23% conversion).

### Separation of Graft Copolymers from Homopolymers

M5VS homopolymer (poly-M5VS) and residual polybutadiene (PBO) were extracted from the polymer mixture by cold solvent extraction with two solvents. The polymer, cut into small pieces, was placed in a weighed Soxhlet thimble. First PBD was extracted with 100 mL of petroleum ether (bp 40-60°C) containing a small amount of MBC antioxidant by shaking the mixture mechanically in the dark at room temperature for at least 2 d. The extract was concentrated to 10 mL and poured into methanol (100 mL). The precipitated polymer was collected in a sintered glass filter, washed, and dried at 0.1 mm.

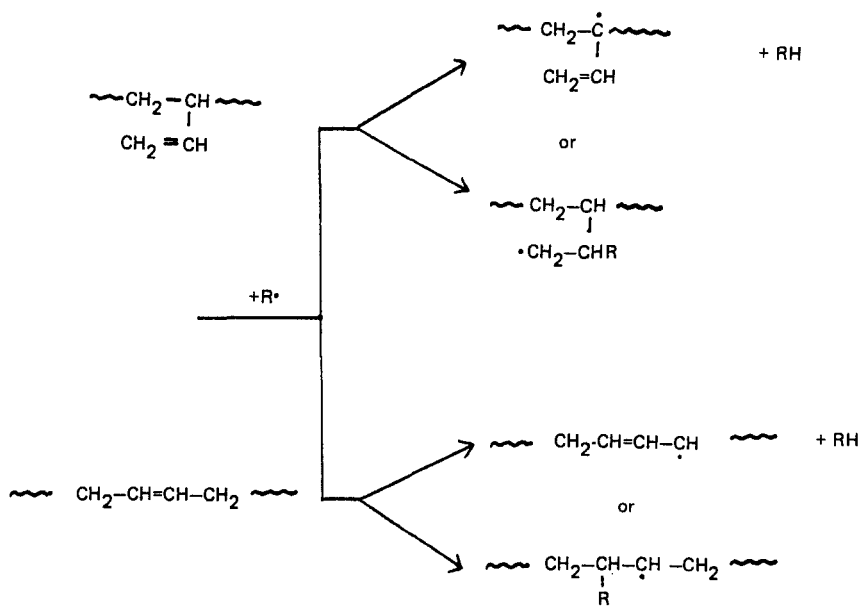
Poly-M5VS was then extracted by shaking the thimble in 100 mL of butanone, containing 2% of MBC, in the dark at room temperature for at least 2 d. The extracted poly-M5VS was recovered the same way as the PBD. The extractions were repeated until no more polymer was found in the extracts. The remaining graft copolymer [poly(BD-g-M5VS)] was isolated by continuing the extraction of the thimble contents with 100 mL of toluene containing 2% of MBC. About 10 extractions were required before a pure graft-product was obtained.

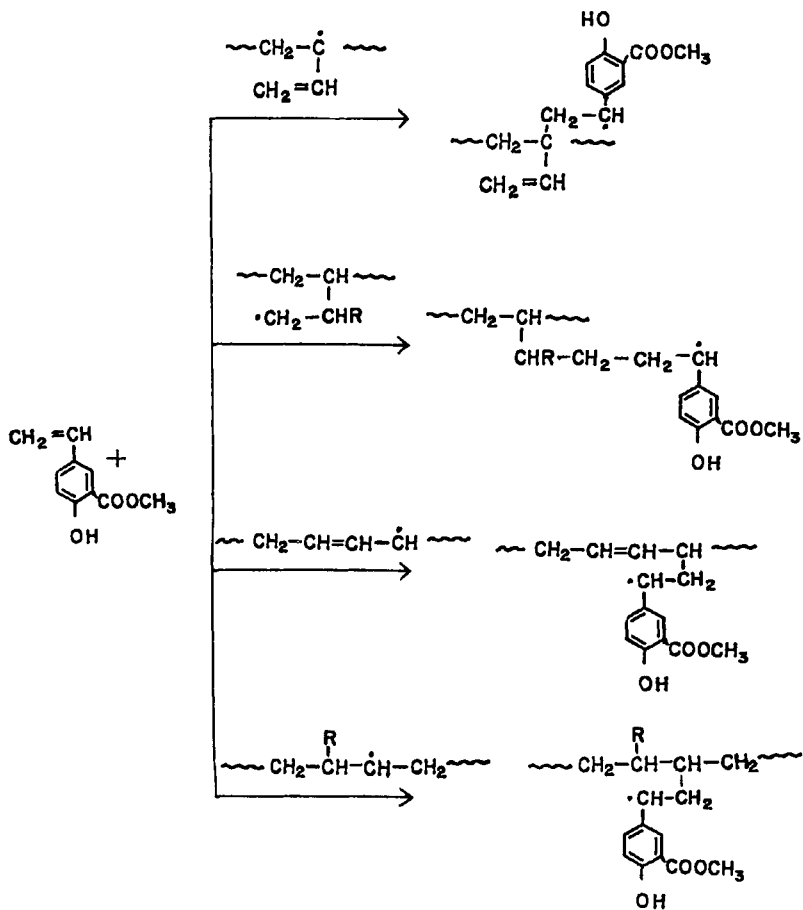
The infrared spectra of both fractions, the petroleum ether extract containing PBD and the butanone extract containing poly-M5VS, indicated that they were contaminated by small amounts of graft copolymer.

## RESULTS AND DISCUSSION

M5VS was successfully grafted onto both 1,2- and *cis*-1,4-PBD. The grafting reactions were carried out under carefully controlled conditions and in the absence of oxygen, otherwise cross-linking occurred and gel formation was observed.

To establish the optimum reaction conditions for grafting M5VS onto the two types of PBD (Eqs. 1 and 2), styrene (St) was used as the grafting monomer. Grafting of St onto isoprene [11, 12] and onto





cis-1, 4-PBD was previously described [7] and, as expected, grafting onto both PBDs took place quite readily but was accompanied by gelation. It was also reported that PBD-St graft polymers could not be separated completely [7] and extracts which should contain only the homopolymer were contaminated with some graft copolymer.

In our hands the separation of the homopolymers from the graft copolymers also proved to be difficult, mainly because the solvent mixtures which are most effective for the precipitation readily formed stable colloids. Similar observations have been reported for the isoprene-styrene system [16]. Comparisons between fractional precipitation and alternating solvent extraction methods finally led to the adoption of cold solvent extraction (usually 10 times) as the method of choice for the separation of homopolymers from graft copolymers. To facilitate complete separation, the grafting of styrene onto the

TABLE 1. Summary of Homopolymerizations of M5VS and Graft Copolymerizations of M5VS onto PBD's. Reaction Conditions: Temperature, 60°C; Reaction Time, 3 d; Solvent, Benzene

M5VS conc (mol/L)	PBD type	PBD conc (mol/L monomer equiv)	Initiator	Initiator conc (mol/L)	M5VS conversion (%)	Poly-M5VS grafting efficiency <sup>a</sup> (%)	PBD grafting efficiency <sup>b</sup> (%)	Poly M5VS content in graft polymer	
								mol%	wt%
0.43	-	-	AIBN	0.85	41	-	-	-	-
0.40	-	-	BPO	0.80	19	-	-	-	-
0.21	1,2-PBD	0.5	AIBN	0.42	29	16	39	5	14
0.41	1,2-PBD	0.5	BPO	0.82	8	8	35	2	5
0.20	cis-1,4-PBD	0.5	AIBN	0.40	32	5	23	3	9
0.42	cis-1,4-PBD	0.5	BPO	0.84	23	22	65	6	18

$$^a \text{Poly-M5VS grafting efficiency} = \frac{\text{wt of poly-M5VS included in graft copolymer}}{\text{total wt of poly-M5VS in homo- and graft copolymer}} \times 100.$$

$$^b \text{PBD grafting efficiency} = \frac{\text{wt of PBD included in graft polymer}}{\text{original wt of PBD}} \times 100.$$

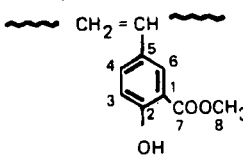
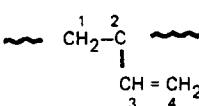


TABLE 2.  $^1\text{H-NMR}$  Chemical Shift Data for Poly(BD-g-M5VS)<sup>a</sup>

Chemical shift data in ppm	
Sample	Chemical shift data in ppm
	-OH
Poly(BD-g-M5VS)	10.2-10.6
	-CH <sub>2</sub> - [ cis-1,4- or 1,2-PBD and poly(M5VS) ]
	-CH- [ 1,2-PBD and Poly(M5VS) ]
	0.8-2.6
	Benzene ring
	6.4-7.3
	-CH= (cis-1,4- and 1,2-PBD)
	=CH <sub>2</sub> (1,2-PBD)
	4.5-5.9
	-COOCH <sub>3</sub>
	3.6-4.0

<sup>a</sup> 15% solution of poly(BD-g-M5VS) in CDCl<sub>3</sub>; 25°C.

TABLE 3.  $^{13}\text{C}$ -NMR Chemical Shift Data for Poly(BD-g-M5VS)<sup>a</sup>

	Chemical shift (ppm downfield from TMS)	Assignment of carbon atoms
Poly(M5VS) in poly(BD-g-M5VS)	170.1	7
	159.7	2
	134.7	4
	117.3	1
	111.6	3
	52.3	8
1,2-PBD in poly(BD-g-M5VS)	142.9	3
	130.6	3
	127.6	3 <sup>b</sup>
	114.9	4 <sup>b</sup>
	114.5	4 <sup>c</sup>
	41.4	2
	38.8	1
	35.7	1
	27.4	1
	25.0	1
cis-1,4-PBD in poly(BD-g-M5VS)	129.6	-CH=
	27.5	-CH <sub>2</sub> -

<sup>a</sup> 10% solution of poly(BD-g-M5VS) in  $\text{CDCl}_3$ ; 25°C.

<sup>b</sup> Syndiotactic triads.

<sup>c</sup> Heterotactic triads.

PBDs was carried out at relatively low St concentrations. To protect against oxidation, MBC was added to the solutions during all workup operations.

Homopolymerization of M5VS as well as its graft copolymerization with the two PBDs was carried out with either BPO or AIBN as the initiator. The concentration of initiator was in all cases 0.2 mol% of the grafting monomer (M5VS). BPO proved inferior to AIBN to initiate both homopolymerization of M5VS and grafting of M5VS onto PBD to give poly(BD-g-M5VS) (Table 1). In homopolymerization and with AIBN as the initiator, 41% of M5VS was converted to poly-M5VS, while with BPO as the initiator only 19% of M5VS was polymerized to poly-M5VS.

In the grafting reactions of M5VS with the PBDs, both grafting and homopolymerization of M5VS occurred simultaneously. For AIBN-initiated grafting, the M5VS concentration was 40 mol% relative to

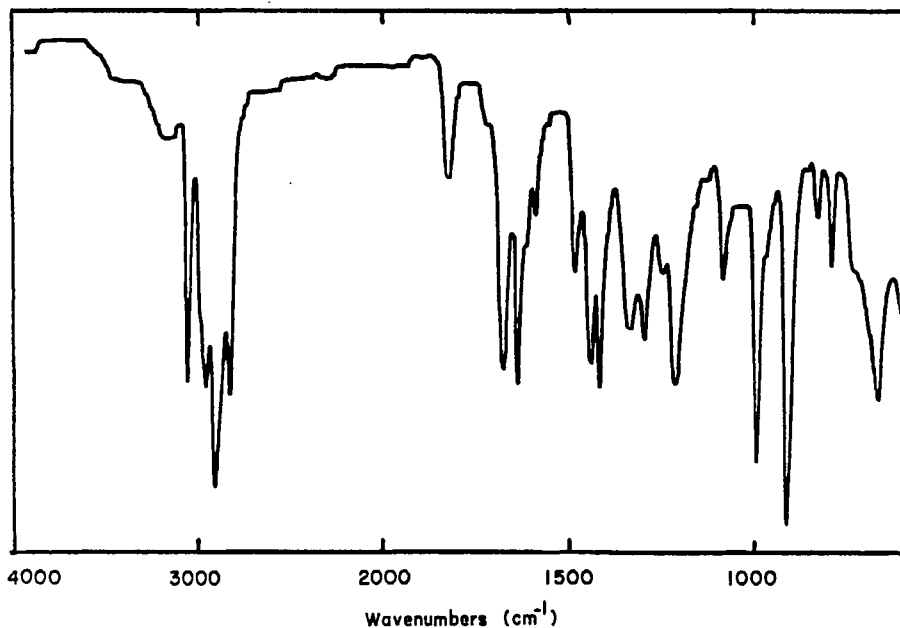


FIG. 1. Infrared spectrum of poly(BD-g-M5VS) (1,2-PBD; AIBN).

the alkene bond in PBD, while for the BPO-initiated grafting it was 80 mol%. In the case of grafting onto 1,2-PBD, 29% of the M5VS underwent polymerization; 16% of this was grafted and formed the graft copolymer poly-(BD-g-M5VS), the remaining 84% was recovered as poly-M5VS. The analogous experiment, but initiated with BPO, resulted in 8% conversion of M5VS to a polymer, and only 8% of that was found in the graft copolymer.

When *cis*-1,4-PBD served as the backbone in the grafting reactions and AIBN as initiator, the conversion of M5VS to a polymer was 32%, 5% of it grafted and 95% homopolymerized. With BPO as initiator, 23% of M5VS was converted; 22% of M5VS showed up as poly(BD-g-M5VS) and 78% homopolymerized. On a molar basis, 2 to 6 mol% of M5VS were incorporated into poly-(BD-g-M5VS); on a weight basis the amount of M5VS was 5 to 18%. With respect to the grafting efficiency onto the PBD-backbone chains, the two initiators did not show a consistent trend. Depending upon reaction conditions, conversion of the PBDs to a graft copolymer ranged between 23 and 65% (w/w).

The separation of graft copolymers from homopolymers or oligomers was less of a problem in the PBD-M5VS graft system than it had been in the PBD-St system. The difference in polarity between PBD

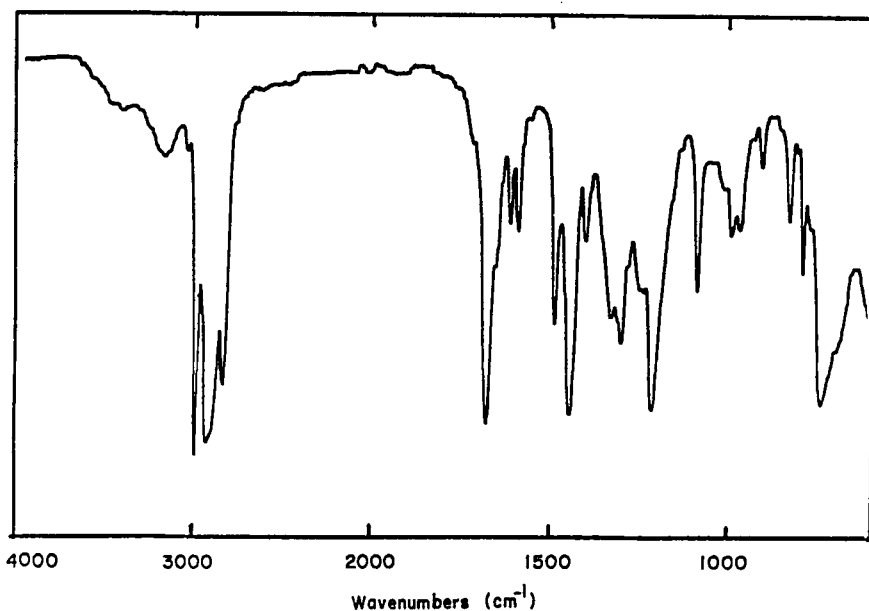


FIG. 2. Infrared spectrum of poly(BD-g-M5VS) (cis-1,4-PBD; BPO).

and the grafting monomer M5VS is substantially greater than that of PBD and St, and consequently the solubilities of the homopolymer and of the graft copolymer are substantially different. The cold extraction method, although tedious, proved very effective to separate any unreacted polybutadiene and the homopolymer of M5VS from the graft copolymer. Under our grafting conditions no gelation occurred, which suggests that recombination of polymer radicals or other cross-linking reactions did not occur to any significant extent.

The grafted polymers were characterized by infrared,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopy. Spectral data of the polymers were in full agreement with the proposed structures (Tables 2 and 3). In our polymer samples the molecular weight of the PBD backbone was high, causing broadening in the  $^1\text{H-NMR}$  spectrum and requiring many transients to obtain an acceptable  $^{13}\text{C-NMR}$  spectrum. The best indication for the incorporation of M5VS was obtained by the IR spectra (Figs. 1 and 2) where the carbonyl and phenolic hydroxy absorption of the M5VS unit are easily recognized.

Preliminary thermal characterizations of our graft copolymers of M5VS with 1,2-PBD or cis-1,4-PBD were carried out by DSC. Only one  $T_g$  was found for each of the graft copolymers: a  $T_g$  of  $-8^\circ\text{C}$

TABLE 4. DSC<sup>a</sup> Data of Transition Temperatures of Poly-M5VS, PBDs, and Poly(BD-g-M5VS)

Sample	$T_g$ ( $^{\circ}\text{K}$ ) <sup>b</sup>	$T_{cr}$ ( $^{\circ}\text{K}$ ) <sup>c</sup>	$T_m$ ( $^{\circ}\text{K}$ ) <sup>d</sup>
Poly-M5VS	-	389	-
1,2-PBD	263	-	-
Poly(1,2-BD-g-M5VS)	265	-	-
cis-1,4-PBD	165	-	204
Poly(cis-1,4-BD-g-M5VS)	165	-	206

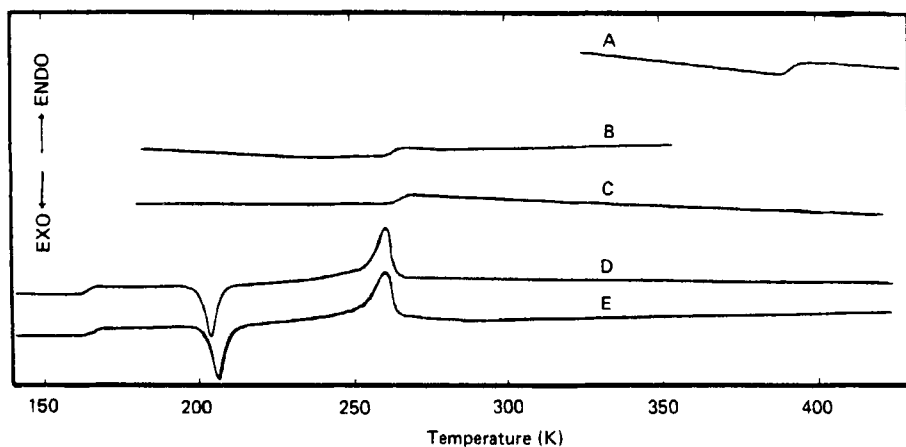
<sup>a</sup>Scanning rate 20 $^{\circ}\text{C}/\text{min}$ .<sup>b</sup>Glass transition temperature.<sup>c</sup>Temperature of crystallization.<sup>d</sup>Melting temperature.

FIG. 3. DSC scans of poly(BD-g-M5VS): (A) Poly(M5VS), (B) 1,2-PBD, (C) Poly(BD-g-M5VS) (1,2-PBD; AIBN), (D) cis-1,4-PBD, (E) Poly(BD-g-M5VS) (cis-1,4-PBD; BPO).

TABLE 5. DSC Data of Transition Temperatures of Blends<sup>a</sup>

Weight of proportion of polymer components in the blends						
cis-1,4-PBD (BR-01)	(I) Poly(M5VS)	(II) Poly(BD-g-M5VS)	T <sub>g</sub> (°K)		T <sub>cr</sub> (°K)	T <sub>m</sub> (°K)
			II	I		
20	80	10	164	394	204	261
50	50	10	163	393	205	261
80	20	10	165	-	205	263
90	10	10	166	-	204	262
80	20	0	165	-	204	262
90	10	0	163	-	201	260
1,2-PBD (BR-820)	Poly(M5VS)	Poly(BD-g-M5VS)				
90	10	10	264	-	-	-
90	10	0	262	-	-	-

<sup>a</sup>Temperature increase: 20°/min; sample size 5-15 mg.

(1,2-PBD) and one of -108°C (cis-1,4-PBD) which correspond to the T<sub>g</sub> for pure 1,2-PBD (-10°C, 263 K) and cis-1,4-PBD (-108°C, 165 K), respectively. No T<sub>g</sub> was found at 116°C (389 K) which is the T<sub>g</sub> of poly-M5VS (Table 4, Fig. 3). This T<sub>g</sub> would be difficult to observe because the proportion of M5VS in the polymer molecule was at most 5 mol% of the total polymer mixture or, possibly, because the poly-M5VS units were present only as short chains and thus unable to form a separate M5VS-rich phase. DSC scans also showed that blends of PBD, poly-M5VS, and their graft copolymer have T<sub>g</sub>'s corresponding to the T<sub>g</sub> for pure 1,2-PBD (-10°C, 263 K) and cis-1,4-PBD (-108°C, 165 K), respectively. The T<sub>g</sub> which corresponds to poly-M5VS was observed only in the case of the higher concentrations of poly-M5VS, possibly for the same reason as discussed before (Table 5). From these results it is concluded that blends of PBD and poly-M5VS are incompatible even in the presence of graft copolymer poly(BD-g-M5VS) with a low M5VS content.

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