



used as the grafting initiators. It was shown that grafting occurs readily, with the grafting efficiency ranging from 23% to 65%, depending on the reaction conditions.

We have continued our efforts in developing general methods for the functionalization of polymers and in this paper report further functionalization of polybutadienes by grafting 2H5V onto the 1,2- and *cis*-1,4-isomer of polybutadiene with AIBN as the initiator. The following reaction scheme suggests a possible mechanism for the free-radical grafting of 2H5V onto 1,2-PBD and *cis*-1,4-PBD, initiated with AIBN (eq 1).

## EXPERIMENTAL

### Materials

Methanol, acetone, 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, water, and dried over phosphorous pentoxide before distillation.

Azobisisobutyronitrile (AIBN) (Eastman Kodak Co.) and benzoyl peroxide (BPO) (Fisher Scientific Co.) were recrystallized and dried at 0.1 mmHg and room temperature.

*cis*-1,4-Polybutadiene (Japan Synthetic Rubber Co.) (BR-01) had the following composition: *cis*-1,4- (97.5%); *trans*-1,4- (1.2%); 1,2- (1.3%); 1,2-polybutadiene (BR-820) consisted of 1,2- (92%); *cis*-1,4- (8%). Both polybutadienes (PBD) were purified by being dissolved in benzene, filtering, precipitation of the polymer solution into methanol, filtering the suspension, and drying the polymer over phosphorous pentoxide at 0.1 mm.

2-(2-Hydroxy-5-vinylphenyl)-2H-benzotriazole (2H5V) was synthesized in this laboratory<sup>4</sup> and purified before use. 2,2'-Methylenebis(6-*tert*-butyl-*p*-cresol) (MBC) (Pfaltz & Bauer, Inc.) was used as received.

### Measurements

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

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured in 10% or 15% deuterated chloroform (Norell Co., Inc.) solutions on a 60 MHz Varian T-60 and 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 thermal behavior of the polymers. DSC scans were recorded at a rate of temperature increase of 20°C min<sup>-1</sup> with sample sizes of 6–7 mg. The temperature at which one-half of the  $\Delta C_p$  transition was noted was registered as the  $T_g$ .

### Procedures

*Homopolymerization of 2-(2-Hydroxy-5-vinylphenyl)-2H-benzotriazole (2H5V).* Polymerization of 2H5V was carried out with BPO as the initiator. A 15 ml polymerization tube was charged with BPO (3.5 mg, 0.014 mmol), 0.5 mol%, 2H5V (0.66 g, 2.8 mmol), and benzene (7 ml). The homogeneous mixture was degassed, sealed at 0.05 mm, and placed in a constant temperature bath of 60°C for 3 days. The homogeneous solution was poured into cold methanol (200 ml), the polymer precipitated and was collected on a sintered glass filter, washed and dried at 0.1 mmHg; poly(2H5V) (0.086 g) (13% yield) was obtained.

This polymer was identical in every respect with the polymer obtained by polymerization of 2H5V with AIBN as the initiator and which gave a 51% yield of poly(2H5V).

### Grafting Procedures.

*Grafting of 2H5V onto cis-1,4-PBD (BR-01) with AIBN as the grafting initiator.* BR-01 (1.35 g, 25 monomer mmol) was dissolved in benzene (45 ml) under dry nitrogen in a 100 ml polymerization tube. 2H5V (1.78 g, 7.5 mmol) and AIBN (3.3 mg, 0.020 mmol), 0.06 mol%, were then added, followed by benzene (5 ml). The homogeneous mixture was degassed, sealed at 0.05 mm and heated to 60°C for three days. The tube was opened and the homogeneous contents were poured into cold methanol (500 ml). The precipitated polymer was collected and purified by a careful separation procedure (see below). From the weight of the total polymer and the weight of BR-01 initially present, the amount of 2H5V polymerized was calculated as 0.28 g, (16% conversion).

Grafting onto 1,2-PBD (BR 820) was carried out in a similar manner and resulted in a 23% conversion of 2H5V to polymers.

*Separation of Polymers.* 2H5V homopolymer [poly(2H5V)] and residual polybutadiene (PBD) were extracted from the mixture of polymers by

leaching them repeatedly with alternative cold solvents. The total polymer, cut into small pieces, was placed in a weighed Soxhlet thimble. First, the unchanged PBD was extracted by shaking the mixture mechanically in the dark at room temperature for at least 2 days with 100 ml of petroleum ether (bp 40–60°C) containing 2% of 2,2'-methylenebis(6-*tert*-butyl-*p*-cresol) (MBC) as an antioxidant. The extract was concentrated to 10 ml and poured into methanol (100 ml). The precipitated polymer was collected in a weighed, sintered glass filter, washed and dried at 0.1 mm to a constant weight. Poly(2H5V) was then extracted by shaking the thimble in 100 ml of a 2% solution of MBC in acetone in the dark at room temperature for a minimum of 2 days. The extracted poly(2H5V) was recovered in the same manner as PBD. Both extractions were repeated until no more polymer could be detected in the extracts. The remaining graft copolymer [poly(BD-*g*-2H5V)] was isolated by repeated thimble extractions with 100 ml of toluene

(containing 2% of MBC) in the dark at room temperature as described above. About ten extractions were required to obtain a pure graft copolymer.

Infrared spectra revealed that both fractions, the petroleum extract containing PBD and the acetone extract containing poly(2H5V), were contaminated with a small amount of graft copolymer.

2H5V could be grafted onto both PBD's, 1,2-PBD and *cis*-1,4-PBD with AIBN as the initiator.

Poly(1,4-BD-*g*-2H5V)

*Anal.* Found: C, 80.68%; H, 8.36%; N, 8.04%.  
Calcd for  $(-C_4H_6)_{0.84}(C_{14}H_{11}N_3O)_{0.16}$ : C, 80.66%; H, 8.21%; N, 8.06%.

Poly(2,2-BD-*g*-2H5V).

*Anal.* Found: C, 82.34%; H, 9.66%; N, 4.16%.  
Calcd for  $(-C_4H_6)_{0.93}(C_{14}H_{11}N_3O)_{0.07}$ : C, 84.29%; H, 9.65%; N, 4.39%.

## RESULTS AND DISCUSSION

Grafting of 2H5V was carried out with AIBN as

**Table I.** Experimental conditions for graft- and homo-polymerizations<sup>a</sup>

PBD type	PBD concentration monomer mol l <sup>-1</sup>	Initiator	Initiator concentration		Monomer 2H5V concentration	
			mmol l <sup>-1</sup>	mol%	mol l <sup>-1</sup>	mol%
1,2-	0.42	AIBN	0.33	0.06	0.13	23
<i>cis</i> -1,4	0.50	AIBN	0.40	0.06	0.15	23
—	—	AIBN	2.0	0.5	0.40	100
—	—	BPO	2.0	0.5	0.40	100

<sup>a</sup> Temperature, 60°C; time, 3 days; solvent, benzene.

**Table II.** Results of graft- and homo-polymerization

PBD type	2H5V conversion %	Poly(2H5V) grafting efficiency <sup>a</sup> %	PBD grafting efficiency <sup>b</sup> %	Poly(2H5V) content in poly(BD- <i>g</i> -2H5V)	
				mol%	wt%
1,2-	23	56	56	7	23
<i>cis</i> -1,4-	16	51	13	16	45
—	51 (AIBN)	—	—	—	—
—	13 (BPO)	—	—	—	—

<sup>a</sup> Poly(2H5V) grafting efficiency =  $\frac{\text{wt of poly(2H5V) included in graft polymer}}{\text{Total wt of poly(2H5V)}} \times 100$ .

<sup>b</sup> PBD grafting efficiency =  $\frac{\text{wt of PBD included in graft polymer}}{\text{Original wt of PBD}} \times 100$ .

**Table III.**  $^1\text{H}$  NMR chemical shift data of poly(BD-*g*-2H5V)<sup>a</sup>

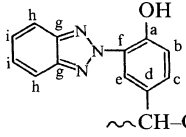
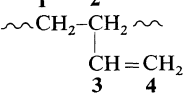
Sample	-OH	Benzene ring	-CH= (1,2-PBD and <i>cis</i> -1,4-PBD) =CH <sub>2</sub> (1,2-PBD)	-CH <sub>2</sub> -[ <i>cis</i> -1,4- and 1,2-PBD and poly(2H5V)] -CH-[(1,2-PBD and poly(2H5V))]
Poly(BD- <i>g</i> -2H5V)	10.5—11.0	6.4—8.5	4.4—6.0	0.8—3.0

<sup>a</sup> In CDCl<sub>3</sub> (15%), 25°C.

the grafting initiator onto both, 1,2- and *cis*-1,4-PBD. The homopolymerization of 2H5V was also performed with either AIBN or BPO as the initiator to give poly(2H5V) in a 51% yield with AIBN and in a 13% yield with BPO. Because of its greater efficiency in homopolymerization, AIBN was used for the grafting of 2H5V onto 1,2- or *cis*-1,4-PBD.

As described for the grafting of methyl 5-vinylsalicylate,<sup>6</sup> the amount of initiator and the grafting conditions have to be carefully controlled in order to avoid crosslinking. These conditions were also very carefully followed in our grafting experiments of 2H5V onto the two PBD's. The initiator concentration for the grafting reaction was usually 0.06 mol%. The experimental conditions of the polymerization and grafting reactions are summarized in Table I and the results in Table II. In the case of grafting of 2H5V onto 1,2-PBD, a 23% conversion of 2H5V to the polymer was achieved, with 56% of the 2H5V grafted and 44% of it homopolymerized. The grafting efficiency onto PBD, the utilization of PBD in the grafting reaction, was also 56%. For the grafting reaction onto *cis*-1,4-PBD, the conversion of 2H5V was only 16%, with a poly(2H5V) grafting efficiency and a PBD grafting efficiency of 51% and 13%, respectively. As a result, the poly(2H5V) content in poly(BD-*g*-2H5V) was 7 mol% for 1,2-PBD and 16 mol% for the *cis*-1,4-PBD. The chemical shift data of both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of poly(BD-*g*-2H5V) (Tables III and IV) confirm the proposed structures as do the elemental analyses, especially the nitrogen analyses. In our polymer samples, the molecular weight of the PBD backbone was high, causing a broadening in the  $^1\text{H}$  NMR spectrum and requiring many transients in the  $^{13}\text{C}$  NMR spectrum. The proton signals due to the 2H5V moiety in the copolymer were weak relative to the proton signals due to the hydrocarbon backbone and their intensity ratios appeared to be consistent with the copolymer composition as calculated on the basis of the elemental analyses.

**Table IV.**  $^{13}\text{C}$  NMR chemical shift data for poly(BD-*g*-2H5V)<sup>a</sup>

Poly 2H5V in poly(BD- <i>g</i> -2H5V)	Chemical shift (ppm downfield from TMS)	Assignment
	147.6	g
	142.1	a
	135.4	d
	129.0	c
	127.0	i
	125.2	f
	119.8	e
	118.9	b
	117.3	h
	1,2-PBD in poly(BD- <i>g</i> -2H5V)	142.9
	130.6	3
	127.6	3
	114.8	4 <sup>b</sup>
	114.4	4 <sup>c</sup>
	41.4	2
	38.8	1
	35.7	1
	27.4	1
25.0	1	
<i>cis</i> -1,4-PBD in poly(BD- <i>g</i> -2H5V)	129.6	-CH=
	27.5	-CH <sub>2</sub> -

<sup>a</sup> In CDCl<sub>3</sub> (10%), 25°C.

<sup>b</sup> Syndiotactic triads.

<sup>c</sup> Heterotactic triads.

However, the best indication of the incorporation of 2H5V were the infrared spectra (Figures 1 and 2) where the phenolic OH-absorption band of 2H5V is easily recognized at 3200 cm<sup>-1</sup>.

Preliminary thermal characterization of our graft copolymers of 1,2-PBD and *cis*-1,4-PBD with 2H5V were carried out by DSC. Only one  $T_g$  was found for each of the graft polymers: a  $T_g$  of -10°C (1,2-PBD) and -107°C (*cis*-1,4-PBD) which correspond to the  $T_g$  for pure 1,2-PBD (-10°C, 263 K) and *cis*-

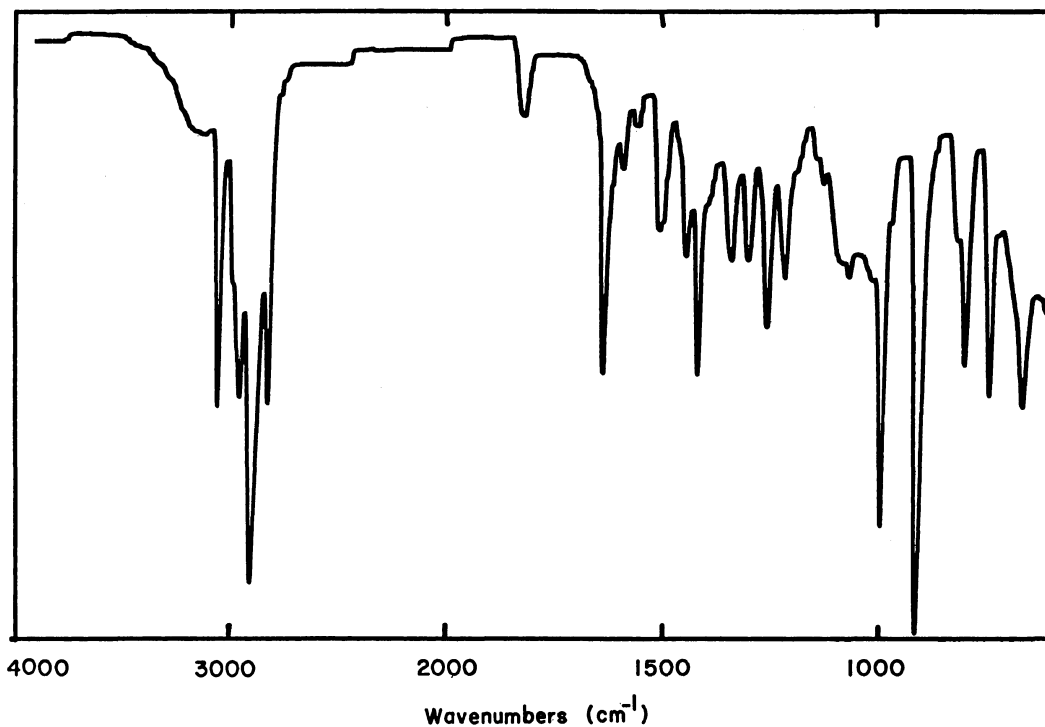


Figure 1. Infrared spectrum of poly(BD-*g*-2H5V) (1,2-PBD).

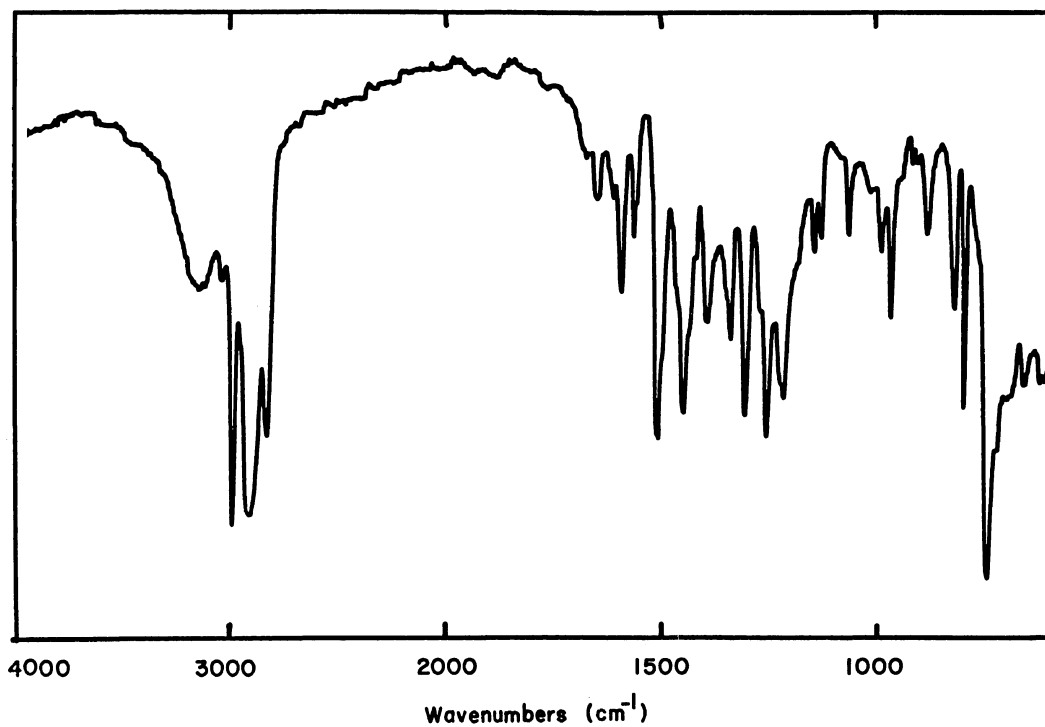


Figure 2. Infrared spectrum of poly(BD-*g*-2H5V) (*cis*-1,4-PBD).

1,4-PBD ( $-108^{\circ}\text{C}$ , 165 K), respectively. No  $T_g$  was found at  $109^{\circ}\text{C}$  (402 K) which is the  $T_g$  of poly(2H5V) (Table V). This  $T_g$  would be difficult to observe, possibly because the poly(2H5V) units are present as short chains only. If so, they would not form a separate 2H5V-phase and hence no separate glass transition could be observed.

Blends of PBD with poly(2H5V) and poly(BD-*g*-2H5V) showed only the  $T_g$ s corresponding to the pure PBDs. A  $T_g$  at  $109^{\circ}\text{C}$  (402 K), corresponding to poly(2H5V), was observed only in the case of the highest concentration of poly(2H5V) in the blend (68 wt%) (Table VI).

We compared also the DSC scans of the graft copolymers of poly(BD-*g*-2H5V) with those of blends of PBD with poly(2H5V). The blends contained the same amounts of PBD and poly(2H5V) as the corresponding graft copolymers (Figure 3). The peak areas due to crystallization and melting are smaller in the graft copolymers than in the corresponding blends. This seems to indi-

cate a short graft length of the grafted poly(2H5V) and consequently no efficient compatibilization between the incompatible homopolymers

Table V. DSC<sup>a</sup> data for transition temperatures of poly(BD-*g*-2H5V)

Sample	$T_g^b$	$T_{cr}^c$	$T_m^d$
	K	K	K
Poly(2H5V)	— 402		
1,2-PBD:			
Original polymer	263 —		
Graft polymer	263 —	—	—
<i>cis</i> -1,4-PBD:			
Original polymer	165 —	204	261
Graft polymer	166 —	207	269

<sup>a</sup> Scanning rate,  $20^{\circ}\text{C min}^{-1}$ .

<sup>b</sup> Glass transition temperature (one half of  $\Delta C_p$  of transition).

<sup>c</sup> Temperature of crystallization (peak temperature).

<sup>d</sup> Melting temperature (peak temperature).

Table VI. DSC data for transition temperature of blends

Blend compositions, in proportions by weight			$T_g$	$T_{cr}$	$T_m$
			K	K	K
1,2-PBD	Poly(2H5V)	Poly(BD- <i>g</i> -2H5V)			
77	23	—	262 —	—	—
<i>cis</i> -1,4-PBD	Poly(2H5V)	Poly(BD- <i>g</i> -2H5V)			
55	45	—	166 —	212	262
25	75	10	166, 404	216	260
55	45	10	166 —	214	261
75	25	10	166 —	210	262

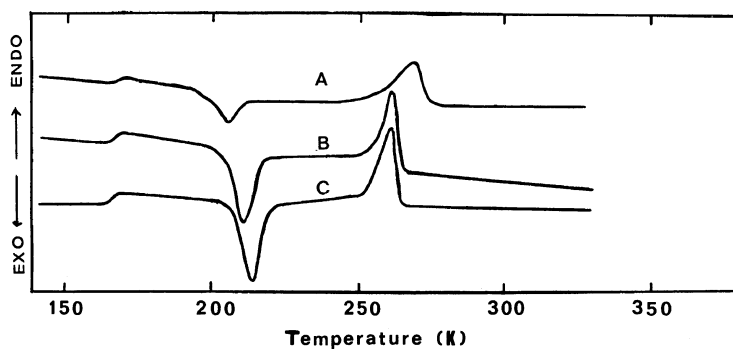


Figure 3. DSC scans of poly(BD-*g*-2H5V) and of blends: A, poly(BD-*g*-2H5V); [55% (wt) of *cis*-1,4-PBD in poly(BD-*g*-2H5V)]; B, blend of *cis*-1,4-PBD/poly(2H5V) (55:45 wt/wt); C, blend of *cis*-1,4-PBD/poly(2H5V)/poly(BD-*g*-2H5V); (55:45:10 wt/wt/wt).

PBD and poly(2H5V) was achieved in the graft copolymer.

*Acknowledgements.* This work was supported by the Bridgestone Tire Company Ltd., Tokyo, Japan and in part by a grant from the National Science Foundation to the Materials Research Laboratory at the University of Massachusetts. 2H5V was synthesized by S. Yoshida. M.K. would like to express his appreciation to the Bridgestone Tire Company, Ltd. for granting a two-year leave of absence to work at the University of Massachusetts.

We would like to thank William J. Harris and Paula Loeffler for their assistance in the preparation of this manuscript.

## REFERENCES

1. S. Yoshida and O. Vogl, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, **21**, 201 (1980).
2. O. Vogl and S. Yoshida, Preprints, Annual Meeting, Society of Polymer Science, Kyoto, 1980, **29**, 648 (1980).
3. S. Yoshida and O. Vogl, *Makromol. Chem.*, **183**, 259 (1982).
4. O. Vogl and S. Yoshida, *Rev. Roum. Chim.*, **7**, 1123 (1980).
5. W. Pradelok, A. Gupta, and O. Vogl, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3307 (1981).
6. M. Kitayama and O. Vogl, *J. Macromol. Sci., Polym. Chem.*, in press.
7. H. Kawaguchi, J. Muggee, and O. Vogl, *Polymer (London)*, in press.