Copolymerization of Butadiene with Vinyl Monomers

USE OF 2-VINYLFURAN, 2-VINYLTHIOPHENE, METHACRYLONITRILE, AND VINYLIDENE CHLORIDE

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Most copolymers of butadiene (75 parts) with vinyl monomers (25 parts) are rubbery, but the quality of the elastomers varies greatly with the nature of the vinyl monomer. Of four comonomers herein described 2-vinylthiophene and methacrylonitrile form copolymers which compare favorably with GR-S; 2-vinylfuran and vinylidene chloride do not. The copolymer with 2-vinylfuran is different from GR-S; it is benzene-insoluble, produces high modulus and low elongation stocks, and has inferior flex-cracking resistance. The copolymer with 2-vinylthiophene is similar in properties to GR-S. The methacrylonitrile copolymer is also similar, but superior to GR-S in respect to the balance between hysteresis-temperature rise and flex-cracking resistance. The butadiene-vinylidene chloride copolymer is poorer than GR-S in this respect.

THE copolymerization of butadiene with a large variety of vinyl monomers has been of much recent interest in the search for new and useful synthetic rubbers. In the present work are described the copolymers of butadiene with two analogs of styrene, 2-vinylfuran, and 2-vinylthiophene, as well as with methacrylonitrile and vinylidene chloride.

STARTING MATERIALS

2-VINYLFURAN was furnished by E. C. Lathrop of the Northern Regional Laboratories and was distilled directly before use; b.p. 99–99.5° C.; n_D^{20} 1.5032.

2-VINYLTHIOPHENE was prepared by the catalytic dehydration with potassium hydroxide of 2-(2-hydroxyethyl)-thiophene. The latter compound was furnished us by C. A. Weisgerber of Pennsylvania State College. The apparatus and technique are those described by Frank, Adams, Allen, Gander, and Smith (*1*). From 258 grams (2.01 moles) of 2-(2-hydroxyethyl)-thiophene were obtained, at 165° C. and a pressure of 120 ± 5 mm., 200 grams of crude 2-vinylthiophene. This was dissolved in chloroform, the water layer separated, and the chloroform solution dried over anhydrous calcium chloride. The dried product was distilled through a 6-inch helix-packed column, and 115.5 grams (53%) of 2-vinylthiophene were obtained; b.p. 75° C. at 75 mm.; n_D^{20} 1.5733; d_4^{20} 1.037; molecular refraction calculated 34.28, found 35.00. Analysis: Calculated for C_6H_6S, C 65.45, H 5.45; found C 65.28, H 5.36. Microanalyses were carried out by Howard Clark of the Illinois State Geological Survey. Kuhn and Dann (*5*) reported the following constants: n_D^{20} 1.5618; d_4^{20} 1.044; molecular refraction 34.20.

METHACRYLONITRILE was supplied by the Rohm & Haas Company and E. I. du Pont de Nemours & Company, Inc. It was redistilled immediately before use; b.p. 90° C.

VINYLIDENE CHLORIDE was furnished by E. C. Britton of The Dow Chemical Company; b.p. 30.5–31° C.

BUTADIENE was the special purity grade supplied by the Phillips Petroleum Company; it was passed over sodium hydroxide pellets and condensed in a dry ice trap.

The other raw materials for polymerization are the same as those used in other recent investigations (*2*).

POLYMERIZATION TECHNIQUE

The recipe for polymerization was that described by Frank, Adams, Blegen, Deanin, and Smith (*2*), using 75 parts by weight of butadiene, 25 parts of the second monomer, 5 parts of Procter and Gamble silica-free soap flakes, 180 parts of water, 0.30 part of potassium persulfate, and 0.35 part of pure *n*-dodecyl mercaptan (used interchangeably with 0.50 part of the commercial mercaptan mixture Naugatuck OEI).

The bottles were charged by dissolving the soap in 170 parts of water and the persulfate in 10 parts of water. The mercaptan modifier was dissolved in the comonomer and the mixture added to the water solutions in 4-ounce screw-cap bottles. The bottles were then thoroughly chilled and the butadiene was added. Air was flushed from the bottles by using a slight excess of butadiene and allowing it to evaporate. The bottles were then sealed, using rubber gaskets lined with heavy tin foil.

Polymerization was carried out by rotating the bottles end over end at 50° C. until a conversion of approximately 70% was reached.

The collected latex was mixed with 25 parts of a 10% suspension of phenyl-β-naphthylamine in soap solution and coagulated with a saturated sodium chloride solution containing 2.3% of concentrated sulfuric acid. The rubber was washed repeatedly with water, cut or broken into small pieces, and dried overnight in an oven at 80° C. In calculating conversions the residual fatty acid and antioxidant were taken into consideration. It was assumed that the unpolymerized monomers were removed by the drying.

Benzene solubilities and intrinsic viscosities of the copolymers were determined as described in a previous paper (*2*).

The polymers were purified for analysis by dissolving them in benzene and reprecipitating with methanol, this procedure being repeated several times. The samples were then dried in a vacuum oven. Determination of the monomer ratios in the copolymers was then made by elementary analysis for chlorine and nitrogen in the cases of vinylidine chloride and methacrylonitrile, respectively, and by sulfur analysis and ultraviolet

TABLE I. COPOLYMERIZATION OF BUTADIENE WITH OTHER MONOMERS

Comonomer	Wt. Ratio Butadiene: Comonomer	Time, Hr.	Conversion, %	Benzene Soly., %	Intrinsic Viscosity	Comonomer, %
2-Vinylfuran	75:25	20	73.5	50	..	....
2-Vinylfuran	75:25	20	75.5	29	..	....
2-Vinylthiophene	75:25	15	77	94	1.98	26.9[a]–28.8[b]
Methacrylonitrile	75:25	4.0–4.5	75	100	1.61	26.8[c]
Vinylidene chloride	75:25	15	71	100	1.74	17.1[d]

[a] By ultraviolet absorption (*7*).
[b] Analysis, 8.38% sulfur.
[c] Analysis, 5.61% nitrogen.
[d] Analysis, 12.5% chlorine.

absorption in the case of 2-vinylthiophene. [Ultraviolet absorption analyses were carried out by Thomas Parks according to the method of Meehan (*7*).] The copolymer of butadiene and 2-vinylfuran was not analyzed as it was too insoluble in benzene, chloroform, high boiling petroleum ether, pyridine, and dioxane for proper purification and determination.

Polymerization data and copolymer analyses are summarized in Table I.

EVALUATION. The copolymers described in Table I were evaluated at The B. F. Goodrich laboratories. The test recipes are summarized in Table II and the evaluation data in Table III.

The processing characteristics of these polymers (as judged by their action on a 4 × 9 inch laboratory mill) were not markedly different from those of GR-S. Stress-strain determinations were run at room temperature on small dumbbell specimens (*3*). Flex-cracking resistance is reported as the number of flexures for a crack initiated by a No. 2 needle to grow to an arbitrary rating of eight (approximately 75% of a 1-inch width). The De Mattia machine is driven at a rate of 300 cycles per minute and with a flexing stroke of $2^1/_4$ inches. Hysteresis temperature rise above 212° F. is determined using the Goodrich flexometer with a 55-pound load and $17^1/_2$% stroke (*6*). Quality index is defined as the ratio of the observed flexures to the flexures calculated from the equation (*4*):

$$\log_{10} \text{flexures} = 0.0126\Delta T + 4.28$$

where ΔT = hysteresis temperature rise above 212° F., determined under the conditions described

Quality index is a measure of the balance between hysteresis temperature rise and flex-cracking resistance. The use of quality index as a means of evaluating rubberlike polymers has been discussed by Juve (*4*).

DISCUSSION

Table I shows that 2-vinylfuran, 2-vinylthiophene, and vinylidene chloride all copolymerize more slowly with butadiene than does styrene. Only methacrylonitrile copolymerized at a faster rate than did similar mixtures of butadiene and styrene.

The analysis of the polymers (Table I) shows that methacrylonitrile and 2-vinylthiophene enter the copolymer at rates approximately proportional to their concentration in the monomer mixture (25%). Both apparently enter the chain at faster rates than does styrene, since butadiene-styrene (75:25) copolymers at 70–80% conversion have a styrene constant of 20.3–21.2% (*8*). Vinylidene chloride enters the chain at a considerably slower rate. It is interesting to compare the various copolymers on the basis of the ratio of the monomer units. These ratios are as follows: butadiene to styrene, 7.2–7.6; butadiene to vinylidene chloride, 8.8; butadiene to methacrylonitrile, 3.4; butadiene to 2-vinylthiophene, 5.1–5.5. As noted in Table I, it was not possible to obtain a measure of the 2-vinylfuran content in its copolymers.

In comparing these copolymers with GR-S it has been found that the 2-vinylthiophene copolymer is similar in properties to GR-S itself. This is perhaps to be expected, as the thienyl nucleus is similar in most of its properties to that of the phenyl group.

The copolymer of butadiene and 2-vinylfuran is different from GR-S. It is insoluble in benzene and produces high modulus, low elongation stocks. The flex-cracking resistance in comparison with that of GR-S of equal hysteresis is inferior, and the quality index assigned to the 2-vinylfuran copolymer is 0.5 to 0.9 (nominal index for GR-S is 1.0).

The rubber obtained from butadiene and methacrylonitrile is more promising (quality index is 4.2 to 4.7). It appears to have a better balance between hysteresis–temperature rise and flex-cracking resistance than does GR-S. However, its low temperature properties would be inferior to GR-S.

The butadiene-methacrylonitrile copolymer was also compared with Perbunan (butadiene-acrylonitrile). It was found to be quite similar in most characteristics, although of a somewhat lower tensile strength than Perbunan of the Standard Oil Company of New Jersey.

The butadiene-vinylidene chloride copolymer appears to be inferior to GR-S. The stress-strain characteristics are good, but the balance between hysteresis–temperature rise and flex-cracking resistance is definitely poorer than that of GR-S. The vinylidene chloride copolymer appears to be particularly sensitive to variations in sulfur content during vulcanization.

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TABLE II. TEST RECIPES FOR COPOLYMERS

	Test Recipe Copolymer	Parts by Weight of Compounding Pigments									
		Copolymer	EPC channel black	MPC black	Paraflux[a]	Zinc oxide	Stearic acid	Santocure[b]	Sulfur	Altax[c]	Soft Cumar[d]
I.	GR-S control for II, IV, and VII–X	100.0	50.0	..	5.0	5.0	1.5	1.2	Variable	..	..
II.	75 butadiene:25 vinylfuran	100.0	50.0	..	5.0	5.0	1.5	1.2	1.75	..	..
III.	75 butadiene:25 vinylthiophene	100.0	50.0	..	5.0	5.0	1.5	1.2	2.0	..	..
IV.	75 butadiene:25 methacrylonitrile	100.0	50.0	..	5.0	5.0	..	1.2	1.75	..	..
V.	Perbunan control for VI	100.0	..	50.0	..	5.0	1.5	..	1.25	1.25	10.0
VI.	75 butadiene:25 methacrylonitrile	100.0	..	50.0	..	5.0	..	..	1.25	1.25	10.0
VII.	75 butadiene:52 vinylidene chloride	100.0	50.0	..	5.0	5.0	1.5	1.2	1.50	..	..
VIII.	Same	100.0	50.0	..	5.0	5.0	1.5	1.2	1.75	..	..
IX.	Same	100.0	50.0	..	5.0	5.0	1.5	1.2	2.00	..	..
X.	Same	100.0	50.0	..	5.0	5.0	1.5	1.2	2.25	..	..

[a] Petroleum-type softener, C. P. Hall Co.
[b] Benzothiazyl 2-monocyclohexyl sulfenamide, Monsanto Chemical Co.
[c] 2,2′-Benzothiazyl disulfide, R. T. Vanderbilt Co.
[d] Coumarone-indene resin, Barrett Div., Allied Chemical & Dye Corp.

TABLE III. EVALUATION OF COPOLYMERS

(Data from B. F. Goodrich laboratories)

Test Recipe	Comonomer with Butadiene	Sulfur, Parts	Cure, Min. at 280° F.	300% Modulus, Lb./Sq. In.	Tensile, Lb./Sq. In.	Elongation, %	ΔT, ° F.[a]	Flexing	Durometer Hardness	Quality Index
II	2-Vinylfuran, sample 1	0.75	30	550	900	450	..	....	..	..
			45	1100	2400	520	68[b]	260,000-8	..	<1.0
			60	1000	2300	515	82[c]	160,000-8	..	<1.0
			75	1600	2600	505	71[d]	90,000-8	..	<1.0
			150	1600	3100	485	..	....	..	..
II	2-Vinylfuran, sample 1	1.00	30	350	2350	845	..	....	..	..
			45	1000	2700	567	..	....	..	..
			60	1300	3200	555	..	....	..	..
			75	1300	3250	505	..	....	..	..
			150	1700	3100	440	..	....	..	..
		1.25	30	950	2000	515	..	....	..	..
			45	1400	3000	505	..	....	..	..
			60	1700	3000	440	..	....	..	..
			75	1700	3400	460	..	....	..	..
			150	2000	3000	345	..	....	..	..
		1.50	30	900	2100	495	..	....	..	..
			45	1500	3100	490	..	....	..	..
			60	1700	3400	460	..	....	..	..
			75	2200	3500	407	..	....	..	..
			150	2500	3500	327	..	....	..	..
		1.75	75	2250	2900	375	37	40,000-8	..	0.7
			150	2350	2450	305	35	20,000-8	..	0.4
II	2-Vinylfuran, sample 2	0.75	30	600	2700	780	..	....	..	..
			45	1300	2000	420	96[e]	130,000-8	..	<1.0
			60	1500	2100	420	74[e]	130,000-8	..	<1.0
			75	1750	2600	420	67[e]	90,000-8	..	<1.0
			150	2100	2800	380	..	....	..	..
II	2-Vinylfuran, sample 2	1.00	30	1700	2700	420	..	....	..	..
			45	1900	2800	407	..	....	..	..
			60	1700	2800	433	..	....	..	..
			75	2200	3300	415	..	....	..	..
			150	2600	2800	320	..	....	..	..
		1.25	30	1800	2900	430	..	....	..	..
			45	2000	2800	375	..	....	..	..
			60	2000	3000	407	..	....	..	..
			75	2200	3200	405	..	....	..	..
			150	2700	2800	285	..	....	..	..
		1.50	30	1400	2400	435	..	....	..	..
			45	2000	3050	390	..	....	..	..
			60	2200	2900	347	..	....	..	..
			75	2500	3200	355	..	....	..	..
			150	2900	2900	300	..	....	..	..
		1.75	75	2400	2700	310	41	30,000-9	..	0.5
			150	2600	2750	310	40	20,000-10	..	0.3
I	GR-S control	..	75	550	2700	740	45[f]	350,000-8	..	5.0[f]
			150	600	3150	750	42[f]	420,000-8	..	6.5[f]
III	2-Vinylthiophene	2.00	75	1100	3500	635	79	750,000-8	62	3.9
			150	1410	3200	500	58	230,000-8	65	2.2
I	GR-S control	..	75	1020	3380	648	79	....	59	..
			150	1040	2810	567	58	....	61	..
IV	Methacrylonitrile	1.75	75	1500	3500	515	62	550,000-8	..	4.7
			150	1600	2750	435	58	440,000-8	..	4.1
I	GR-S control	..	75	780	3500	730	58	160,000-8	..	1.5
			150	860	3200	680	52	140,000-8	..	1.6
VI	Methacrylonitrile	1.25	30	800	3560	640	..	....	..	..
			45	850	4050	640	..	....	..	..
			75	900	4000	600	..	....	..	..
V	Perbunan	1.25	30	1450	4950	560	..	....	..	..
			45	1525	4950	570	..	....	..	..
			60	1875	4950	570	..	....	..	..
VII	Vinylidene chloride	1.50	30	325	1600	725	..	....	..	..
			45	500	2050	700	..	....	..	..
			75	775	2600	560	..	....	..	..
			150	875	2300	325	..	....	..	..
VIII	Vinylidene chloride	1.75	30	375	1650	705	..	....	..	..
			45	500	2500	725	137	140,000-8	..	0.1
			75	1100	3175	567	64	90,000-9	..	0.7
			150	1250	2350	310	..	....	..	..
IX	Vinylidene chloride	2.00	30	250	1000	640	..	....	..	..
			45	2000	2000	300	..	....	..	..
			75	2000	1800	290	..	....	..	..
			150	..	1550	150	..	....	..	..
X	Vinylidene chloride	2.25	30	250	900	625	..	....	..	..
			45	1800	1800	300	..	....	..	..
			75	..	1950	260	..	....	..	..
			150	..	1850	180	..	....	..	..

[a] Hysteresis–temperature rise above 212° F., using a 55-pound load and a 17½% stroke.
[b] Broke at 4 minutes.
[c] Broke at 14 minutes.
[d] Blew out.
[e] Broke, time unknown.
[f] Hysteresis–temperature rise abnormally low for GR-S control.

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