POLYMERIZATION OF 2-FLUOROBUTADIENE-1,3 AND PROPERTIES OF POLYMERS[1]

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ABSTRACT

Fluorobutadiene has been copolymerized with styrene in emulsion at 5°C. The rate of mercaptan consumption, rate of conversion, copolymer composition, and the intrinsic viscosity of the copolymer have been measured. Reactivity ratios and regulating indices were calculated for this temperature. Copolymerization reactions at 50°C. were studied in solution, and the reactivity ratios calculated. These were, for the following monomers as monomer 2: styrene at 5°C., $r_1 = 1.61 \pm 0.24$ and $r_2 = 0.16 \pm 0.08$; styrene at 50°C., $r_1 = 1.55 \pm 0.10$ and $r_2 = 0.50 \pm 0.10$; acrylonitrile at 50°C., $r_1 = 0.59 \pm 0.10$ and $r_2 = 0.07 \pm 0.03$; isoprene at 50°C., $r_1 = 2.05 \pm 0.19$ and $r_2 = 0.19 \pm 0.10$; α-methyl styrene at 50°C., $r_1 = 1.77 \pm 0.19$ and $r_2 = 0.38 \pm 0.11$; and methyl methacrylate at 50°C., $r_1 = 1.54 \pm 0.08$ and $r_2 = 0.64 \pm 0.08$. Polyfluorobutadiene has a cohesive energy density of 90–100 cal./cc., a second order transition point of -62.5°C., and some units formed by 1,2 or 3,4 addition.

INTRODUCTION

There are few data on the polymerization of 2-fluorobutadiene or on the physical properties of its polymers. The patent literature contains information on preparation of the polymers in emulsion and their properties (8, 9, 10, 16, 17, 18, 19, 24). Other papers have appeared summarizing the properties and preparations of the polymers (21, 33).

Fluorobutadiene lies between butadiene and chlorobutadiene in its properties. It polymerizes nearly as rapidly as chlorobutadiene, but unlike the latter copolymerizes with many monomers readily. Homopolymers have been found to be resistant to crystallization on stretching but require reinforcement for development of high tensile properties. Methods of synthesis of the monomer have been reported in a number of patents (2, 11, 12, 25, 26, 27, 28, 29).

EXPERIMENTAL RESULTS

Copolymerization Rates

The rate of conversion was measured as a function of monomer ratio for copolymerization with styrene at 5°C.; the results are given in Table I. The conversion rate is unaffected by the per cent diene in the charge. The time–conversion relation is quite linear, showing a rate of conversion considerably more rapid than during the polymerization of butadiene.

Chain Transfer Reactions

The intrinsic viscosities of the polymers prepared to different conversions, from various charge ratios and mercaptan contents, were measured in benzene and ethylene dichloride. The mercaptan used was a mixture of tertiary mercaptans of an average molecular weight 220. The data are in Table II. The disappearance of mercaptan (RSH) over the course of the polymerization was determined by amperometric titration. The results are in Table III.

TABLE I

CONVERSION RATES FOR STYRENE–FLUOROBUTADIENE COPOLYMERIZATION

% Diene in charge	Hours	% Conversion
100	3.75	43
78	1.00	11
	2.50	40
60	1.00	18
	1.50	26
	2.25	36
	3.25	49
20	1.00	10
	3.00	40

TABLE II

INTRINISIC VISCOSITIES OF FLUOROBUTADIENE POLYMERS AND COPOLYMERS

% Diene in charge	Mercaptan parts	% Conv.	Solvent	$[\eta]$
100	0	18		0.49
		23		0.50
		30		0.49
		36	Ethylene dichloride	0.67
		38		0.50
		45		0.50
		48		0.84
		58		0.43
		43		0.3
	0.9	46		0.6
	2.0	40		0.7
78	2.3	18	Benzene	0.90
		34		0.88
		48		0.65
60	2.3	21		0.80
		38		0.79
		49		0.80
20	2.3	14		0.4
		36		1.0
		42		0.7

TABLE III

MERCAPTAN DISAPPEARANCE IN STYRENE–FLUOROBUTADIENE COPOLYMERIZATION

% Diene	% Conversion	$[RSH]/[RSH]_0$
78	18	0.79
	34	0.31
	48	0.36
60	21	0.85
	38	0.61
	49	0.33

Polymer Compositions from Emulsion and Solution Polymerizations

Polymers from polymerizations in emulsion and solution, at 5° and 50°C. respectively, were analyzed for per cent diene.

Styrene was the comonomer at 5°C. and the comonomers at 50°C. were styrene, acrylonitrile, isoprene, α-methyl styrene, and methyl methacrylate.

The emulsion polymers were obtained at varying conversions. The polymers prepared in solution were as low conversion as possible. The results of the analyses are in Table IV.

TABLE IV

POLYMER COMPOSITIONS FOR FLUOROBUTADIENE (M_1) COPOLYMERS

Weight % M_1 in initial monomer		% Conv.	Weight % diene	Weight % diene at 0 % conv. (calc.)
78	M_2 = styrene at 5°C.	33	87.5	87.2
		47	87.0	
60		11	72.0	72.5
		15	71.5	
		38	73.0	
		49	73.0	
30		6.5	53.5	53.5
		30	53.5	
		50	51.2	
20		14	41.0	41.0
		36	33.0	
		42	31.0	
60	M_2 = styrene at 50°C.	<3	73.9	75.3
		<3	74.6	
		<3	78.6	
50		<3	62.2	61.3
		<3	60.5	
40		<3	55.8	52.7
		<3	48.1	
20		<4	38.0	37.4
		<4	36.8	
68	M_2 = α-methyl styrene at 50°C.	6.36	81.9	80.0
		13.78	78.0	
52		2.66	67.9	68.5
		11.37	69.0	
36		2.20	47.9	50.8
		8.55	43.8	
20		1.19	31.2	36.0
		5.28	40.6	
68	M_2 = methyl methacrylate at 50°C.	8.12	76.2	78.1
		11.60	80.0	
52		10.17	50.3	56.9
		11.23	63.5	
36		9.97	48.2	49.5
		15.27	50.8	
20		15.60	20.5	27.3
		17.36	34.2	
68	M_2 = isoprene at 50°C.	<4	85.7	83.8
		12.7	81.9	
52		6.8	73.7	73.7
36		5.3	65.2	65.2
20		<4	38.4	40.8
		<4	43.2	
60	M_2 = acrylonitrile at 50°C.	4.7	67.6	67.6
50		2.3	63.6	63.6
40		5.0	61.1	61.1
20		6.9	50.4	50.4

Effect of Solvents on Vulcanized Polyfluorobutadiene

The tendency of this polymer to swell in a series of solvents of varying cohesive energy densities was determined. The per cent swell was determined by soaking a strip of the rubber in the solvent and determining the weight increase. The equilibrium weight was used to determine the amount of swelling.

Some of the cohesive energy density values were taken from publications (14, 31). Those unavailable were calculated from the relation c.e.d. $= \Delta H_{vap} - RT$. In Table V are given the results.

TABLE V

SWELL BEHAVIOR OF VULCANIZED POLYFLUOROBUTADIENE

Solvent	c.e.d. (Ref.)	% Swell
Toluene	80 (14)	115
Benzene	82 (14)	110
Methyl ethyl ketone	86	93
Ethylene dichloride	96	219
Carbon disulphide	97	134
Acetone	100 (14)	110
Pyridine	100 (31)	203
Dioxane	100 (14)	199
Dimethyl formamide	140 (31)	100
Nitromethane	160 (31)	183

Second Order Transition Temperature

This was determined by a dilatometric method as being $-62.5°C$. There was no evidence of crystallization at this temperature.

Infrared Spectra of Polyfluorobutadiene

All infrared spectroscopic work had to be done on the solid films since the polymers were insoluble in carbon disulphide. No quantitative conclusions were possible but qualitative results could be obtained. In Fig. 1 are curves for polyfluoro- and polychloro-butadiene. These are compared with the spectra of polybromoprene (20). Since all spectra were determined in polyethylene, no data were obtained below 7.8 microns where polyethylene begins to interfere.
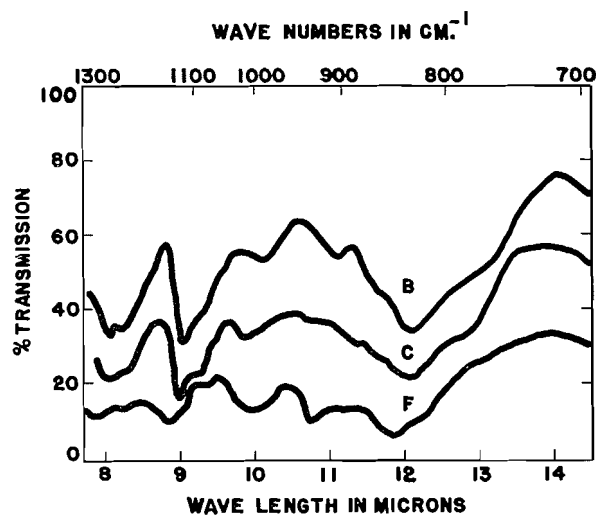

FIG. 1. Infrared spectra of polyfluorobutadiene (F), polychlorobutadiene (C), and polybromobutadiene (B).

DISCUSSION

Emulsion Polymerizations

Emulsion copolymerization rates are quite rapid compared to butadiene (3, 6) indicating either efficient utilization of initiating radicals or a high solubilization of monomers by soap. The independence of rate with per cent fluorobutadiene in the charge suggests polymerization rates similar to those of styrene. The low intrinsic viscosities of the polymers may be due to low molecular weight, a highly gelled polymer, or an improper choice of solvent. Since the values did not change markedly for measurements using two liquids of a different cohesive energy density, the choice of solvent could not have been responsible. There seems little possibility that the polymers were gelled since the intrinsic viscosity of polyfluorobutadiene prepared in the absence of mercaptan did not show the peak characteristic of gelation, even at very low conversion. The low intrinsic viscosities must be characteristic of low molecular weights due to chain transfer reactions. These cannot be due to mercaptan since the intrinsic viscosity is independent of the mercaptan content of the original charge. Either the fluorobutadiene itself, or some impurity difficult to remove, such as difluorobutene, must be responsible. The mercaptan does react during polymerization at a rate indicating the same reactivity toward the fluorobutadienyl radical as toward butadienyl (6). If this reaction is first order with respect to mercaptan over the first part of the reaction, the regulating indices would be 1.8 and 0.6 for 78/22 and 60/40 fluorobutadiene–styrene charge ratios respectively.

Structure of Polyfluorobutadiene

The dominant band in the spectra near 12 microns must be due to the C–H on the CH=CF group. This completely obscures that portion of the spectra which would give a measure of the proportion of *cis* 1,4 addition (by analogy with the spectrum of Hevea). Some 1,2 or 3,4 addition is indicated by the band at 10.75 microns. This is different from polychlorobutadiene which is 100% 1,4 (20).

Solubility of Polyfluorobutadiene

One method of determining the cohesive energy density (c.e.d.) of a polymer is to find the liquid in which the swelling of the vulcanized polymer is a maximum (31). From the data in Table V, the cohesive energy density of polyfluorobutadiene was estimated as 90–100 cal./cc. Acetone and nitromethane gave anomalous results. The cohesive energy density is of the order of that for polyvinyl chloride and is larger than the value for polychlorobutadiene and 75/25 butadiene–acrylonitrile copolymers. Fluorine changed the cohesive energy density of the polymer in the same direction but to a greater extent than did chlorine. This does not correlate well with the low values obtained with other fluorine containing polymers (31). The structure of the polymer chain may affect the part that fluorine plays in determining the cohesive energy density.

Reactivity Ratios of Fluorobutadiene in Copolymerization

The reacted monomer data from the emulsion polymerizations were extra-

polated to zero conversion. Solution polymerizations were stopped at low conversions and the polymer composition assumed to be identical with that formed at zero conversion. These values, with the corresponding charge ratio, were substituted in the copolymerization equation, the r_1–r_2 lines calculated, and the values of r_1 and r_2 determined. The error was estimated from the size of the triangle of intersection. A typical r_1–r_2 plot is shown in Fig. 2. In Table VI are the values which were determined.
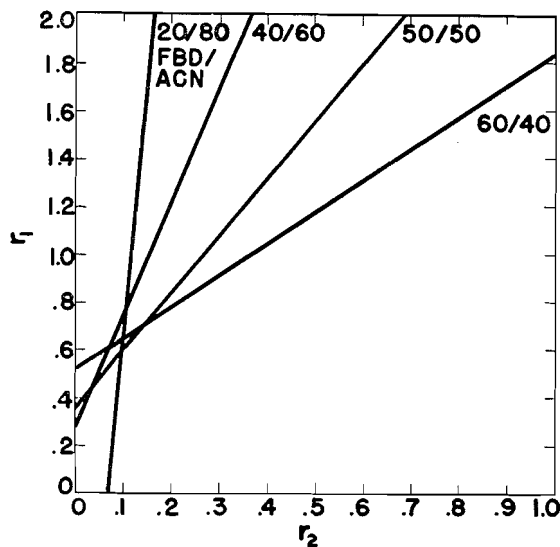

FIG. 2. r_1–r_2 lines for fluorobutadiene–acrylonitrile copolymerization at 50°C.

TABLE VI

REACTIVITY RATIOS OF FLUOROBUTADIENE WITH COMONOMERS

Comonomer (M$_2$)	T (°C.)	r_1	r_2	$r_1 \times r_2$
Styrene	5	1.61 ± 0.24	0.16 ± 0.08	0.26
Styrene	50	1.55 ± 0.10	0.50 ± 0.10	0.78
Acrylonitrile	50	0.59 ± 0.10	0.07 ± 0.03	0.04
Isoprene	50	2.05 ± 0.19	0.19 ± 0.10	0.39
Alpha methyl styrene	50	1.77 ± 0.19	0.38 ± 0.11	0.67
Methyl methacrylate	50	1.54 ± 0.8	0.64 ± 0.08	0.99

The influence of temperature on r_2 seems much more pronounced than on r_1. There is a strong tendency to alternate in the copolymers, reaching a maximum with acrylonitrile and a minimum with methyl methacrylate. The ratio of r_1 and r_2 indicates a general tendency to enter the copolymer more rapidly than the comonomer.

The Q and e Values of Fluorobutadiene

These values were calculated from the Alfrey-Price equation and are in Table VII. The values for fluorobutadiene were determined using styrene as the primary standard with $Q = 1.0$ and $e = -0.8$. Those for the other comonomers were determined using the fluorobutadiene as a secondary standard.

TABLE VII

Q AND e VALUES FOR FLUOROBUTADIENE AND THE COMONOMERS

Monomer	T (°C.)	Q	e
Fluorobutadiene	5	1.39	+0.36
Fluorobutadiene	50	1.32	−0.30
Methyl methacrylate	50	0.85	−0.30
Acrylonitrile	50	2.5	+1.5
Isoprene	50	0.86	−1.27
Alpha methyl styrene	50	0.98	−0.93

Agreement with the values reported previously (1) is within experimental error except for the e value of methyl methacrylate which was reported as 0.4. The Q and e values for isoprene at 50°C. were not previously reported but the deviation from butadiene at this temperature is in accord with that observed at −18°C. (22, 23).

It is of interest to compare the relative effects of chlorine and fluorine substitution on the polarity of the double bond and the resonance stabilization of the dienyl free radical. The reactivity ratios for chlorobutadiene have been reported as $r_1 = 3.41$, $r_2 = 0.59$ for butadiene and $r_1 = 3.65$, $r_2 = 0.133$ for isoprene (chlorobutadiene being monomer-1) at 50°C. (30). Using butadiene as a secondary standard with $Q = 1.33$ and $e = -0.8$, then Q and e for chlorobutadiene are 1.5 and −0.24 respectively. It may be seen that the change in Q and e caused by the substitution of the fluorine group is in the same direction, but not as pronounced as it was for the chlorine. Fluorobutadienyl radical is less resonance stabilized and the double bond of the monomer is poorer in electrons than that of the chlorobutadiene.

EXPERIMENTAL METHODS

The recipe was similar to one developed previously for butadiene copolymerization (6) and is:

Monomers	100 parts by weight, active material
Water	180
Potassium fatty acid soap flakes	5.0
Mixed tertiary mercaptans	Variable
Cumene hydroperoxide	0.10
Ferrous sulphate heptahydrate	0.14
Potassium pyrophosphate	0.177

An emulsion of ditertiary butyl hydroquinone was used as the stopping agent.

Fluorobutadiene was prepared by the Defence Research Chemical Laboratory through the courtesy of Dr. H. Sheffer. It was subjected to simple distillation before use. Other monomers were commercial materials which were fractionated, taking the center fraction. All polymerization chemicals were standard Commercial grade. Analytical reagents were C.P. grade.

The mercaptan in the latex was determined by amperometric titration (13). Intrinsic viscosities were measured at 30.0°C. by dissolving the latex directly in an 80:20 benzene–ethanol or ethylene dichloride – ethanol solution. Dilutions were made with pure benzene (or ethylene dichloride) so that intrinsic viscosities could be calculated (4, 7, 15).

The polyfluorobutadiene was synthesized at 5°C., coagulated in brine acid, stabilized with BLE, compounded in the test recipe, and vulcanized. Swelling indices were done on the vulcanized stock. Second order transition points were determined on uncured samples by a dilatometric technique. Polymers were purified for analysis by swelling in benzene and extracting in methanol.

A normal Parr bomb combustion using 50 mgm. polymer, 15 gm. sodium peroxide, and 0.5 gm. benzoic acid was used. The ignition was electrical and it was found that the position of the fuse wire in respect to the top of the combustion mixture was critical. Potassium perchlorate was omitted from the combustion mixture since it was found to have a deleterious effect in the subsequent colorimetric analysis for fluoride ion.

Fluoride was determined on aliquots of the solution containing the soluble combustion products by the extent of bleaching brought about by the addition of fluoride ions to a ferric thiocyanate solution (5, 32). The amount of bleaching is definite and reproducible but not a linear function of fluoride ion concentration. There is a slow but distinct decrease in the colorimeter reading with time and the color varies considerably with pH. The combustion mixture was brought to pH = 7.0 with nitric acid and further adjusted to 2.0 with hydrochloric acid. The method was standardized against sodium fluoride solution with readings taken on a Klett-Summerson colorimeter and a Beckman DU ultraviolet spectrophotometer set at 4900 Å wavelength. Analysis of polyfluorobutadiene indicated complete recovery and identification of organic fluorine.

ACKNOWLEDGMENT

REFERENCES

1. ALFREY, T. and PRICE, C. C. J. Polymer Sci. 2: 101. 1947.
2. COFFMAN, D. D. and SALISBURY, L. F. (duPont) U.S. Patent No. 2,451,612. Oct. 19, 1948.
3. EMBREE, W. H., SPOLSKY, R., and WILLIAMS, H. L. Ind. Eng. Chem. 43: 2553. 1951.
4. FORDHAM, J. W. L., O'NEIL, A. N., and WILLIAMS, H. L. Can. J. Research, F, 27: 119. 1949.
5. FOSTER, M. D. Ind. Eng. Chem. Anal. Ed. 5: 234. 1933.
6. GILBERT, R. D. and WILLIAMS, H. L. J. Am. Chem. Soc. 74: 4114. 1952.
7. HENDERSON, D. A. and LEGGE, N. R. Can. J. Research, B, 27: 666. 1949.
8. HILL, F. B., Jr. (duPont) U.S. Patent No. 2,436,213. Feb. 17, 1948.
9. HILL, F. B., Jr. (duPont) Can. Patent No. 459,661. Sept. 13, 1949.
10. IMPERIAL CHEM. INDUSTRIES Brit. Patent No. 591,086. Aug. 6, 1947.
11. IMPERIAL CHEM. INDUSTRIES Brit. Patent No. 603,855. June 24, 1948.
12. JOHNSON, F. W. (duPont) U.S. Patent No. 2,398,181. April 9, 1946.
13. KOLTHOFF, I. M. and HARRIS, W. E. Ind. Eng. Chem. Anal. Ed. 18: 161. 1949.
14. MARK, H. and TOBOLSKY, A. V. Physical chemistry of high polymeric systems. Vol. 2. Interscience Publishers, Inc., New York. 1940. p.261.
15. MITCHELL, J. M. and WILLIAMS, H. L. Can. J. Research, F, 27: 35. 1949.
16. MOCHEL, W. E. (duPont) U.S. Patent No. 2,426,560. Aug. 26, 1947.
17. MOCHEL, W. E. (duPont) U.S. Patent No. 2,429,838. Oct. 28, 1947.
18. MOCHEL, W. E. (duPont) U.S. Patent No. 2,446,382. Aug. 3, 1948.
19. MOCHEL, W. E. (duPont) Can. Patent No. 459,955. Sept. 27, 1949.

20. MOCHEL, W. E. and HALL, M. B.　J. Am. Chem. Soc. 71: 4082.　1949.
21. MOCHEL, W. E., SALISBURY, L. F., BARNET, A. L., COFFMAN, D. D., and MIGHTON, C. J.
　　　Ind. Eng. Chem. 40: 2285.　1948.
22. ORR, R. J. and WILLIAMS, H. L.　Can. J. Chem. 29: 270.　1951.
23. ORR, R. J. and WILLIAMS, H. L.　Can. J. Chem. 30: 108.　1952.
24. SALISBURY, L. F.　(duPont) U.S. Patent No. 2,416,456.　Feb. 25, 1947.
25. SALISBURY, L. F.　(duPont) U.S. Patent No. 2,426,792.　Sept. 2, 1947.
26. SALISBURY, L. F.　(duPont) U.S. Patent No. 2,437,307.　Mar. 9, 1948.
27. SALISBURY, L. F.　(duPont) U.S. Patent No. 2,437,308.　Mar. 9, 1948.
28. SALISBURY, L. F.　(duPont) U.S. Patent No. 2,469,948.　May 10, 1949.
29. SALISBURY, L. F.　(duPont) U.S. Patent No. 2,519,199.　Aug. 14, 1950.
30. SIMHA, R. and WALL, L. A.　J. Research Natl. Bur. Standards, 41: 521.　1948.
31. SMALL, P. A.　J. Appl. Chem. (London), 3: 71.　1953.
32. SMITH, H. V.　Ind. Eng. Chem. Anal. Ed. 7: 23.　1935.
33. STARKWEATHER, H. W., BARE, P. O., CARTER, A. S., HILL, F. B., Jr., HURKA, V. R.,
　　　MIGHTON, C. J., SANDERS, R. A., WALKER, H. W., and YOUKER, M. A.　Ind. Eng.
　　　Chem. 39: 210.　1947.