Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Polymerization of Some 1-Alkyl-1-hydroperfluoroalkyl Acrylates

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Recent investigations of fluorine-containing acrylates for use as high temperature elastomers resistant to diester-type lubricants prompted this study of acrylates prepared from fluorine-containing secondary alcohols. A detailed description of the preparation and polymerization reactions of a series of six 1,1-dihydroperfluoroalkyl acrylates has been published (*5–9*). One of these acrylates, 1,1-dihydroperfluorobutyl acrylate, is now commercially available. Bittles (*2*) has described the preparation of ω,1,1-trihydroperfluoroalkyl acrylates. Some polymerization work has also been reported on 1,1,3-trihydroperfluorobutyl acrylate (*3*). This report describes the preparation and properties of the homopolymers and copolymers of three 1-alkyl-1-hydroperfluoroalkyl acrylates. The quantity of the monomers prepared was small and consequently only a preliminary examination of their polymerization reactions was possible.

MATERIALS

The fluorine-containing acrylates were prepared by the method of Codding and others (*6*) for the preparation of 1,1-dihydroperfluoroalkyl acrylates. The physical properties and yields of the three monomers are shown in Table I. A sample of poly(1,1-dihydroperfluorobutyl acrylate), 1F4, was obtained from the Minnesota Mining and Manufacturing Co.

METHODS

Bulk Polymerization. Bulk polymerizations were run at 60°C. in small borosilicate glass bottles with screw-cap lids and Buna-N gaskets. Catalyst and monomer were added and air was displaced by dry oxygen-free nitrogen. Polymerization time was generally estimated by change in viscosity of the reaction mixture. After the desired time, the polymerization bottles were cooled and the polymer was precipitated with methanol. Purification was accomplished by dissolving the polymer in benzotrifluoride or *N,N'*-dimethylformamide and reprecipitating with methanol and water, respectively. The polymers were then washed thoroughly and dried overnight in a vacuum oven at 70°C. Copolymers were prepared using 1-gram monomer charge and 1% benzoyl peroxide as catalyst.

Emulsion Polymerization. Emulsion polymerizations were carried out at 50°C. using the standard recipe (*5*).

Standard Emulsion Recipe

	Grams
Monomers	5
Water	9
Sodium lauryl sulfate	0.15
Potassium persulfate	0.025

In some homopolymerization reactions, 0.015% acrylic acid was added to facilitate curing of the polymer. Polymerization and purification procedures were similar to those for bulk polymerization.

EVALUATION

Copolymer Evaluation. The copolymers prepared were characterized by inherent viscosity, elemental analysis, and appearance of the polymer. The infrared spectra of all copolymers were recorded and used as further evidence of copolymer formation.

Compounding and Vulcanization. The homopolymers were processed on a 1.25 × 1.25 × 4 inch mill with a roll temperature of 110°F.

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Table I. Physical Properties of Monomers

$CH_2{=}CHCO_2R$ R−	Yield, %	B.P., °C./Mm.	n_D^{20}	d_4^{20}	Carbon, % Calcd.	Carbon, % Found	Fluorine, % Calcd.	Fluorine, % Found
$—CH(CH_3)CF_3$	36	48/120	1.3573	1.158	42.86	42.90	33.93	34.19
$—CH(CH_3)C_3F_7$	52	63/73	1.3400	1.352	35.82	35.87	49.63	49.80
$—CH(C_2H_5)C_3F_7$	65	66/45	1.3512	1.319	38.30	38.33	47.16	47.06

Table II. Bulk Copolymerizations of Fluorine-Containing Acrylates

Comonomer	Polym. Time, Hr.	Conversion, %	Inherent Viscosity[a]	Acrylate Incorp.,[b] Wt. %	Appearance of Solid
1-Methyl-1-hydroperfluoroethyl acrylate					
Acrylonitrile	8	90	3.25[c]	51	Tough elastomer
Vinyl acetate	5	70	1.91	67	Soft elastomer
Maleic anhydride	72	65	0.95	87	Tacky elastomer
Styrene	8	85	1.78	48	Brittle
Benzalacetophenone	72	60	1.50	83	Tacky
1-Methyl-1-hydroperfluorobutyl acrylate					
Acrylonitrile	8	95	3.21[c]	43	Tough elastomer
Vinyl acetate	5	70	1.98	74	Soft elastomer
Maleic anhydride	72	65	1.04	92	Tacky elastomer
Styrene	8	50	2.36	59	Brittle
Benzalacetophenone	72	55	1.84	84	Tacky
1-Ethyl-1-hydroperfluorobutyl acrylate					
Acrylonitrile	8	40	3.06[c]	34	Tough elastomer
Vinyl acetate	5	75	1.64	67	Soft elastomer
Maleic anhydride	72	65	0.94	93	Tacky elastomer
Styrene	8	50	3.50	69	Brittle
Benzalacetophenone	72	65	1.97	89	Tacky

[a] Determined in benzotrifluoride
[b] Calculated from fluorine analysis.
[c] Determined in *N,N'*-dimethylformamide.

Standard Compounding Recipe

	Parts
Polymer	100
Paraffin	1
Sulfur	1
Philblack O	40
Triethylenetetramine	1.25

The stock without amine was aged overnight before acceleration and curing to wet the filler and aid dispersion. The amine was then added and the stock cured for 30 minutes at 320°F.

Vulcanizates of the polyacrylates were tested for stress-strain, permanent set 2 minutes after break, Shore A hardness, and low temperature retraction. These tests were patterned after ASTM Standards on Rubber Products (*1*).

RESULTS AND DISCUSSION

Copolymerization. The 1-alkyl-1-hydroperfluoroalkyl acrylates copolymerize with a variety of vinyl monomers and butadiene. In general, their reactivity does not differ widely from the 1,1-dihydroperfluoroalkyl acrylates. Copolymerization occurs readily with styrene, acrylonitrile, vinyl acetate, maleic anhydride, and benzalacetophenone. The monomer charge (1 gram) with styrene, vinyl acetate, and acrylonitrile contained 0.5 gram of acrylate; 0.8 gram of acrylate was charged with benzalacetophenone and maleic anhydride. Copolymers with vinyl acetate softened from 80° to 110°C. and had poor strength and chemical resistance. The acrylonitrile copolymers darkened from 150° to 200°C. and charred around 285°C. Copolymers with benzalacetophenone, maleic anhydride, and vinyl acetate appeared promising as adhesives. Other properties of these acrylate copolymers are shown in Table II.

Rubbery copolymers of the fluorine-containing acrylates with butadiene were prepared in very small quantities by the emulsion recipe. Infrared data indicated that copolymers also were formed with isoprene, 2-vinylpyridine, *n*-butyl vinyl ether, and perfluoropropyl propenyl ketone.

Homopolymerization. Homopolymerization of the 1-alkyl-1-hydroperfluoroalkyl acrylates resulted in transparent latices and the rubbery nature of the polymer increased as the chain length of the perfluoroalkyl group increased. Conversions from 60 to 90% were easily obtained and the inherent viscosity in methyl perfluorobutyrate ranged from 0.5 to 1.5. The homopolymer of 1-methyl-1-hydroperfluoroethyl acrylate was a tough material and resembled a plastic more than an elastomer. It softened at 100°C. and gave no evidence of cross linking with heat. The 1-methyl- and 1-ethyl-1-hydroperfluorobutyl acrylate homopolymers were tough white elastomers.

A qualitative heat stability test was carried out on the raw polymers by heating them in air for 2 days at 187°C. and an additional day at 204°C. Duplicate samples were tested. Poly-(1-ethyl-1-hydroperfluorobutyl acrylate) showed a weight loss in the range of 10 to 20%, while the other two experimental polymers and 1F4 showed a 40 to 50% weight loss. Because traces of water or residual soap could cause some differences in thermal stability, these results cannot be considered absolute. However, the differences in weight loss are large enough to indicate some increased thermal stability of the 1-ethyl derivative over the other acrylates studied.

Evaluation. The polymers tested in this study are identified in Table III. The homopolymer of 1-methyl-1-hydroperfluoroethyl acrylate was not evaluated because of its extreme toughness.

The stocks processed easily to give excellent sheets. However, the standard recipe resulted in blown uncured stock. Previous work on 1F4 (*9*) indicated that in the curing reaction, the fluoroalcohol is liberated by hydrolysis and the polyamine takes part in the cross linking by forming amide linkages between polymer chains. Consequently, the curing of the acrylates of secondary fluorinated alcohols should be more difficult, because of steric hindrance of the hydrolysis reaction. Attempts to use other curing agents such as dicumyl peroxide, ethylenediamine, methylene

Table III. Polymers Evaluated

Sample No.	$CH_2=CHCO_2R$ R-	Acrylic Acid, %
101	$—CH(C_2H_5)C_3F_7$	...
102	$—CH(C_2H_5)C_3F_7$	0.015
103	$—CH(CH_3)C_3F_7$	...
104	$—CH(CH_3)C_3F_7$	0.015
1F4	$—CH_2CF_2CF_2CF_3$	0.015

Table IV. Evaluation of Vulcanizates

	101		1F4	
	Original	Aged[a]	Original	Aged[a]
Tensile strength, lb./sq. inch	950	1000	1050	900
Elongation, %	120	90	170	100
Modulus, 100%, lb./sq. inch	730	...	...	...
Permanent set[b], %	10	10	10	3
Shore A hardness	77	85	72	75
Volume swell, %	...	2.5	...	1.5
TR_{10}, °C.	0		+5	

[a] Aged 100 hours at 350°F. in MIL-L7808 diester type fluid.
[b] Two minutes after break.

iodide, and dimethylethanolamine-calcium oxide were unsuccessful. These results are in agreement with an earlier attempt to cure poly-(1-methyl-1-hydroperfluorobutyl acrylate) (*4*).

A vulcanizate using the standard recipe was ultimately obtained on only one experimental sample, 101, by preheating the raw polymer 12 hours at 250°F. Properties of this vulcanizate and a 1F4 vulcanizate are given in Table IV.

Although no physical properties were measured, data on the partially cured 102, 103, and 104 samples indicated very low volume swell in diester fluids.

No further work was done on obtaining optimum polymerization or curing techniques, as the physical properties of the experimental vulcanizate were similar to those of the commercial 1F4 and only marginal improvement in thermal stability might be expected.

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Polyelectrolytic Properties of Ligninsulfonic Acids

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Lignin sulfonates from spent sulfite liquor were separated into eight fractions of osmotic molecular weights ranging from 3500 to 58,000 by ultrafiltration and fractional dialysis. The methoxyl, sulfur, and phenolic hydroxyl contents, neutralization equivalent weights, reducing powers, and ultraviolet absorption spectra of the fractions were determined.

The concentration dependence of the reduced viscosities, specific conductivities, and dyestuff-absorbing powers of the individual fractions in aqueous solutions indicates that they behave as flexible polyelectrolytes. There is evidence that lignin sulfonates of molecular weight less than 5000 associate in solution in a manner analogous to micelle formation in colloidal electrolytes. The dependence of intrinsic viscosities and of diffusion coefficients on molecular weight indicates that sodium lignin sulfonates in solution form flexible coils which are impermeable to water in the presence of sufficient amounts of sodium chloride and permeable to water in absence of added electrolytes.

One of the aims of this work was to find the fundamental properties of lignin sulfonates from the sulfite pulping of wood, which make possible their use as dispersants and binders. The broader aim was to investigate their solution behavior and get information on their molecular shape and molecular weight distribution.

The present research can logically be divided into three parts: (1) preparation of fractions of different molecular weights and determination of their analytical properties, (2) determination of molecular weights and diffusion coefficients, and (3) investigation of viscosities, conductivities, and dyestuff-adsorbing powers of solutions prepared from the fractions.

Figure 1 shows the process of fractionation. The starting material was spray-dried spent sulfite liquor drawn from cooks of a mixture of approximately equal amounts of balsam and spruce. This material was dissolved in water, ion-exchanged to remove the inorganic materials, and exhaustively dialyzed through denitrated nitrocellulose membranes of low porosity. Four fractions of low molecular weight were prepared from dialyzates corresponding to different dialysis times by precipitating the barium salts with alcohol (*1*). The dialyzed liquor was separated into four fractions by ultrafiltration (*1*, *2*) through cellophane and parchment membranes. All fractions were converted into sodium salts and dried at 60°C. under vacuum.

Table I gives analytical data of the fractions. There is strong indication that fractions 1 to 4 are pure lignin sulfonates. All acidic groups on these fractions are sulfonic; they have high methoxyl contents and high ultraviolet extinctions. The reducing power of these fractions is low, in the range of 3.5% equivalent glucose, and is probably