

NOTE

*Preparation and Polymerizability of Substituted
 α,β,β -Trifluorostyrenes*

The oxidative instability of polystyrene and its copolymers has been the subject of many reviews and publications for the past three decades. Alternate molecules similar in structure but having greater oxidative resistance (e.g., elimination of benzylic hydrogen) have been sought as replacements for polystyrene, and it is the purpose of this note to review research work directed toward this goal.

Although still expensive, poly- α,β,β -trifluorostyrene is one such alternate material offering good oxidative stability. The monomer α,β,β -trifluorostyrene was first synthesized by Cohen¹ in 1949 and was successfully converted to high molecular weight polymer by Prober,² who described several conversion difficulties encountered. Livingston³ evaluated copolymerizations of α,β,β -trifluorostyrene with styrene and chlorotrifluoroethylene.

This note presents data on the preparations, polymerizability, and copolymerizability of substituted α,β,β -trifluorostyrenes.

Dixon⁴ synthesized α,β,β -trifluorostyrene by reacting phenyl lithium and tetrafluoroethylene, thus discovering a general reaction between organolithiums and fluorinated olefins. We used the Dixon method to prepare the fluorostyrenes listed in Table I. These monomers were then subjected to variable catalysis and medium experiments to determine their polymerizabilities (for both homo- and copolymers). Table II is a summary of the homopolymerizations attempted. Polymers having an intrinsic viscosity of 0.5 dl./g. or higher (measured in benzene at 30°C.) were sought, and those not meeting this requirement are listed as low molecular weight materials.

By heat-induced persulfate decomposition in an emulsions system using 100 g. monomer, 11.69 dodecylamine hydrochloride, 0.44 g. potassium persulfate, all in 600 ml. of distilled water, attempts were made to copolymerize α,β,β -trifluorostyrene with the following monomers: β -chloro- α,β -difluorostyrene, 1-phenylperfluoropropylene, 2-methyl- α,β,β -trifluorostyrene. In each case, only the homopolymer of α,β,β -trifluorostyrene was found, regardless of the ratios of comonomers.

On the other hand, copolymerization of an equimolar mixture of 4-methyl- α,β,β -trifluorostyrene and α,β,β -trifluorostyrene yielded a random copolymer in 80% conversion. No attempt was made to determine reactivity ratios for this copolymerization.

It appears from the results shown that steric hindrance, exerted by groups on or near the substituted vinyl side chain, is the primary factor influencing the ring- and side-chain-substituted fluorostyrenes. The conversion of substituted perfluoro alkyl styrenes to macromolecules by emulsion polymerization is directly related to the size of substituent groups on both the vinyl chain and the ring. For instance, although styrene and α,β,β -trifluorostyrene homopolymerize readily by emulsion techniques, the substitution of even one chloro group for a fluoro group in the β position renders the monomer inactive to free-radical polymerization. Only unreacted monomer was recovered after attempted emulsion polymerizations using this monomer with the larger chloro substituent on the vinyl group.

Also, attempts to bulk polymerize the above monomers by free-radical initiation again showed that the monomers exhibited marked differences in reactivity, α,β,β -trifluorostyrene was converted principally (60–70%) to its dimer (1,3-diphenylperfluorocyclobutane). Dimerization also occurred during attempts to bulk polymerize 4-methyl- α,β,β -trifluorostyrene or 4-fluoro- α,β,β -trifluorostyrene. In contrast, attempted bulk polymerizations of 2-methyl- α,β,β -trifluorostyrene, 1-phenylperfluoropropylene, or

TABLE I
The Boiling Points and Yields of Substituted α,β,β -Trifluorostyrenes Prepared by the Direct Reaction of Substituted Phenyl Lithium Compounds and Fluoroethylene Monomers⁴






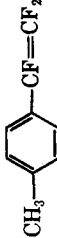
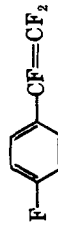
Monomer	Structure	B.p., °C.	% Yield
1. α,β,β -Trifluorostyrene		69/69 mm.	20
2. β -Chloro- α,β -difluorostyrene		77-80/28 mm.	78
3. α,β -Difluorostyrene		87-89/60 mm.	Prepared from 2 by dehydrogenation and dehydrohalogenation
4. 1-Phenyl perfluoropropylene		62-64/31 mm.	
5. 2-Methyl- α,β,β -trifluorostyrene		60/26.5 mm.	33
6. 4-Methyl- α,β,β -trifluorostyrene		84-86/65 mm.	17
7. 4-Fluoro- α,β,β -trifluorostyrene		47-48/28 mm.	9

TABLE II
The Polymerizability Under Various Conditions of Catalysis for Substituted α,β,β -Trifluorostyrenes

Monomer	Catalyst and reaction conditions	Yield of polymer obtained, %	Intrinsic viscosity of polymer in benzene at 30°C., $[\eta]$, dl./g.	Remarks
α,β,β -Trifluorostyrene	100 g. monomer, 11.6 g. dodecylamine 0.44 g. potassium persulfate, 600 ml. distilled water. temp. = $55 \pm 1^\circ\text{C}$.	82	0.80	
β -Chloro- α,β -difluorostyrene	"	None	—	Monomer recovered
1-Phenyl perfluoropropylene	"	None	—	"
2-Methyl- α,β,β -trifluorostyrene	"	None	—	"
4-Methyl- α,β,β -trifluorostyrene	"	75	0.94	"
4-Fluoro- α,β,β -trifluorostyrene	"	77	1.03	"
α,β,β -Trichlorostyrene	"	None	—	"
α,β,β -Trifluorostyrene	100 g. monomer, 11.6 g. dodecylamine hydrochloride, 0.44 g. potassium persulfate, 0.15 g. potassium hydro- sulfite, 600 ml. distilled water temp. = $27 \pm 1.0^\circ\text{C}$.	69	1.35	
3-Chloro- α,β -difluorostyrene	"	None	—	
1-Phenyl perfluoropropylene	"	None	—	

(continued)

TABLE II (continued)

Monomer	Catalyst and reaction conditions	Yield of polymer obtained, %	Intrinsic viscosity of polymer in benzene at 30°C., $[\eta]$, dl./g.	Remarks
4-Methyl- α,β,β -trifluorostyrene	100 g. monomer, 11.6 g. dodecylamine hydrochloride, 0.44 g. potassium persulfate, 0.15 g. potassium hydro-sulfite, 600 ml. distilled water temp. = $27 \pm 1.0^\circ\text{C}$.	78	Not characterized	
4-Fluoro- α,β,β -trifluorostyrene	"	59	Not characterized	
α,β,β -Trichlorostyrene	"	None	—	
α,β,β -Trifluorostyrene	Bulk polymerization 100 g. monomer 0.075 g. benzoyl peroxide or 0.075 g. azobisisobutyronitrile temp. = $60 \pm 1.0^\circ\text{C}$.	None	—	Nearly quantitative conversion to 1,3-diphenyl perfluorocyclobutane (dimer)
4-Methyl- α,β,β -trifluorostyrene	"	"	—	Nearly quantitative conversion to 1,3-di-4-methyl phenyl perfluorocyclobutan (dimer)
4-Fluoro- α,β,β -trifluorostyrene	"	"	—	Nearly quantitative conversion to 1,3-di-4-fluoro phenyl perfluorocyclobutane
β -Chloro- α,β -difluorostyrene	Bulk polymerization: 100 g. monomer, 0.075 g. benzoyl peroxide or 0.075 g. azobisisobutyronitrile temp. = $60 \pm 1.0^\circ\text{C}$.	None	—	Monomer recovered
α,β -Difluorostyrene	"	"	—	"

1-Phenyl perfluoropropylene	"	—	"
2-Methyl- α,β,β -trifluorostyrene	"	—	"
α,β,β -Trichlorostyrene	"	—	"
α,β -Difluorostyrene	17	0.09	Low MW gummy polymer
α,β,β -Trifluorostyrene	None	—	
4-Methyl- α,β,β -trifluorostyrene	"	—	
4-Fluoro- α,β,β -trifluorostyrene	"	—	
β -Chloro- α,β -difluorostyrene	"	—	
1-Phenyl perfluoropropylene	"	—	
2-Methyl- α,β,β -trifluorostyrene	None	—	
α,β,β -Trichlorostyrene	"	—	
α,β,β -Trifluorostyrene	"	—	

Bulk polymerization: 100 g. monomer,
 0.10 g. boron trifluoride ether complex
 temp. = $27 \pm 1^\circ\text{C}$.

Bulk polymerization 100 g. monomer
 0.075 g. benzoyl peroxide or
 0.075 g. azobisisobutyronitrile
 temp. = $60 \pm 1.0^\circ\text{C}$.

Anionic catalysts sodium naphthenate
 or sodium 0.1 g. in 100 g. monomer
 temp. $27-60 \pm 1.0^\circ\text{C}$.

(continued)

TABLE II (continued)

Monomer	Catalyst and Reaction conditions	Yield of polymer obtained, %	Intrinsic viscosity of polymer in benzene at 30°C., $[\eta]$, dl./g.	Remarks
4-Fluoro- α,β,β -trifluorostyrene	"	"	—	
β -Chloro- α,β -difluorostyrene	"	"	—	
α,β -Difluorostyrene	"	"	—	
1-Phenyl perfluoropropylene	"	"	—	
2-Methyl- α,β,β -trifluorostyrene	"	"	—	
α,β,β -Trichlorostyrene	"	"	—	
α,β,β -Trifluorostyrene	Light at 3600 Å.; temp. = $30 \pm 0.1^\circ\text{C}$. time = 88 hr.	None	—	
4-Methyl- α,β,β -trifluorostyrene	"	"	—	
4-Fluoro- α,β,β -trifluorostyrene	"	"	—	
β -Chloro- α,β -difluorostyrene	"	"	—	
α,β -Difluorostyrene	"	"	—	
1-Phenyl perfluoropropylene	"	"	—	
2-Methyl- α,β,β -trifluorostyrene	"	"	—	
α,β,β -Trichlorostyrene	"	"	—	
α,β -Difluorostyrene	Heat ranging between 50 – 100°C . time = 48 hr.	8	Not characterized but <0.05	Sticky solid obtained
α,β,β -Trifluorostyrene	"	None	—	
4-Methyl- α,β,β -trifluorostyrene	"	"	—	
4-Fluoro- α,β,β -trifluorostyrene	"	"	—	
β -Chloro- α,β -difluorostyrene	Heating ranging between 50 – 100°C . time = 48 hr.	None	—	
1-Phenyl perfluoropropylene	"	"	—	
2-Methyl- α,β,β -trifluorostyrene	"	"	—	
α,β,β -Trichlorostyrene	"	"	—	

α,β,β -trichlorostyrene yielded only unreacted monomer. Table II is a summary of these reactions.

Clearly, α,β,β -trifluorostyrene is a monomer which is close to being nonpolymerizable because of steric hindrance, having just enough spacial volume to add monomer and form a high molecular weight linear polymer in a free-radical emulsion system. The substitution of Cl, CF₃, and presumably any other bulky group larger than H or F on the vinyl group totally inhibits free-radical polymerization in emulsion systems. Such large substituents also prevent dimerization in attempted bulk polymerization by free-radical initiators. The presence of a bulky group on the aromatic ring ortho to the perfluorovinyl group also inhibits emulsion free-radical polymerization as well as bulk free-radical dimerization. However, the same bulky group, when substituted on the aromatic ring in the position para to the perfluorovinyl group, does not interfere with either free-radical emulsion polymerization or free-radical bulk dimerization.

The conversion of substituted perfluorovinylbenzenes to high molecular weight polymers (emulsion system) or dimers (bulk system) is extremely sensitive to steric effects.

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RUSSELL B. HODGDON, JR.
DAVID I. MACDONALD

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General Electric Company
West Lynn, Massachusetts

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