

The Stability of Fluorine-Containing Polymers to Amines

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INTRODUCTION

Previous work has shown that perfluorocarbon liquids containing small amounts of hydrogen-bearing fluorocarbon impurities, can be purified by treating the liquid mixtures with amines.¹ In the present study, a number of fluorine-containing polymers and copolymers have been heated in the presence of *n*-butyl amine and large differences in reactivity have been observed.

EXPERIMENTAL

Amine Treatment

The amines were distilled at atmospheric pressure through a 2-foot spinning-band column, and 60-ml. portions were placed in 100-ml. round-bottomed flasks fitted with a condenser and nitrogen inlet. One-inch-square strips of film from the polymers or copolymers were dropped into the amine at reflux temperatures and the time required for embrittlement of the polymer was noted. The samples that reacted also became black during this treatment. These simple, but significant, observations gave an effective measure of the reactivity of the various polymers to these reagents.

Preparation of Polymers

The polymers and copolymers examined in this study were film strips from either commercial polymers or polymers prepared by procedures described in the published literature. These comprised the following: polyethylene, Alathon-10 polyethylene resin as sold by E. I. du Pont de Nemours & Co.; poly(vinyl fluoride) synthesized by procedures described in U. S. Patent 2,510,783, F. L. Johnson and D. C. Pease to E. I. du Pont de Nemours & Co.; poly(vinylidene fluoride) synthesized by procedures described in U. S. Patent 2,435,537, T. A. Ford and W. E. Hanford to E. I. du Pont de Nemours & Co.; polytrifluoroethylene synthesized by procedures described in U. S. Patent 2,409,274, W. E. Hanford and G. W. Rigby to E. I. du Pont de Nemours & Co.; polytetrafluoroethylene skived tape fabricated from Teflon TFE-fluorocarbon resin as sold by E. I. du Pont de Nemours & Co.; tetrafluoroethylene hexafluoropropylene copolymer, Teflon FEP-fluorocarbon resin as sold by E. I. du Pont de Nemours & Co.; poly-1,1,2-trifluorobutadiene as described in Wright Air Development Center Report #19, Contract AF 33 (038)-515 ED Number 602-192;

TABLE I
Stability of Hydrofluorocarbon Polymers to *n*-Butylamine (78°C.)

Polymer	Structural formula	Time required for embrittlement
Polyethylene	$-(\text{CH}_2-\text{CH}_2)_n-$	stable (test stopped at 24 hr.)
Poly(vinyl fluoride)	$-(\text{CH}_2-\text{CHF})_n-$	stable (test stopped at 24 hr.)
Poly(vinylidene fluoride)	$-(\text{CH}_2-\text{CF}_2)_n-$	4 hr. (black)
Polytrifluoroethylene	$-(\text{CHF}-\text{CF}_2)_n-$	10 min. (black)
Polytetrafluoroethylene	$-(\text{CF}_2-\text{CF}_2)_n-$	stable (test stopped at 24 hr.)
Hexafluoropropylene/tetrafluoroethylene copolymer	$\left[\begin{array}{c} \text{CF}_3 \\ \\ \text{CF}-\text{CF}_2(\text{CF}_2-\text{CF}_2)_m \end{array} \right]_n$	stable (test stopped at 24 hr.)
Poly-1,1,2-trifluorobutadiene	$-(\text{CF}_2-\text{CF}=\text{CH}-\text{CH}_2)_n-$	10-15 min. (black)
Tetrafluoroethylene/ethylene ^a	$-(\text{CF}_2-\text{CF}_2)_n-(\text{CH}_2-\text{CH}_2)_m-$	24 hr. (dark brown)
Tetrafluoroethylene/vinylidene fluoride copolymer ^a	$-(\text{CF}_2-\text{CF}_2)_n-(\text{CH}_2-\text{CF})_m-$	3 hr. (black)

^a Random copolymers.

tetrafluoroethylene/ethylene copolymer, 1/1, synthesized by procedures described in U. S. Patent 2,468,664, W. E. Hanford and J. R. Roland, Jr. to E. I. du Pont de Nemours & Co.; and tetrafluoroethylene/vinylidene fluoride copolymer, 1/1, also synthesized by procedures described in U. S. Patent 2,468,664.

Results

The time required for complete embrittlement (excessive degradation) of the various polymers and copolymers under the conditions of the amine treatment is presented in Table I.

To determine the effect of amine basicity on the relative reactivity toward hydrofluorocarbon polymers, a second series was studied, poly(vinylidene fluoride) being used as the "standard" polymer with amines of varying base strengths. The results, which show the decrease in reactivity with decreasing basicity of the amine, are presented in Table II.

TABLE II
Relation of Amine Basicity to Reactivity toward Poly(vinylidene Fluoride)^a

Amine	Color	Time required for embrittlement, hr. ^b
<i>n</i> -Butylamine	black	4
<i>n</i> -Dibutylamine	dark brown-black	19
<i>n</i> -Tributylamine	yellow-tan	>19
Pyridine	white	>20
Aniline	white	>20

^a All experiments conducted at 78°C.

^b Test stopped at time designated.

DISCUSSION

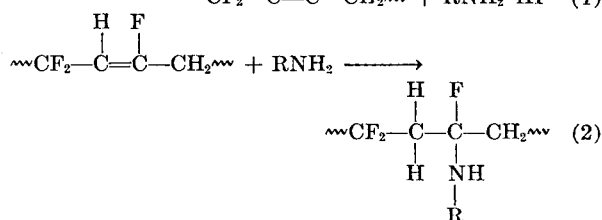
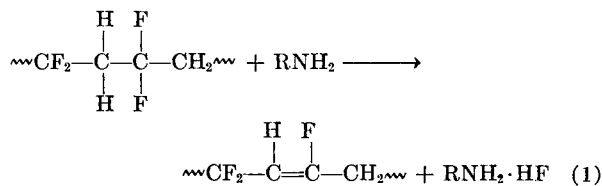
In Table I we see that polyethylene is unreactive toward *n*-butylamine. Moreover, poly(vinyl fluoride) is unaffected under the conditions of the experiment. In polymers of increasing fluorine content, i.e., poly(vinylidene fluoride) and polytrifluoroethylene, we see a progressive increase in reactivity toward this reagent. (These polymers are predominantly of the head-to-tail type according to Haszeldine.²) The completely fluorinated polymers, polytetrafluoroethylene and the copolymer of tetrafluoroethylene with hexafluoropropylene, are completely inert toward this reagent.

As the hydrogen atoms are replaced by fluorine in these polymers, those hydrogen atoms remaining become increasingly electrophilic in nature. The

fluorine atoms have a strong electron-withdrawing power, leaving the carbon to which they are attached in an electron-deficient state. This decrease in electron density about the carbon is compensated, in part, by a shift of the electrons away from the hydrogen, increasing the proton character of this atom.

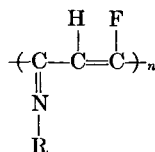
The increased reactivity toward amines increases directly with increasing amounts of fluorine in the series described so far and explains, to some degree, the unreactivity of the hydrocarbon and perfluorocarbon polymers. This becomes even more apparent when one considers the relation of position and proximity of fluorine to hydrogen in reactivity toward amines. Thus, a 1:1 (mole basis) random copolymer of tetrafluoroethylene and ethylene, which may be considered a head-to-head type poly(vinylidene fluoride), is much less reactive toward amines than is poly(vinylidene fluoride), yet their elemental analyses are identical. In this case, we see that the carbon bearing hydrogen is adjacent to only one carbon carrying fluorine and thus is less electrophilic in character. The increased reactivity of the tetrafluoroethylene/vinylidene fluoride copolymer over poly(vinylidene fluoride), suggests that this effect may extend beyond the nearest neighbors. Polytrifluoroethylene appears to be swollen somewhat by amines. This may also contribute to its unusually high reactivity.

The embrittlement of the polymers and the accompanying change in coloration suggest that a complex sequence of reactions occurs. While additional experiments are required to elucidate the mechanism in detail, it appears that the first step involves the removal of HF *via* an E₂-type elimination, with formation of an unsaturated link and a molecule of amine hydrofluoride. This is followed by the addition of a second amine molecule to the double bond formed.

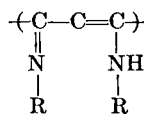


The reaction sequence presented above cannot, however, account for the appearance of color or the embrittlement in the presence of monoamines. Coloration is not restricted to the systems studied here, but occurs when perfluoroolefins (terminal or internal) or perfluorodimethylcyclohexane (containing hydrogen-bearing fluorocarbon impurities) are treated with excess amine.

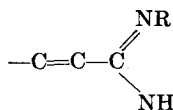
The coloration suggests conjugated unsaturation and possible carbonization, while embrittlement indicates that degradation or extensive cross-linking occurs. In the presence of excess amine, the product from reaction (2) probably reacts further, yielding more unsaturated linkages by a mechanism similar to that of reaction (1). More amine adds to the double bonds so formed and this process is repeated until a highly unsaturated system is obtained. Conjugated imino structures of the type



or



may be formed. Aminolysis of compounds of this type would be expected to result in chain cleavage to produce amidines



This degradative reaction would produce low molecular weight polymer.

The product from reaction (2) is a secondary amine and may also add to the double bond formed on another portion of the chain or on neighboring chains. Such crosslinking reactions would produce considerable stiffening in the polymer films.

In the case of the 1,1,2-trifluorobutadiene polymer (believed to be of the 1,4 type) the first reaction probably involves the addition of the amine to the double bond as shown in step (2).

Additional experiments which will elucidate further the nature of these reactions are contemplated. Low molecular weight hydrofluorocarbon compounds of known structure will be allowed to react with controlled amounts of amine and the products isolated and identified.

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References

1. U.S. Patent 2,738,371, H. M. Parmelee assignor to E. I. du Pont de Nemours & Co.
2. R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, **1957**, 2800.

Synopsis

The reactivity of hydrofluorocarbon polymers toward organic amines increases, generally, with increasing fluorine content and with increasing basicity of the amine. The position of fluorine in the molecule with respect to hydrogen strongly affects the electrophilic character of the hydrogen atom. A discussion of the effects of neighboring groups on this reactivity is presented.

Résumé

La réactivité des polymères hydrofluorocarbonés vis à vis des amines organiques s'accroît généralement lorsque le taux en fluor et la basicité de l'amine augmentent. La position du fluor dans la molécule par rapport à l'hydrogène affecte fortement le caractère électrophile de l'atome d'hydrogène et on discute l'influence des groupes voisins sur cette réactivité.

Zusammenfassung

Die Reaktionsfähigkeit von Fluorkohlenwasserstoffpolymeren gegen organische Amine nimmt im allgemeinen mit zunehmendem Fluorgehalt und mit zunehmender Basizität des Amins zu. Der elektrophile Charakter des Wasserstoffatoms wird durch die Stellung des Fluors in Molekül stark beeinflusst. Eine Diskussion des Einflusses von Nachbargruppen auf die Reaktionsfähigkeit wird durchgeführt.

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