

**THERMALLY STABLE PERFLUOROALKYL SUBSTITUTED POLYMERS**

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**INTRODUCTION**

The perfluoroalkyl-substituted sym. triazine molecule has been shown to have exceptional stability to high temperatures and strong oxidizing agents. The formation of this ring structure from the condensation of perfluoroalkyl amidines and some of its characteristics have been described<sup>1,2</sup>. The incorporation of the perfluoroalkyl-substituted triazine group into a polymer structure was reported at the previous conference and has been described in the literature<sup>3</sup>. Condensation polymerization of a difunctional perfluoroalkylamidine produced hard, infusible, insoluble products that were obviously completely cross linked. Copolymerization of perfluoroadipamide or perfluoroglutarimide with perfluorobutyramide produced elastomeric gums, presumably with the structure shown in Fig. 1, where the values of x and y depend on the

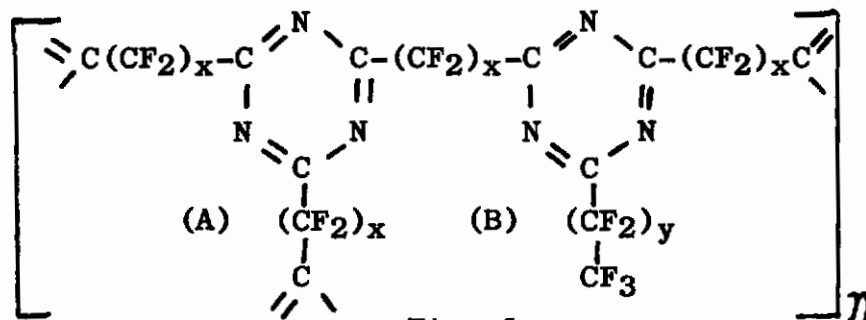


Fig. 1

particular diamidide or monoamidide used, and the groups at (A) and (B) may be continuing or terminal, depending on the monomer which reacted at this point. These polymerizations were carried out with melts or solutions of the two solid monomers.

The structure shown in Fig. 1 is randomly crosslinked, and, by the method of preparation used, this crosslinking apparently cannot be prevented. Obviously, to attain the maximum desired physical properties, a completely linear structure in which (A) and (B) were always terminal would be desirable in the original product, though subsequent partial crosslinking might be used for modification.

This report describes work carried out on the perfluoroalkyl-triazine polymer system since the last conference. Three areas of research are described: (1) the mechanism of triazine ring

formation in this system; (2) the preparation of intermediate or prepolymer; (3) catalytic trimerization and polymerization of perfluoroalkylnitriles. All areas have as their objective the attainment of a more complete understanding of this polymer system.

**MECHANISM OF FORMATION OF THE TRIAZINE RING FROM CONDENSATION OF PERFLUOROALKYLAMIDINES.**

A simple picture of the overall reaction to produce tris-(perfluoroalkyl)sym. triazines is shown in Fig. 2.

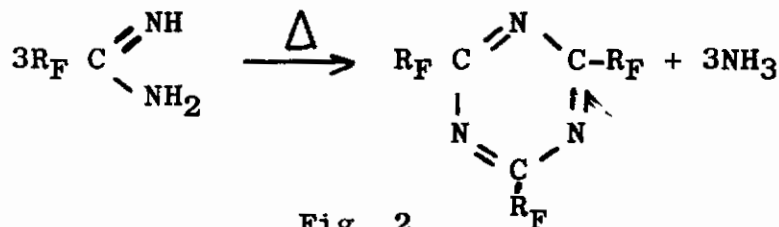


Fig. 2

Here three moles of a perfluoroalkylamidine condense upon heating to form the tris-perfluoroalkyl sym. triazine with the evolution of ammonia.

The first approach to the problem of the mechanism of this reaction was to obtain kinetic data by determining the rate of evolution of ammonia when a solution of the perfluoroalkylamidines in toluene was heated at 100°C. Since a termolecular reaction seemed quite improbable, an assumption was made that the initial step was the reaction of two molecules of amidine to produce one molecule of ammonia and a condensation product represented by the tautomeric structures shown as A + B in Fig. 3.

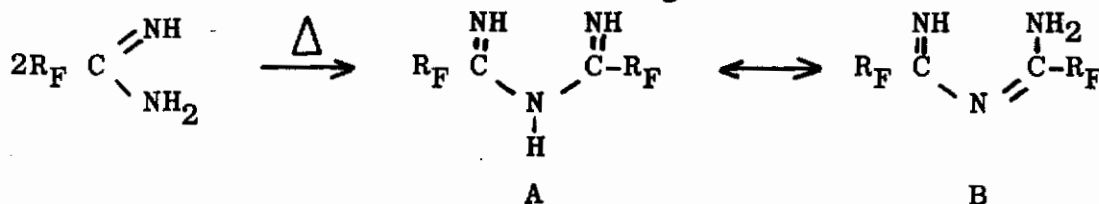


Fig. 3

Graphing of the rate data obtained definitely indicated a bimolecular or second order reaction for the initial stages of the deammonation. A fairly uniform value for the reaction rate constant was obtained during this initial stage and it was assumed that the intermediate shown was being formed.

If we examine the structure of this intermediate, particularly the form shown as B, it is obvious that there is a possibility of chelate formation with metal ions. The solutions used in the rate

studies were, therefore, treated with a solution with cupric acetate and a stable, water-insoluble chelate was isolated.

For the purposes of determining the overall mechanism of triazine formation from the perfluoroalkylamidines, it was obviously necessary to learn something of the intermediate products formed and their properties. Although isolation of this intermediate, which we have termed an N'(perfluoroacylimino)perfluoroalkylamidine, is possible from the deamination solutions of the original amidine, the procedure is difficult and cumbersome. It was, therefore, desirable that this intermediate be synthesized directly and this was done as shown in Fig. 4.

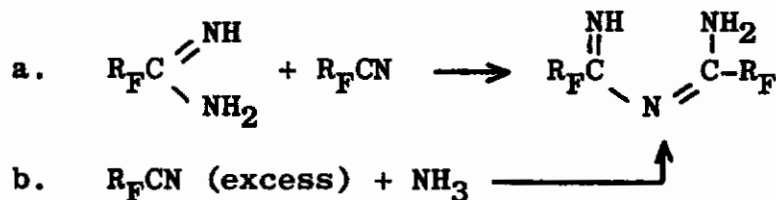


Fig. 4

In reaction (a), a perfluoroalkylamidine is simply reacted with an excess of perfluoroalkylnitrile at a relatively low temperature and the resulting N'(perfluoroacylimino)perfluoroalkylamidine is formed in good yield. The reaction can be carried out even more simply by reacting an excess of the nitrile with the desired amount of ammonia as shown in reaction (b). Reaction (a), of course, offers the opportunity of placing unlike perfluoroalkyl groups in the structure.

In Table 1 are shown some of the properties of the N'(perfluoroacylimino)perfluoroalkylamidines prepared to date.

TABLE 1

N' (PERFLUOROACYLIMINO)PERFLUOROALKYLAMIDINES

$$\begin{array}{c}
 \text{NH} \quad \text{NH}_2 \\
 \parallel \quad | \\
 \text{R}_F\text{-C-N=C-R}'_F
 \end{array}$$

$\text{R}_F$	$\text{R}'_F$	BP, °C	MP, °C	$d^{25}$	$N_D^{25}$	Nitrogen	
						calc.	found
$\text{CF}_3$	$\text{CF}_3$		38-42 <sup>a</sup>			20.28	19.16
$\text{C}_2\text{F}_5$	$\text{C}_2\text{F}_5$	35.9-36.1 (6.8 mm)		1.6128	1.3438	13.67	13.41

TABLE 1 (continued)

$C_3F_7$	$C_3F_7$	44.3-44.7 (1.5 mm)	1.6854	1.3386	10.31	10.05
$CF_3$	$C_3F_7$	50.0-50.8 (13.0 mm)	1.6521	1.3508	13.67	13.51
$C_2F_5$	$C_3F_7$	39.2-40.0 (3.8 mm)	1.6561	1.3398	11.76	11.38

$C_7F_{15}$      $C_3F_7$     b

a            Decomposes at room temperature

b            Viscous liquid, isolated as its copper II chelate

If both of the perfluoroalkyl groups were  $CF_3$ , a low melting solid was obtained which was not stable for any length of time at room temperature. If these groups were  $C_2F_5$  or  $C_3F_7$ , liquids were obtained which, surprisingly enough, can be distilled without appreciable decomposition. The last three compounds do not have identical perfluoroalkyl groups. Their properties are in line with what we might expect. The last compound, in which one of the perfluoroalkyl groups is  $C_7F_{15}$ , was a viscous liquid and could not be distilled. It was actually isolated and purified as a copper chelate.

Fig. 5 shows the formation of the copper chelate of a (perfluoroacylimino)perfluoroalkylamidine.

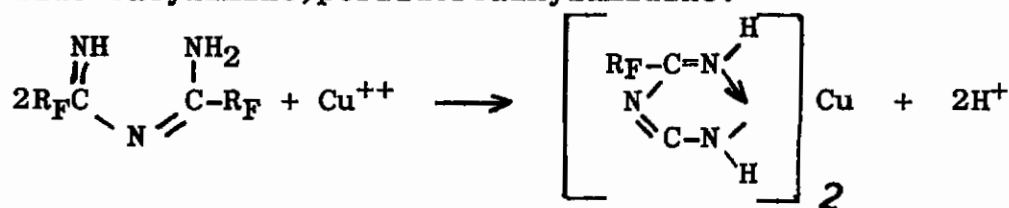


Fig. 5

The structure of the chelates shows one covalent copper-nitrogen bond, one coordinate covalent copper-nitrogen bond and the equation shows the production of hydrogen ion on chelate formation. This is a true picture and the course of this chelate formation can be followed by the determination of the hydrogen ion concentration of the solution.

The absorption spectra of the metal chelates in the visible region was determined as a method of characterization. The copper and nickel chelates are colored where the mercury and zinc chelates are not.

The absorption spectra in the ultra-violet region is of

considerably more interest in helping to understand the structure of the chelate and of the ligand itself. In Fig. 6 the structure of the metal chelate is shown at (B), and the log of the molar extinc-

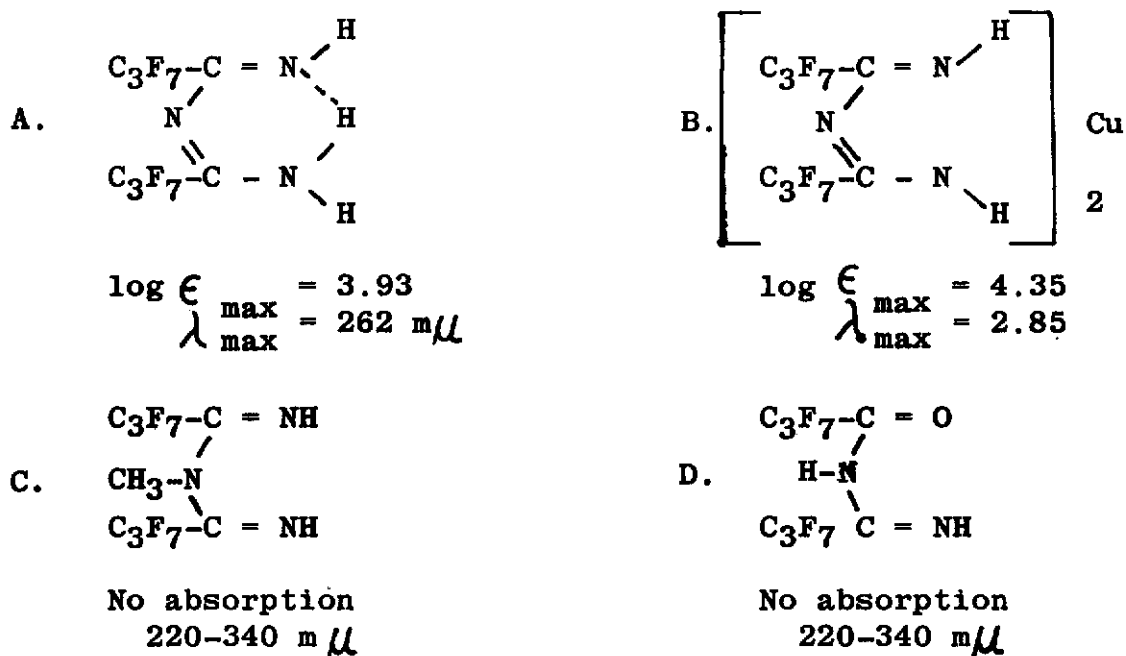


Fig. 6

tion coefficient shown as 4.35 at a maximum wave length of 285 m $\mu$ . Obviously, the absorption in this region cannot be attributed simply to the two conjugated C=N bonds. The C=N bond is reported to absorb in the region of 190 m $\mu$  with a log molar extinction coefficient of about 3.7. Conjugation might shift this absorption maxima towards the red by about 30 m $\mu$  but certainly not to the extent shown by the results obtained. The picture, therefore, of the structure of the chelate indicates considerable delocalization of the  $\pi$  electrons from the carbon-nitrogen double bond, but probably not a completely conjugated ring structure since this would involve an unlikely contribution to the bond formation from the metal atom. The ring must have some aromatic character.

Subsequent to the determination of the ultra-violet absorption spectra of the metal chelates, the ultra-violet spectra of the ligand itself, the (perfluorobutyrimino)perfluorobutyramidine, (A) was determined and somewhat unexpectedly showed a fairly intense absorption maxima with the  $\log \epsilon = 3.93$  at 262 m $\mu$ . Resonance structures might be proposed for the ligand to account for absorption in this region and this, of course, brings up the question of the position of the hydrogen atom which is involved in the hydrogen bonding as shown. It seems likely at present that this is one of the rare incidences where the hydrogen is actually equi-distant



between the two nitrogen atoms, although this is not usually the case in hydrogen bonding.

The compound shown at (C) is N'(perfluorobutyrimino)N-methyl perfluorobutyramidine and at (D) is N'(perfluorobutyryl)perfluorobutyramidine. Neither of these compounds showed absorption in the ultra-violet region between 220 and 340 m $\mu$ . Compound (C) was prepared by the reaction of a perfluorobutyronitrile on N-methyl perfluorobutyramidine. The attack of the nitrile on the N-methyl amidine was obviously on the amino nitrogen and resulted in the CH<sub>3</sub> group being attached to the central nitrogen atom. An alternative attack on the imino nitrogen would have resulted in an NHCH<sub>3</sub> group being formed and this structure should have shown the characteristic ultra-violet absorption spectra of the unsubstituted compound and also the chelate formation. No chelate formation was observed when compound (C) was treated with metallic ions.

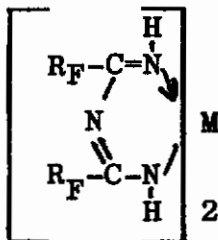
Compound (D) could be produced either by hydrolysis of the N'(perfluoroacylimino)perfluoroalkylamidine or by acylation of a perfluoroalkylamidine with the appropriate anhydride. The structure shown has been selected rather than the tautomeric form in which an OH group would be present on the basis of its infrared spectra which shows a strong absorption for C=O and also on the basis of the inability of this compound to form a metal chelate.

Typical metal chelates that have been formed from the N'(perfluoroacylimino)perfluoroalkylamidine are shown in Table 2.

TABLE 2

N' (PERFLUOROACYLIMINO)PERFLUOROALKYLAMIDINE

Metal Chelates



R <sub>F</sub>	Metal	MP, °C	Analysis			
			Metal calc.	Metal found	Nitrogen calc.	Nitrogen found
CF <sub>3</sub>	Cu	223 dec.	13.35	13.19	17.67	17.52
C <sub>2</sub> F <sub>5</sub>	Cu	134-135	9.40	9.34	12.43	12.02

TABLE 2 (continued)

C <sub>3</sub> F <sub>7</sub>	Cu	148.5-149.5	7.26	7.21	9.58	9.67
C <sub>3</sub> F <sub>7</sub>	Zn	108.5-108.8	7.41	7.31	9.58	9.39
C <sub>3</sub> F <sub>7</sub>	Ni	152-153	6.77	6.66	9.64	9.52
C <sub>3</sub> F <sub>7</sub>	Hg	126-127	19.93	20.39	8.30	8.53

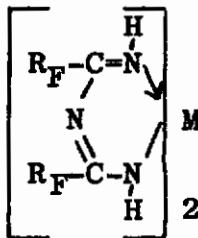
These are all solid compounds that are not wetted by water but are soluble in a variety of organic solvents.

Electronic Spectra

Table 3 shows the ultra-violet and visible spectra of representative chelates.

TABLE 3

ULTRA-VIOLET AND VISIBLE SPECTRA OF REPRESENTATIVE CHELATES



Ligand, R <sub>F</sub>	Metal	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$
CF <sub>3</sub>	Cu	500	1.69	394	1.87	282	4.13
C <sub>2</sub> F <sub>5</sub>	Cu	485	1.65	400	1.85	285	4.00
C <sub>3</sub> F <sub>7</sub>	Cu	490	1.69	405	1.89	285	4.35
C <sub>3</sub> F <sub>7</sub>	Zn	---	---	---	---	290	4.18
C <sub>3</sub> F <sub>7</sub>	Ni	492	1.72	241	4.37	305	3.75
C <sub>3</sub> F <sub>7</sub>	Hg	---	---	---	---	289	3.83
C <sub>3</sub> F <sub>7</sub>	H	---	---	---	---	262	3.93

Spectroscopic data were determined on methanol solutions of the

metal chelates and ligand using a Beckman DK-2 recording spectrophotometer. It can be seen that there are two absorption maxima in the visible region for the copper chelates in the region of 500 m $\mu$  and 400 m $\mu$  and that the log of the molar extinction coefficients at this maximum range from 1.65 to 1.9. The ultra-violet absorption maxima for the copper chelates in the region of 280 to 285 m $\mu$  show much higher extinction coefficients with log  $\epsilon$  values of around 4. The nickel chelates are of approximately the same color and, therefore, show absorption in the visible about the same region as the copper chelates. In the ultra-violet region, however, the two absorption maxima for Ni chelates at 241 m $\mu$  and 305 m $\mu$  again are much more intense than those in the visible region. The mercury and zinc chelates as mentioned before are colorless, but absorb in the ultra-violet region of about 290 m $\mu$  with a fairly high extinction coefficient. In the last line is shown the ultra-violet absorption maxima for the ligand at 262 m $\mu$  with the log  $\epsilon_{\max}$  3.93. for comparison.

#### Infra-Red Absorption Spectra

A considerable effort has been made to establish assignments in the infra-red region for the various N-H and C-N structural features found in the compounds that are pertinent to the objectives of this research. As an aid in establishing these assignments, infra-red spectral data was obtained on several representative compounds and their deuterated analogs in which deuterium has been exchanged for hydrogen. Preparation of the deuterated compounds made use of ammonia-d<sub>3</sub> which was synthesized by the reaction of magnesium nitride with deuterium oxide.

Table 4 shows the infra-red absorptions spectra assignments made to date in the 2.5-7.4 $\mu$  region. Absorption bands at higher wave lengths are not generally useful in this series of compounds since the carbon-fluorine absorption frequencies obscure the other bands which would be of interest. With the exception of those spectra indicated by footnotes, all of these spectra were obtained by observation of the sample in a mull in Kel F Polymer Oil.

A shift to lower vibration frequencies would be expected upon exchanging deuterium for hydrogen in an NH group.

According to Hooke's Law:

$$\nu = \left( \frac{1}{2\pi C} \right) \left( \frac{K}{\mu} \right)^{1/2}$$

in which  $\nu$  = frequency in cm.<sup>-1</sup>, C = velocity of light, K = force constant of the bond, and  $\mu$  = reduced mass.



For the bond X-H,

$$\mu = \frac{M_X M_H}{M_X + M_H} \quad \text{where } M = \text{atomic weight}$$

The force constants of X-H and X-D are not significantly different, but the reduced mass changes greatly when D is substituted for H. Therefore the approximate shifts to be expected upon deuteration of an X-H bond may be calculated by:

$$\frac{\nu_{X-D}}{\nu_{X-H}} = \left( \frac{\frac{K_1}{\mu_D}}{\frac{K_2}{\mu_H}} \right)^{1/2} = \left( \frac{\mu_H}{\mu_D} \right)^{1/2} \quad (\text{since } K_1 = K_2)$$

$$\frac{\nu_{X-D}}{\nu_{X-H}} = \left( \frac{\frac{M_X M_H}{M_X + M_H}}{\frac{M_X M_D}{M_X + M_D}} \right)^{1/2} = \left( \frac{(M_X)^2 + 2M_X}{2(M_X)^2 + 2M_X} \right)^{1/2} = \left( \frac{M_X + 2}{2M_X + 2} \right)^{1/2}$$

For X = Nitrogen

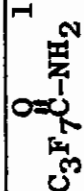

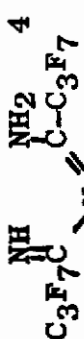
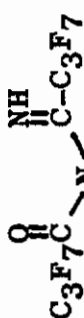
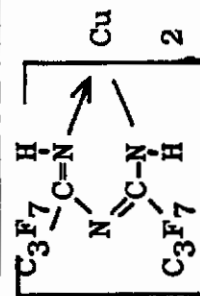
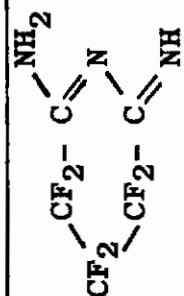
$$\frac{\nu_{N-D}}{\nu_{N-H}} = \left( \frac{16}{30} \right)^{1/2} = \sqrt{.534} = 0.732$$

The frequency shifts found for the N-H to N-D stretching absorption are shown in Table 5. The shifts obtained agree in general with the values that would be expected.

The N-H stretching frequencies of the compounds listed in Table 4 fall within a rather narrow range; the ND stretching frequencies are somewhat more spread but are fairly consistent.

Deuteration of an NH group should cause a similar shift in the deformation frequency to that described above for the stretching absorption. Since this shift would place the absorption maxima at wave lengths greater than  $7.4 \mu$  (in which region it would be obscured by other absorption of the fluorocarbon molecule), we would not expect to see the ND deformation maximum. The net result, of course, would be the disappearance of a maximum observed in the NH compound upon deuteration. In the compounds observed, with the exception of perfluorobutyramide, there were no strong and distinct absorption bands which could be assigned to NH deformation. In perfluorobutyramide, a band at  $6.15 \mu$  (distinct and of medium strength) disappeared completely upon deuteration. In N' (perfluorobutyrimino)-

TABLE 4  
INFRA RED ABSORPTION SPECTRA ASSIGNMENTS IN THE 2.5-7.4  $\mu$  REGION (IN  $\mu$ )

Compound	NH			ND		
	asym. str.	sym. str.	assoc.	asym. str.	sym. str.	assoc.
	2.82(m) (3546)	3.03(m) (3300)		4.00(m) (2500)	4.30(m) (2326)	
	2.86(m) (3497)	3.05(m) (3279)		3.85 to 4.01(m) <sup>2</sup> (2545)	4.20(m) (2370)	
	2.86(m) (3497)	3.00(w) (3333)	3.20(w-b) (3125)	3.87(m) (2584)	4.07(m) (2457)	4.24(w) (2358)
	2.99(s)		3.31(m) (?)	---	---	---
	2.93(w) (3413)			4.00(w) (2500)		
	2.89(m) <sup>3</sup> (3460)	3.12(m) (3205)		3.95(m) (2532)		4.25(m) (2353)

(1) Nujol Mull (2) triplet (3) shoulder (4) liquid state

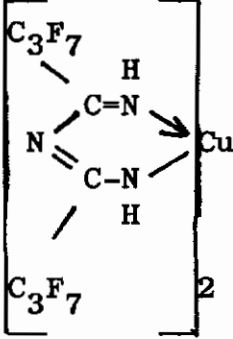
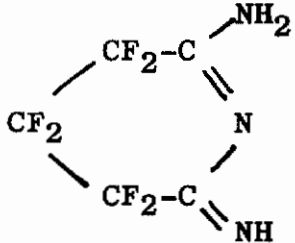
TABLE 4 (cont.)  
 INFRA RED ABSORPTION SPECTRA ASSIGNMENTS IN THE 2.5-7.4μ REGION (IN μ)

Compound	$\begin{matrix}   \\ \text{C=N str.} \\ \text{-C=NH} \end{matrix}$	$\begin{matrix}   \\ \text{C=N str.} \\ \text{-C=N-} \end{matrix}$	$\begin{matrix}   \\ \text{C=N str.} \\ \text{-C=N-} \end{matrix}$	N-H def.	N-D def.	Unas- signed
$\begin{matrix} \text{O} \\    \\ \text{C}_3\text{F}_7\text{C-NH}_2 \end{matrix}$	$\begin{matrix} \text{C=O} \\ 5.85(\text{s}) \end{matrix}$	$\begin{matrix} \text{C=O} \\ 6.02(\text{s}) \end{matrix}$	$\begin{matrix} \text{C=O} \\ 6.02(\text{s}) \end{matrix}$	6.15(m)	$\lambda > 7.4\mu$	$\begin{matrix} 7.00(\text{m}) \\ \text{for (d)} \\ 6.70(\text{w}) \\ 7.00(\text{m}) \end{matrix}$
$\begin{matrix} \text{NH} \\    \\ \text{C}_3\text{F}_7\text{C-NH}_2 \end{matrix}$	$\begin{matrix} 5.71(\text{m})^3 \\ 5.97(\text{s}) \\ 6.10(\text{m})^3 \end{matrix}$	$\begin{matrix} 5.75(\text{w})^3 \\ 6.02(\text{s}) \\ 6.20(\text{w})^3 \end{matrix}$				$\begin{matrix} 6.90 \\ \text{for (d)} \\ 7.00 \end{matrix}$
$\begin{matrix} \text{NH} \\    \\ \text{C}_3\text{F}_7\text{C} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{C-C}_3\text{F}_7 \end{matrix}$	$\begin{matrix} 6.13(\text{s}) \\ 6.30(\text{s}) \\ \text{(conj.)} \end{matrix}$	$\begin{matrix} 6.17(\text{s}) \\ 6.36(\text{s}) \\ \text{(conj.)} \end{matrix}$	$\begin{matrix} 6.60(\text{w}) \\ 6.60(\text{w}) \\ \text{(conj.)} \end{matrix}$	$\lambda > 7.4\mu$		$\begin{matrix} 6.80 \\ 7.00 \\ \text{for (d)} \\ 6.80 \\ 7.00 \end{matrix}$
$\begin{matrix} \text{NH} \\    \\ \text{C}_3\text{F}_7\text{C} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{C-C}_3\text{F}_7 \end{matrix}$	$\begin{matrix} \text{C=O} \\ 5.82(\text{s}) \\ 6.02(\text{s}) \end{matrix}$					
$\begin{matrix} \text{H} \\   \\ \text{C=N} \\   \\ \text{N} \\   \\ \text{C-N} \\   \\ \text{H} \end{matrix}$	$\begin{matrix} 6.25(\text{s}) \\ 6.45(\text{s}) \\ \text{(conj.)} \end{matrix}$	$\begin{matrix} 6.29(\text{s}) \\ 6.47(\text{s}) \\ \text{(conj.)} \end{matrix}$	$\begin{matrix} 6.54(\text{m})^3 \\ 6.54(\text{m})^3 \\ \text{(conj.)} \end{matrix}$	$\lambda > 7.4\mu$		$\begin{matrix} 6.70 \\ 6.95 \\ \text{for (d)} \\ 6.90 \end{matrix}$
$\begin{matrix} \text{NH}_2 \\   \\ \text{C} \\ / \quad \backslash \\ \text{N} \quad \text{N} \\   \quad   \\ \text{H} \quad \text{H} \end{matrix}$	$\begin{matrix} 6.10(\text{m}) \\ 6.30(\text{s}) \\ \text{(conj.)} \end{matrix}$	$\begin{matrix} 6.10(\text{m})^3 \\ 6.30(\text{s}) \\ \text{(conj.)} \end{matrix}$				$\begin{matrix} 5.87 \\ \text{(N-H)} \\ \text{def. ?} \end{matrix}$

(1) Nujol Mull (2) triplet (3) shoulder (4) liquid state

TABLE 5

FREQUENCY SHIFTS ON DEUTERATION OF N-H BONDS

Compound	Frequency Shift, $\frac{\nu_{\text{cm}^{-1}} \text{N-D}}{\nu_{\text{cm}^{-1}} \text{N-H}}$		
	<u>asym. str.</u>	<u>sym. str.</u>	<u>assoc.</u>
$\text{C}_3\text{F}_7\text{C}(=\text{O})\text{NH}_2$	.705	.705	
$\text{C}_3\text{F}_7\text{C}(=\text{NH})\text{NH}_2$	.728	.724	
$\text{C}_3\text{F}_7\text{C}(=\text{NH})\text{N}(\text{C}_3\text{F}_7)\text{C}(=\text{NH}_2)\text{C}_3\text{F}_7$	.739	.744	.753
		.732	
	.732	.733	

perfluorobutyramidine, a weak band appeared at  $6.60\mu$  which was not apparent in the deuterated structure. The copper chelate of this compound exhibited an absorption maxima of  $6.54\mu$  as a shoulder that disappeared on deuteration. A somewhat puzzling absorption at  $5.87$  microns in the spectra of perfluoroglutarimidine disappeared upon deuteration. The assignment of this maxima to NH deformation, however, does not agree with the assignment made from our previous work with the N(methyl) substituted perfluoroglutaramidines.

Assignments for C=N stretching are divided into those attributed to C=NH and to C=N-; all of those in the latter category are conjugated double bonds. The assignments for C=N are consistent when the variation in structures of the compounds recorded are taken into account. In all cases the C=N in a conjugated chain absorbed at lower frequencies. The exchange of deuterium for hydrogen has very little effect on the C=N stretching frequency as is shown by the data in the table.

During the preparation of the mulls of the compounds listed in Table 4 for determination of their infra-red spectra the following observations were made on the rate of exchange of hydrogen for deuterium when the compounds were exposed to atmospheric moisture:

- (a) perfluorobutyramidine-detectable exchange in 24 hrs.
- (b) perfluoroglutarimidine-detectable exchange in 15 min.
- (c) N(perfluorobutyrimino) perfluorobutyramidine Cu II chelate-no exchange in 24 hrs.
- (d) N(perfluorobutyrimino)perfluorobutyramidine-considerable exchange in 2 min.

## PERFLUOROALKYL-TRIAZINE POLYMERS

The structure of the perfluoroalkyl-triazine polymer shown in Fig. 1 indicates a considerable degree of crosslinking. Since a linear structure would be desirable in terms of improved physical properties, efforts to produce a polymer in which all groups at (A) and (B) were terminal were made by reacting perfluoroglutaronitrile with perfluorobutyramidine to produce a prepolymer with subsequent cyclization along the chain to form triazine rings. An idealized picture of this reaction is shown in Fig. 7. In this reaction, the primary amino group of the perfluorobutyramidine adds to the nitrile of perfluoroglutaronitrile with a subsequent tautomeric shift to give III.

The primary amino group of this structure then adds to another molecule of perfluoroglutaronitrile to continue chain formation, IV; such a linear polymer could then form the triazine ring in the chain by deamination.

The first experiments were carried out in benzene by adding a dilute solution of perfluorobutyramidine to a solution of perfluoroglutaronitrile. Samples were taken periodically from this reaction



# Contrails

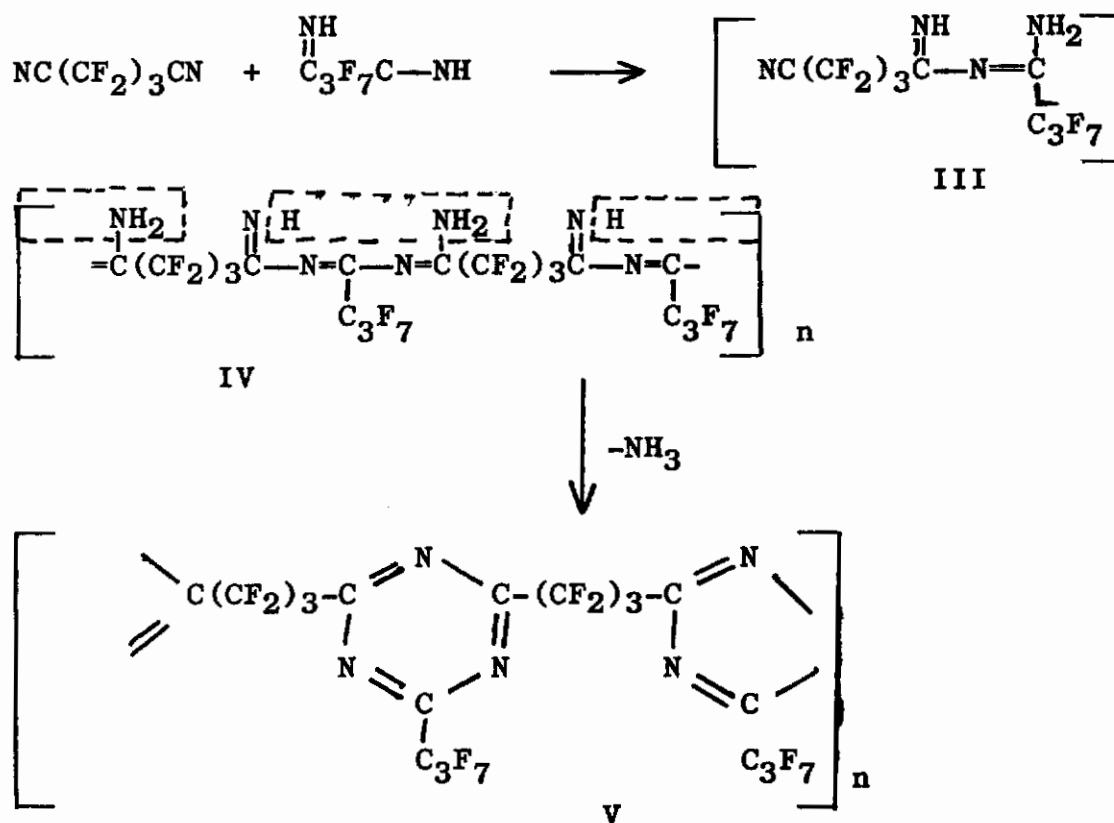


Fig. 7

mixture and the infrared spectra examined. Disappearance of the C=N absorption band at  $4.3 - 4.4\mu$  was followed easily as the reaction took place.

Evaporation of the solvent from a portion of this reaction solution produced a tacky, fusible material which has been termed the intermediate polymer. Subsequent heating of the intermediate polymer at  $150^\circ$  for 2 1/2 days and at  $300^\circ$  for several hours produced an amber, thin, homogenous sheet which was elastic and had appreciable tensile strength.

Toluene was chosen as a solvent for subsequent prepolymer preparations with the thought that the higher boiling point of this solvent would favor complete reaction in a shorter time. A few examples of these prepolymers and their subsequent treatment are described below.

Polymer No. 39 was prepared in toluene with no attempt at protection from the effects of atmospheric oxygen or moisture. The reaction solution was not refluxed but, after stirring briefly, was distilled until about 85% of the solvent was removed. The remainder of the solvent was removed under reduced pressure and the intermediate polymer was then placed in an oven at  $150^\circ$  for 4 hours,  $200^\circ$

# Contrails

for 15 hours, and 250° for 6 hours. The final product obtained was a thin, soft, flexible, somewhat elastic sheet that was a clear, light amber color. A portion of this polymer was heated further at 400° for 48 hours with very little change other than a slight darkening in color.

Polymer No. 343 was prepared from perfluoroglutaronitrile and perfluorobutyramidine in toluene and after removal of the solvent the intermediate polymer was divided and used for a variety of subsequent treatments. The intermediate polymer No. 343 was a clear, pale yellow-green, very viscous and very tacky material.

A portion of No. 343 (designated No. 343.2) was heated in an oven at 150° for 3 hours and at 200° for 16 hours. The product from this treatment was a light amber sheet, containing some large bubbles, that was elastic and very slightly tacky.

A portion of the polymer sheet No. 343.2 was heated at 375° for 24 hours with no physical change except a darkening to a clear amber color.

Other portions of Polymer No. 343.2 were reacted with perfluoroglutaronitrile by sealing the polymer sample and various percentages of perfluoroglutaronitrile in previously evacuated tubes and heating the tubes at 250° for 16 hours. The amounts of perfluoroglutaronitrile employed in this procedure ranged from over 200% to 10% by weight of the polymer. In each case, all of the perfluoroglutaronitrile was reacted with the polymer. The high percentages produced a very brittle but very hard product, with properties for the lower percentages ranging down to the 10% sample which was somewhat stiffer than the original polymer but was not broken by repeated flexing. These polymer samples after reaction with perfluoroglutaronitrile were heated at 375° for 24 hours with no further physical change except a slight darkening of color.

A small amount of the intermediate polymer No. 343 was placed in a 4" test tube and heated in an oven at increasing temperatures up to a maximum of 170°. When it was apparent that the intermediate polymer was beginning to gel, a glass plunger was forced into the tube to compress the gel and prevent bubble formation. The compressed product was then heated for 1 hour at 170° and cooled to room temperature. The test tube was broken, the pellet removed and placed in an oven at 200° for 1 hour at 250° for 12 hours. There was no deformation or bubble formation in the polymer pellet after this heat treatment and it is evident from this procedure that molding of the intermediate polymer after a suitable heating cycle would be possible.

The infrared spectra of polymer No. 343.2 was typical. There was strong absorption at 5.7 $\mu$ , probably due to the C=O group, and at 6.45 $\mu$  due to C=N stretching in the triazine rings. The treatments of this polymer with 40% by weight of perfluoroglutaronitrile

produced no appreciable change in the spectra. The dinitrile evidently reacted completely with the NH or NH<sub>2</sub> groups in the polymer, since there were no evidence of the C≡N in the spectra. All of the samples heated at 375-400° showed quite similar infrared spectra with absorption at 6.45 μ, which is characteristic of a triazine ring.

#### Intermediate Polymer Preparation in Sealed Tubes

From a series of experiments in which preparation of the intermediate polymer was carried out simply by sealing the required quantities of perfluoroglutaronitrile and perfluorobutyramidine in a previously evacuated glass tube and allowing the reaction between the two to take place as the tube warmed, it appeared that this might be a more desirable method of preparation of the intermediate polymer than that described above with the use of solvents. The work to date in this area has not included a detailed study of the properties of the intermediate polymer, such as molecular weight determination, but has dealt principally with the characteristics of the products obtained by oven heating procedures.

Polymer No. 47a was prepared by sealing equimolar quantities of perfluoroglutaronitrile and perfluorobutyramidine in a tube, warming the tube to room temperature and allowing the exothermic reaction to take place. This intermediate polymer was a clear yellow-green liquid that was not viscous immediately following the initial reaction but on standing at room temperature became very viscous after approximately 1 hour and finally set to a hard resin. Subsequent heating of this intermediate polymer, after removal from the reaction tube, at 150° for 2 hours and at 200° for 2 hours produced a clear, water-white elastic, non-tacky sheet with scattered bubble formation. A small portion of this polymer product was heated at 375° for 24 hours and retained all of its previous characteristics with the exception of a slight darkening in color.

A qualitative examination of the product produced by the procedure described above indicates that the final polymer is quite similar to those produced in the best runs made in solvents.

Polymer No. 47b was a repeat of No. 47a with the exception that the sealed tube was heated to 150° for 30 minutes before opening. This procedure produced a marked change in the appearance of the intermediate polymer, which became an opaque white, and subsequent oven heating of the intermediate polymer did not produce a gel but rather a stiff, tacky gum which was partially fusible. Heating this material at 375° caused foaming and the formation of a cellular product.

Small portions of No. 47b were reacted with additional perfluoroglutaronitrile as previously described, and upon this treatment, became infusible and considerably harder.



Polymer No. 348 was prepared in approximately the same manner as No. 47a but with somewhat more extensive investigation of the effect of various treatments on the intermediate polymer.

A portion of No. 348 (designated 348a) was heated in an oven at 100° for 1 hour, 150° for 3 hours, and 200° for 12 hours. The final product from this treatment was an elastic, leathery sheet, containing some bubbles, and very pale amber in color. No. 348a was heated at 375° for 24 hours with no change in physical characteristics. Further reaction of No. 348a with 10% by weight of perfluoroglutaronitrile produced a product that was somewhat stiffer but not brittle. This nitrile treated product appeared to be completely stable when heated at 375° for 24 hours.

The infrared spectra of the polymers obtained in this experiment show all of the characteristic peaks found in the spectra of similar polymers prepared originally in solvents. For example, No. 348a showed a very weak absorption in the NH stretching region (2.6-3.0  $\mu$ ), a strong absorption peak at 5.75 $\mu$  and another strong absorption peak at 6.48 $\mu$ . After heating at 375° the NH stretching absorption had disappeared and there was no significant peak at 5.75  $\mu$ . The characteristic triazine absorption peak at 6.45 $\mu$  remains.

## Determination of the Volatile Products from Controlled Heating of the Intermediate or Pre-Polymer

Since it was quite evident from the work described above on the intermediate or pre-polymers produced from perfluoroglutaronitrile and perfluorobutyramidine that further knowledge was needed concerning the subsequent heat treatment of these products, a detailed study was started in this area with the objective of determining a suitable heating schedule for the pre-polymer in which the loss of the fluorocarbon monomers would be at a minimum and in which the deammonation would be carried to its maximum with a minimum amount of gel formation in the polymer. The pre-polymer product was prepared by reacting equal molar quantities of perfluorobutyramidine and perfluoroglutaronitrile in an evacuated tube at temperatures below 0°. The intermediate product was then held at 0° for 2 - 3 days before the heating schedule was begun. The pre-polymer product was then heated in a glass tube and the volatile products swept out with a constant flow of nitrogen which passed through a trap to collect sublimed solids or high boiling liquids, then through tubes containing a chemical reagent to combine with the evolved ammonia, and finally through a liquid air trap to condense perfluoroalkylnitriles.

In a typical run, No. 20, the first trap was cooled to -30° to trap the higher boiling liquids or sublimed solids. This particular temperature, slightly above the boiling point of ammonia, was chosen in the hope that no ammonia would condense. Liquid ammonia has been found to react rapidly with perfluoroalkylnitriles but

ammonia in the gas phase is very slow to react.

Table 6 shows the evolution of ammonia during the various stages of heating in Run No. 20.

TABLE 6  
EVOLUTION OF AMMONIA IN RUN NO. 20

<u>Temp., °C. (furnace)</u>	<u>Total NH<sub>3</sub> Collected, g.</u>	<u>Total NH<sub>3</sub> Collected, g. (at °C.)</u>	<u>Time of Collection, hrs.</u>	<u>Rate of Evolution g./hr</u>
100	.0027	---	1.5	.0018
100	none	.0027 (100)	2.0	---
125	.0096	---	1.0	.0096
125	.1182	---	2.0	.0591
125	.0272	---	1.3	.0204
125	.0187	.1737 (125)	1.17	.0160
150	.0167	---	0.5	.0334
150	.0775	---	1.0	.0775
150	.0419	---	1.0	.0419
150	.0136	.1497 (150)	0.5	.0272

Total NH<sub>3</sub> .3261

It is apparent from these data that deammonation is not appreciable until a temperature of 100° is reached.

Table 7 shows the various volatile compounds collected during the heating schedule of Run No. 20. In Run No. 20 the combined nitrile portion from the liquid air trap apparently contained about 23% perfluorobutyronitrile and 77% perfluoroglutaronitrile. Thus the weight of perfluoroglutaronitrile (0.0305 g.) represents only 0.61% of the dinitrile originally charged to the reaction tube. The loss of perfluorobutyramidine, however, was high, both at 125° and at 150°. The solid amidine and the C<sub>3</sub>F<sub>7</sub> substituted triazine collected in the -30° trap represent, of course, loss of the original perfluorobutyramidine. If one assumes that the materials trapped



at  $-30^{\circ}$  from the  $125^{\circ}$  heating are 50% perfluorobutyramidine and 50%  $C_3F_7$  substituted triazine and that the material from the  $150^{\circ}$  heating is 50%  $C_3F_7$  substituted triazine, one can calculate that 0.918 g. of perfluorobutyramidine has been lost. This represents 17.5% of the original charge.

TABLE 7  
VOLATILE MATERIALS COLLECTED IN RUN NO. 20

<u>Source of Recovered Volatile Material</u>	<u>Furnace Temp., <math>^{\circ}C.</math></u>	<u>Wgt. of Collected Fraction, g.</u>	<u>Identification</u>
AlCl <sub>3</sub> trap	100	0.0027	NH <sub>3</sub>
AlCl <sub>3</sub> trap	125	0.1737	NH <sub>3</sub>
AlCl <sub>3</sub> trap	150	0.1497	NH <sub>3</sub>
$-30^{\circ}$ trap	100	0.0357	Unidentified liquid.
$-30^{\circ}$ trap	125	0.6526	$C_3F_7C(NH)NH_2$ and $(C_3F_7CN)_3$ <sup>1</sup>
	150	0.4349	$(C_3F_7CN)_3$ + unidentified liquid.
Liquid Air trap	100	0.0347	$(CF_2)_3(CN)_2$ , $C_3F_7CN$ and unidentified liquid.

<sup>1</sup>This mixture appears to be about 50%  $C_3F_7C(NH)NH_2$

A member of subsequent runs established the fact that gelation of the polymer occurred when 45-55% of the ammonia had been liberated from the perfluoroglutaronitrile-perfluorobutyramidine system. Heating the prepolymer in a sealed tube to  $150^{\circ}$ - $165^{\circ}$  with subsequent removal of ammonia produced a fusible product but intrinsic viscosity measurements indicated a very low molecular weight.

The perfluorocaprylamidine-perfluoroglutaronitrile polymer system was investigated in order to study the effect of lengthening of the perfluoroalkyl chain of the monoamidine on this type of polymerization reaction and also to provide a monoamidine that was less

volatile than those previously used in order to minimize sublimation of the starting materials. The reaction of perfluorocaprylamidine with perfluoroglutaronitrile was slower than that of perfluorobutyramidine; the prepolymer prepared from the C<sub>8</sub> amidine required three hours to gel when heated at 150° while that formed from the C<sub>4</sub> amidine gelled in approximately seventy five minutes. The total weight losses, representing in large part sublimed solids, were also significantly lower in runs made employing the C<sub>8</sub> amidine; the total loss was less than 6%. Another apparent advantage of this system is the fact that the polymer does not reach a gel point until approximately 83-85% of the total contained ammonia has been evolved. This should be an advantage in future fabrication of the polymer.

Table 8 shows the volatile products produced from a typical run (No. 50). At the gel point (after heating 1.5 hours at 150°), 84.7% of the ammonia had been liberated and at the end of the run 90.3% of ammonia was evolved.

TABLE 8  
VOLATILE PRODUCTS FROM RUN NO. 50

<u>Temp., °C.</u> <u>Time, hrs.</u>	<u>Source of Collected Material</u>	<u>Wgt. g.</u>	<u>Identification</u>
Room Temp.	AlCl <sub>3</sub> trap	0.0039	NH <sub>3</sub> (Mol. Wgt. 139)
	Liq. Air Trap	0.0323	
100/2.0	AlCl <sub>3</sub> trap	0.0005	NH <sub>3</sub> HCl <sup>1</sup>
	Liq. Air Trap	0.0144	
125/2.5	AlCl <sub>3</sub> trap	0.0845	NH <sub>3</sub> (Mol. Wgt. 19.5) <sup>1</sup> HCl
	-30° Trap	0.0069	
	Liq. Air Trap	0.0211	
150/2.0	AlCl <sub>3</sub> trap	0.0988	NH <sub>3</sub> (Mol. Wgt. 16) <sup>1</sup> HCl
	-30° Trap	0.0052	
	Liq. Air Trap	0.0128	
Sublimed solids (entire run)		<u>.1618</u>	
Total volatile		<u>.4422</u>	

Total NH<sub>3</sub>- 0.1877 g. (90.3% of NH<sub>3</sub> present in starting materials)  
Total wgt. loss of prepolymer 0.4428 g.

1. The material collected in the  $-30^{\circ}$  trap was not identified. There is a possibility, however, that it was HF since the  $C_7F_{15}$  group of the  $C_8$  amidine is not a solely straight chain and some HF may be formed by decomposition in this reaction environment. If this happens, then sweeping of a portion of the HF through the  $AlCl_3$  trap would account for the HCl formed in the liquid air trap.

The perfluoroacetamide-perfluoroglutaronitrile system was investigated in the hope that the increased reactivity of perfluoroacetamide (as compared with perfluorobutyramide) would more than offset its increased volatility, and make possible the preparation of copolymers with lower weight losses than were encountered with the  $C_4$  monoamide.

The reaction of perfluoroacetamide with perfluoroglutaronitrile was difficult to control. At a temperature  $-45^{\circ}$  the reaction apparently does not take place; upon warming to  $-40^{\circ}$  the reaction is virtually complete and about 25 seconds. Stirring the reaction mixture to obtain an homogeneous product is not possible.

A further difference in the activity of perfluoroacetamide as compared to perfluorobutyramide was evident in the time required for gelation of the prepolymer. The perfluoroacetamide product required approximately forty minutes at  $150^{\circ}$  while the average time for the perfluorobutyramide product was around seventy five minutes at this same temperature. This more rapid gelation may be due in part to the tendency for the perfluoroacetamide group to react with itself to form the volatile N-(perfluoroacetimino) perfluoroacetamide and tris(trifluoromethyl) sym. triazine which are then removed from the reaction zone. This, of course, requires that the original prepolymer product chain be broken; an examination of the volatile products produced and of the final polymers indicates that this is probably taking place. All of the final polymers were amber colored and brittle, resembling more the homopolymers of perfluoroglutaronitrile than previously described copolymers.

## CATALYTIC TRIMERIZATION AND POLYMERIZATION OF PERFLUOROALKYLNITRILES

In the course of our study of the perfluoroalkyltriazine polymer system, the question arose as to whether a small amount of ammonia could function as a catalyst for the trimerization of perfluoroalkylnitriles or the polymerization of the dinitriles to give final products of the same type as those obtained by heating the ammonia addition products.

A study was begun, therefore to determine the effect of catalytic amounts (0.1-10.0 mole% of ammonia on the various perfluoro-

alkylnitriles at elevated temperatures; this study was later extended to other weakly basic or nucleophilic catalysts (with preferential selection of volatile compounds since the conditions chosen indicated a gas phase reaction) in order to gain more information concerning the variables influencing the rate and direction of the reaction.

The results of the work on the mononitriles, particularly the indication of the formation of an activated complex, led to the extension of this type of reaction to the cotrimerization of perfluoroalkylnitriles with aromatic nitriles. Further extension involved the homopolymerization of perfluoroglutaronitrile and the copolymerization of perfluoroglutaronitrile with perfluorobutyronitriles.

Catalytic Trimerization of Perfluoroalkylnitriles

Perfluoroacetonitrile was trimerized at 300° in the presence of 10 mole % or less of weakly basic compounds, or compounds capable of functioning as nucleophiles, to give 2,4,6-tris(trifluoromethyl)-triazine. The reactions were carried out under uniform conditions so that a comparison could be made between the efficiencies of the various catalysts; no attempt was made to find conditions of maximum yield for a given catalyst. The results of these experiments are shown in Table 9.

TABLE 9

TRIMERIZATION OF  $CF_3CN$  WITH VARIOUS CATALYSTS

(300°C./24 hrs.)

<u>Catalyst</u>	<u>Mole %</u>	<u>Yield, 2,4,6, <u>tris</u>(trifluoromethyl)-1,3,5-triazine, %</u>
Ammonia	1	9
	10	85
Triethylamine	1	6
	10	45
p-Toluidine	1	4
	10	55
Diethyl ether	10	trace
Water	10	63

TABLE 9 (continued)

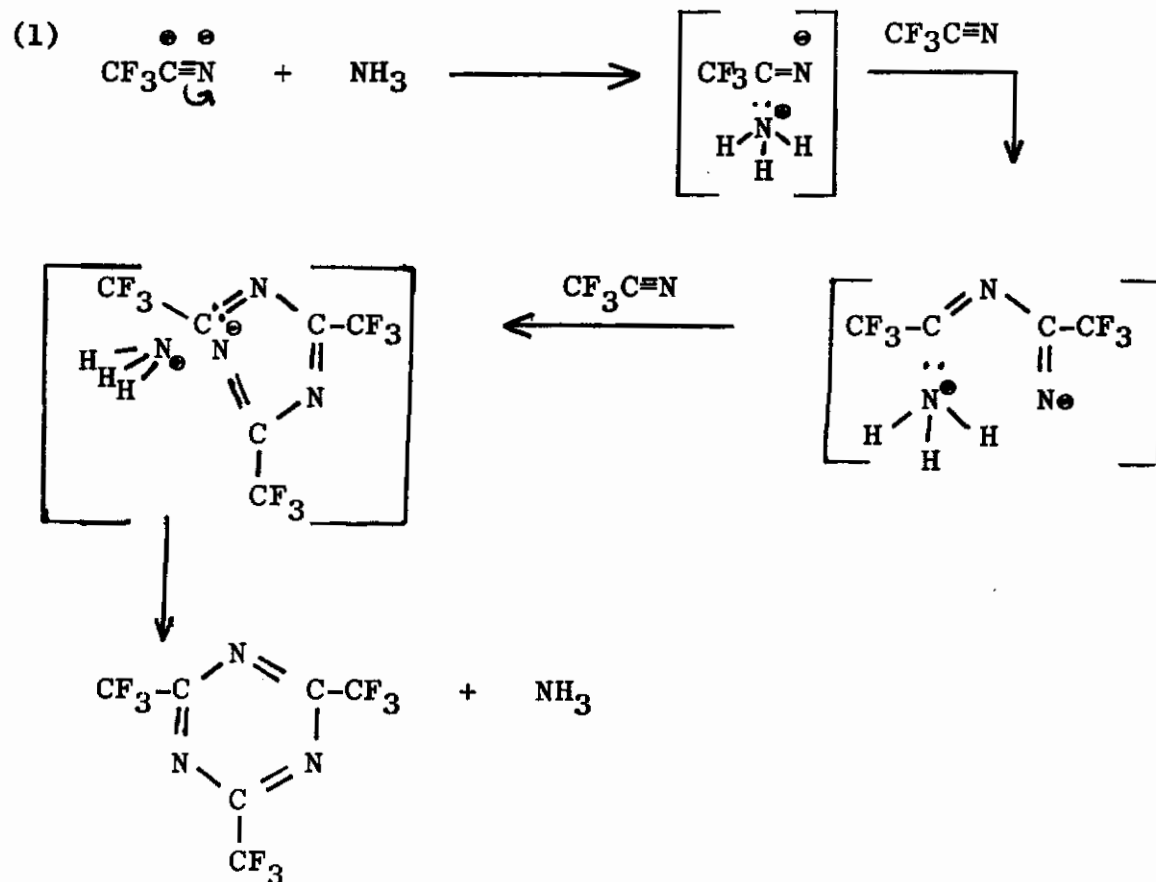
Perfluoroacetamide

1  
10

4  
65

Ammonia also was found to be an excellent catalyst for the conversion of perfluoropropionitrile and perfluorobutyronitrile to the corresponding s-triazines.

A mechanism for reaction under these conditions has been considered; two possibilities present themselves as shown in (1) and (2) of Fig. 8.





# Contrails

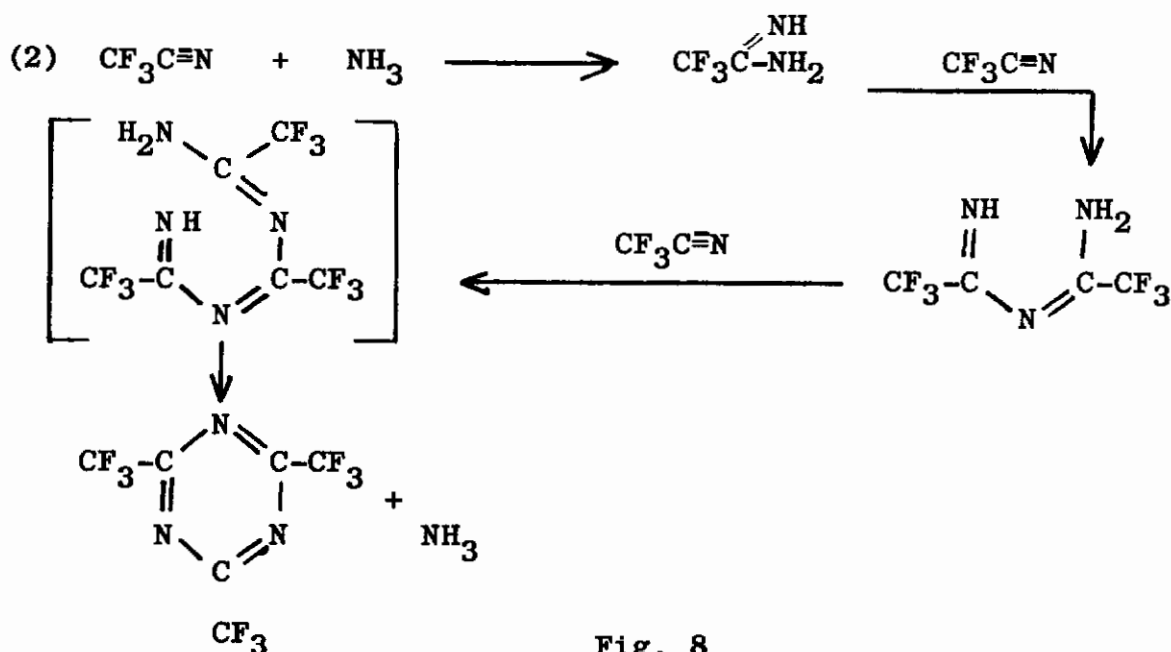


Fig. 8

A mechanism similar to that shown in (2) has been previously discussed by Schaefer *et al*<sup>4</sup> to explain triazine formation from heating amidines; our initial work on the N'(perfluoroacylimino)-perfluoroalkylamidines led toward a similar conclusion. However, the trimerizations in the present work occurred in the gas phase at a high temperature and neither the perfluoroalkyl amidines nor the N'(perfluoroacylimino)perfluoroalkylamidines are stable under these conditions. In addition, this reaction was catalyzed by trimethylamine, where formation of addition products as shown in (2) is not possible.

We therefore propose the mechanism shown in (1), wherein a nucleophilic attack by ammonia, trimethylamine, water or other nucleophile results in the formation of an activated complex; this complex then reacts with another molecule of nitrile to give an activated dimer, then a trimer. At this stage cyclization occurs to give the resonance-stabilized triazine ring with release of the nucleophile.

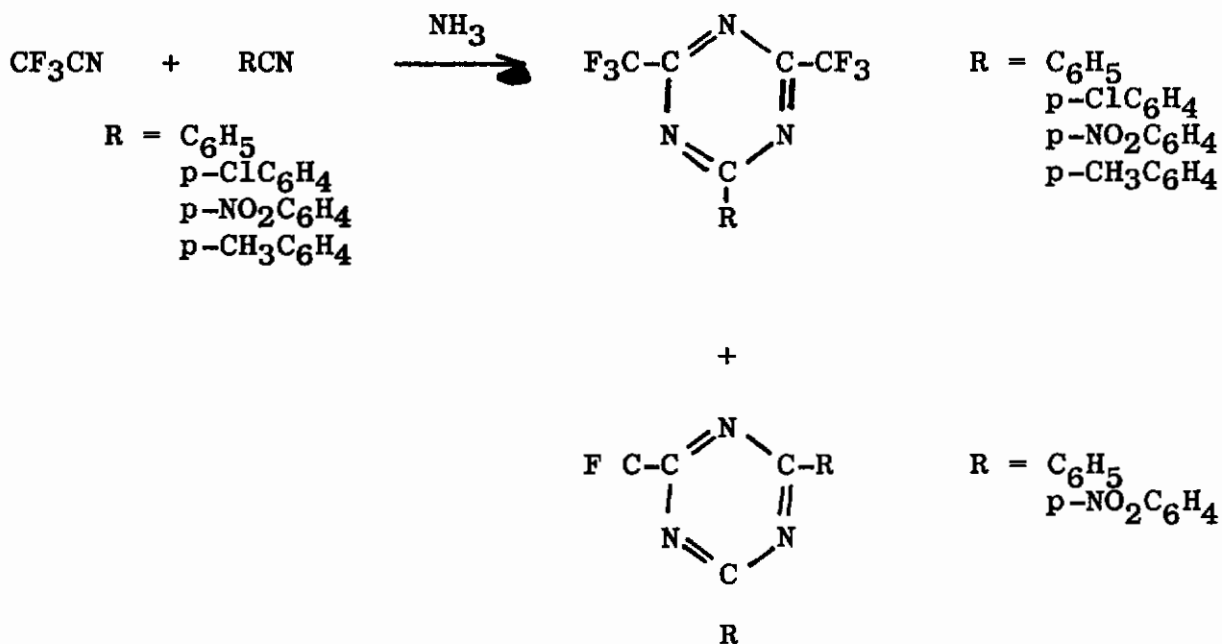
The highest yield of tris(perfluoroalkyl)-s-triazine was obtained with ammonia; triethylamine, a slightly stronger base, gave lower yields, as did p-toluidine, with some decomposition. Steric effects possibly prevented these amines from functioning as effectively as ammonia.

Ethyl ether was an ineffective catalyst and must be considered a poor nucleophile under these conditions. Water was quite effective; perfluoroacetamide, which must be a considerably weaker nucleophile than water, probably is unstable at 300° and the actual catalyst in this experiment was water.

Nitriles containing no fluorine, for example, acetonitrile and benzonitrile, were not trimerized by this procedure.

## Catalytic Cotrimerization of Perfluoroacetonitrile with Aromatic Nitriles

Perfluoroacetonitrile was found to cotrimerize with several aromatic nitriles in sealed Pyrex tubes at 300° in the presence of 1-5 mole % ammonia.



Yields of the s-triazines with unlike substituents were less than 30% with the exception of 2-phenyl-4,6-bis(trifluoromethyl)-1,3,5-triazine, which was recovered in 53% yield. tris(Trifluoromethyl) s-triazine was produced in each reaction; no s-triazines of the aromatic nitriles were detected.

Since the aromatic nitriles do not trimerize under the conditions of these experiments, the cotrimerization with trifluoroacetonitrile must have been promoted by the formation of an activated complex, as previously described, of the ammonia and perfluoroalkyl nitrile.

It is anticipated that these cotrimers may furnish useful monomers for polymers incorporating both triazine and phenyl rings in the polymer structure.

## Catalytic Polymerization of Perfluoroalkyl nitriles

Our report at the previous conference discussed briefly catalytic polymerization of perfluoroglutaronitrile by basic

(ammonia), Lewis acid (aluminum chloride), and free radical (benzoyl peroxide) catalysts.

It is obvious from our work on trimerization of nitriles that the principal interest now lies in the area of basic or nucleophilic catalysts. The present extension of this type of polymerization has involved the use of ammonia, various amines and water. Table 10 shows the catalysts, conditions and yield of homopolymers of perfluoroglutaronitrile obtained. In general, the yields shown are average values of the runs made.

TABLE 10  
CATALYTIC POLYMERIZATION OF PERFLUOROGLUTARONITRILE  
AT 200°C.

<u>Catalyst (Mole %)</u>	<u>Relative Pressure of PFGN</u>	<u>Polymer Yield %</u>
None	1.0	7.4*
None	2.0	9.1*
Ammonia (0.1)	1.0	26.5
Ammonia (0.1)	2.0	14.0
Ammonia (0.5)	0.5	77.3
Ammonia (0.5)	1.0	48.6
Ammonia (0.5)	2.0	36.1
Ammonia (1.0)	0.5	91.2
Ammonia (1.0)	1.0	84.0
Ammonia (1.0)	2.0	51.5
Methylamine (1.0)	0.5	89.6
Methylamine (1.0)	1.0	85.4
Dimethylamine (1.0)	0.5	47.8

TABLE 10 (continued)

Dimethylamine (1.0)	1.0	52.6
Trimethylamine (1.0)	0.5	18.6
Trimethylamine (1.0)	1.0	37.4
Pyridine (3.2)	1.0	46.7
p-Toluidine (1.0)	1.0	87.9**
Piperidine (1.0)	1.0	52.8**
p-Phenylendiamine (1.0)	1.0	91.7**
Perfluoroacetamide (1.0)	1.0	13.4
Perfluoroglutaramide (1.0)	1.0	98.9

\*reproducibility poor

\*\*possibly decomposition of the catalyst

For the polymerizations catalyzed by ammonia, the yield of polymer increased, as expected, with increase in catalyst concentration; for each catalyst concentration, it will be noted however, that yields increased with decreasing initial pressure. Additional study of the nature of the activated complex formed in this polymerization would help explain this effect.

The decreasing yields in the series  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$  may be explained by steric hindrance to formation of the complex. Some of the other amines may have decomposed under the conditions of the reaction. No significant conclusions may be drawn concerning the effect of the basicity of the catalyst on this reaction.

The polymerization catalyzed by perfluoroglutaramide almost certainly indicates that water derived from catalyst decomposition was the effective nucleophile. At this temperature ( $200^\circ$ ) dehydration of perfluoroacetamide appears to be much less extensive than in the trimerization experiments at  $300^\circ$ .

Copolymers of the type previously described in this report were prepared by catalytic copolymerization of perfluoroglutaronitrile with perfluoroalkylmononitriles. Table 11 shows the results obtained.

TABLE 11  
 CATALYTIC COPOLYMERIZATION OF PERFLUOROGLUTARONITRILE  
 WITH PERFLUOROALKYLNITRILES AT 300° WITH  
 1.0 MOLE % AMMONIA

<u>Perfluoroalkylnitrile</u>	<u>Molar Ratio PFGN : PFAN</u>	<u>% Yield (of total reactants)</u>
CF <sub>3</sub> CN	1 : 1	86
CF <sub>3</sub> CN	1 : 2	77
CF <sub>3</sub> CN	1 : 3	50
C <sub>2</sub> F <sub>5</sub> CN	1 : 1	66
C <sub>3</sub> F <sub>7</sub> CN	1 : 1	89
C <sub>3</sub> F <sub>7</sub> CN	1 : 2	53

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