# Poly(perfluoroether) Oxadiazole Elastomer System Cured with Terephthalonitrile Oxide

ROBERT E. COCHOY, *Air Force Materials Laboratory (AFSC), Wright-Patterson AFB, Ohio 45433*

## Synopsis

The terpolymerization of N,N′-terephthalonitrile oxide (TPNO), 1,3,5-tricyanobenzene, and oligomeric perfluoroalkylene dinitriles derived from the oligomerization of tetrafluoroethylene oxide yields poly(perfluoroether)-1,2,4-oxadiazole polymers which are soluble in Freon TF and bear pendent nitrile groups as curing sites. The polymerization is a two-step, ambient-temperature reaction. Several different perfluoroether dinitriles are shown to polymerize using this procedure. The syntheses and certain structure/property relationships of the polymers are discussed. Increasing the chain length of the perfluoroalkylene oxide dinitriles results in polymers which range from paraffin-like solids through tough elastomers and, finally, to tacky gums. Tough, crepe elastomer gum with a $T_g$ of −64°C may be obtained in yields of 60–70%. The poly(perfluoroether) oxadiazoles may be milled with additional TPNO and press cured at 95°C (200°F). The following physical properties of the cured polymers are given: compression set, tensile strength, per cent elongation at break, set at break, and Shore A hardness. Thermal stability, moisture stability, and low-temperature flexibility data are also presented for the cured elastomeric polymer.

## INTRODUCTION

Polymer chemists have recognized for some time the value of incorporating poly(perfluoroalkylene oxide) units (1)

$$\left[ OCF\!\!-\!\!\underset{\underset{Y}{|}}{CF} \right]_x \qquad Y = F, \text{ or } CF_3$$
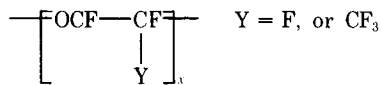
1

into elastomer systems in order to obtain low temperature flexibility (low $T_g$), thermo-oxidative stability, and fuel or oil resistance in the resulting elastomers. However, the same lack of chemical reactivity that imparts thermo-oxidative stability to an elastomer gum containing units of polymer 1 also precludes curing the elastomer gum into a useful elastomeric material such as a hydraulic seal.

Poly(perfluoroether) diacid fluorides (referred to as EDAF's in this paper) are readily prepared[1,2] as shown on page 1036:

$$F-\overset{\overset{\displaystyle O}{\|}}{C}-(CF_2)_3-\overset{\overset{\displaystyle O}{\|}}{C}-F \ + \ CsF\cdot \ + \ (m \ + \ n \ + \ 2)CF_2-\overset{\displaystyle O}{\overset{\diagup\diagdown}{C}}F-Y$$

$$\Big\downarrow$$

$$F-\overset{\overset{\displaystyle O}{\|}}{C}-CF-\Big(O-CF_2-CF\Big)_m-O-(-CF_2)_5-O-\Big(CF-CF_2-O\Big)_n-CF-\overset{\overset{\displaystyle O}{\|}}{C}-F$$
$$\phantom{xxx}| \phantom{xxxxxxx} | \phantom{xxxxxxxxxxxxxxxxxxxx} | \phantom{xxxxx} |$$
$$\phantom{xxx}Y \phantom{xxxxxxx} Y \phantom{xxxxxxxxxxxxxxxxxxxx} Y \phantom{xxxxx} Y$$

an EDAF                               Y = F, or CF$_3$

The EDAF's are easily converted to the corresponding dinitriles (2).[3]  Previous workers[4] have shown that these dinitriles (2, Y = CF$_3$) oligomerize with terephthalonitrile oxide (TPNO) to yield polymers (3) containing the 1,2,4-oxadiazole linkage:

$$N\equiv C-CF-\Big(OCF_2-CF\Big)_m-O(CF_2)_5-O-\Big(CFCF_2O\Big)_n-CF-C\equiv N \ + \ \overset{\ominus}{O}-\overset{\oplus}{N}\equiv C-\langle\bigcirc\rangle-C\equiv\overset{\oplus}{N}-\overset{\ominus}{O}$$

an EDAF  dinitrile (2)                                                   TPNO

$$\Big\downarrow$$

$$\Big[-CF-\Big(OCF_2CF\Big)_m-O(CF_2)_5O\Big(CFCF_2O\Big)_n CF-C\overset{N}{\underset{O-N}{\diagup\diagdown}}C-\langle\bigcirc\rangle-C\overset{N}{\underset{N-O}{\diagdown\diagup}}C-\Big]_x$$

poly(perfluoroether) oxadiazole (3)                    Y = F or CF$_3$

Since polymer 3 contains no chemically reactive "handles" along the backbone of the polymer, it cannot readily be cured into a useful elastomeric material.

This report describes an approach for preparing polymeric gums similar to structure 3 (Y = F) but containing nitrile cure sites along the polymer backbone.  This report also describes the curing of these gums with additional TPNO as a crosslinking agent and the physical properties of the resulting elastomers.

## RESULTS AND DISCUSSION

Tables I through IV summarize the results obtained with this elastomer system.  Table I summarizes the experimental procedure and results for a series of polymerization runs with 5-EDAF, 8-EDAF, and 9-EDAF dinitriles (2; Y = F; m + n = 3, 6, and 7, respectively).  Table II gives the physical properties of the cured elastomers derived from this same series of polymerization runs in order to compare the synthesis of the polymer gum and the physical properties of the cured polymer.  Tables III and IV present moisture stability and thermal stability data for a representative elastomer gum (from run F) press cured with 3% TPNO.

N,N-Terephthalonitrile dioxide (TPNO) has been shown to cure ethylenic and acetylenic polymers[5] as well as saturated nitrile polymers.[6]  The curing

TABLE I
Summary of Polymerizations[a]

| Run | EDAF dinitrile/ mmoles charged | Mmoles 1,3,5-tricyano-benzene charged | Mmoles TPNO charged | Freon TF solvent, ml | Oligomer-ization time, days | $CH_2Cl_2$ solvent, ml added | Chain extension time, days | Polymer appearance (yield, %)[b] |
|---|---|---|---|---|---|---|---|---|
| A | 8-EDAF dinitrile/2.3 | 0 | 2.27 | 21 | 5 | 0 | — | colorless oil (93) |
| B | 8-EDAF dinitrile/3.2 | 1.4 | 4.9 | 26 | 4 | 0 | — | colorless oil[c] |
|  |  | 1.4 | 4.9 | 26 | 8 | 0 | — | viscous oil |
|  |  | 1.4 | 4.9 | 26 | 8 | 25 | 2.5 | elastomeric gum |
| C | 8-EDAF dinitrile/4.6 | 1.5 | 6.2 | 35 | 6 | 15 | 5 | crepe gum elastomer (61) |
| D | 8-EDAF dinitrile/9.4 | 3.0 | 12.5 | 70 | 6 | 40 | 4 | crepe gum elastomer (50) |
| E | 5-EDAF dinitrile/9.4 | 3.0 | 12.5 | 70 | 6 | 40 | 4 | paraffin-like white solid (54) |
| F | 8-EDAF dinitrile/9.4 | 3.0 | 12.5 | 70 | 4 | 40 | 3 | tough gum (71) |
| G | 9-EDAF dinitrile/9.4 | 3.0 | 12.5 | 70 | 4 | 40 | 3 | tacky gum (59) |
| H | 9-EDAF dinitrile/9.4 | 0.75 | 10.3 | 70 | 4 | 40 | 3 | sticky sealant grade material (82) |
| I | 8-EDAF dinitrile /11.35 | 3.6 | 14.8 | 70 | 4 | 40 | 3 | tough gum (70) |
| J | 8-EDAF dinitrile/11.3 | 3.6 | 15.2 | 70 | 4 | 40 | 3 | tough crepe gum elastomer (55)[d] |
| K | 8-EDAF dinitrile/11.3 | 3.6 | 15.5 | 70 | 5 | 40 | 3 | tough crepe gum (68) |
| L | 8-EDAF dinitrile/11.3 | 3.6 | 15.7 | 70 | 5 | 40 | 3 | slightly tacky gum (61) |
| M | 8-EDAF dinitrile/5.75 | 1.8 | 8.0 | 35 | 3 | 20 | 5 | tough gum (28)[e] |
| N | 8-EDAF dinitrile/5.75 | 1.8 | 8.0 | 35 | 7 | 5 | — | (0)[f] |
| O | 8-EDAF dinitrile/22.6 | 7.5 | 31.2 | 105 | 4 | 55 | 3 | tacky gum (60) |
| P[a] | 8-EDAF dinitrile/18.1 | 7.2 | 26.2 | 84 | 4 | 44 | 3 | tacky gum (60) |
| Q | 8-EDAF dinitrile/7.0 | 5.0 | 12.5 | 70 | 4 | 40 | 3 | tough gum (37) |
| R | 8-EDAF dinitrile/7.0 | 5.0 | 12.5 | 70 | 6 | 40 | 4 | tough, crepe gum (30) |

[a] Polymer reactions were magnetically stirred in a stoppered single-necked, indented round-bottom flask at ambient temperature (25°C), except for run P which was vigorously shaken on a Burrel wrist shaker.

[b] Except for runs A and B, all yields are of fractionated polymer and are based on the EDAF dinitrile charged.

[c] No yields are reported on run B since aliquots were removed periodically.

[d] Inadvertent heating of the gum in contact with TPNO during the fractionation caused some loss in yield of the final gum.

[e] Polymer partially crosslinked during the long chain extension time causing large loss during filtration.

[f] The 5 ml $CH_2Cl_2$ was added at the beginning of the polymerization along with the other reactants. Polymer crosslinked in pot.

TABLE II
Curing Results[a]

| Run[b] | TPNO, wt % in Polymer | Filler, % | Press cure, min/°F | Tensile strength, psi | Elongation at break, % | Shore A hardness | Compression set 24 hr at 400°F, 25% deflection, % | Comments |
|---|---|---|---|---|---|---|---|---|
| B | 1 | — | 120/200 | 580 | 765 | 40 | — | unfractionated gum, no scorching |
|   | 0 | — | 60/160 | — | — | — | — | sample did not cure without the additional TPNO |
| C | 3 | — | 20/200 | 1267 | 625 | 66 | — | fractionated gum, TGA on cured sample flat up to 500°F |
| D | 3 | — | 10/200 | 1455 | 560 | 45–50 | 100 | doubly fractionated gum, TR-10 = −73°F |
| E | 5 | — | 15/200 | 1450 (1090) | 480 (380) | — | 105 (67) | TPNO dispersed in Freon TF solution of gum. Freon then removed under vacuum; set at break = 300% (245%) on cured and postcured samples |
|   | 3 | — | 15/160 | 1120 | 400 | — | — | |
|   | 3 | — | 20/200 | 1705 (1815) | 430 (435) | — | 76 (64) | |
| F | 3 | — | 20/200 | 1215 (1045) | 640 (465) | 40–45 | (84) | TR-10 = −73°F, TR-20 = −67°F, TR-30 = −64°F |
| G | 3 | — | 30/200 | 410 | 660 | 50 | — | set at break = 18%; cured sample stiffened or crystallized upon standing |
|   | 3 | — | 30/200 (air cured) | — | — | — | — | used at 50:50 blend of gum from runs G and H; TNPO was mixed with warm gum and mixture trowled onto B-120 titanium test strip, cured well in air oven; no corrosion of test strip after 200 hr at 400° |
| H | 3 | — | 30/200 (air cured) | — | — | — | — | sealant strip prepared as in run G; no stress corrosion of B-120 titanium test strip after 1000 hr at 400°F |

| Run[b] | | Filler | Cure, min/°F | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|
| | 3 | — | 120/200 (air cured) | 240 | 475 | 22 | — | sealant test strip cured in air oven; strip contained pinholes from escaping air or solvent; set at break = 0% |
| I | 3 | — | 20/200 | 1160 | 685 | 40 | — | $T_g = -83°F$ |
| J | 3 | — | 30/200 | 1045 | 215 | — | — | slightly scorched |
| | 3 | HiSilEP (20) | 30/200 | 2425 (2270) | 260 (400) | 71 (70) | — | scorched |
| K | 3 | HiSilEP (20) | 30/200 | 2175 (2085) | 420 (410) | 75 (68) | 120 (100) | 100% modulus = 505 psi; set at break = 20% (10%) on cured and postcured samples, respectively. |
| | 5 | HiSilEP (20) | 30/200 | 1775 | 350 | 75 | 113 (105) | sample judged to be overcured; set at break = 15% |
| | 3 | HiSilEP (20) | 45/200 | — | — | — | — | two 214-size O-rings were molded for compression set determination; comp. set (24 hr at 325°F) = 84.4%; comp. set (24 hr at 350°F) = 94.4%; O-rings were postcured at 350°F before tests |
| L | 3 | HiSilEP (20) | 45/200 | 2200 (1920) | 595 (650) | 70 (65) | 125 (103) | set at break = 30% (10%) on cured and postcured samples, respectively |
| O | 3 | HiSilEP (20) | 45/200 | — | — | — | — | two 214-size O-rings were molded for compression set determination; both O-rings were spongy and were not tested |
| P | 3 | — | 30/200 | 790 | 705 | 53 | — | set at break = 5% |
| | 3 | — | 30/200 | 725 | 645 | 48 | — | set at break = 10% |
| | 6 | — | 30/200 | 1000 | 835 | 52 | — | set at break = 10% |
| Q | 3 | — | 30/200 | 1145 | 600 | 52 | 110 | set at break = 5% |
| R | 3 | — | 30/200 | 1330 | 370 | 65 | — | set at break = 0% |

a Physical properties were determined on three test specimens averaged. Values in parentheses indicate test values obtained after postcuring 24 hr at 400°F. Except for compression set, all tests were in accordance with applicable ASTM standards.

b Run numbers correspond to run numbers in Table I.

reaction occurs at moderate temperature via a 1,3-cycloaddition reaction without the elimination of volatile by-products. The reaction is unaffected by the presence of moisture or air. Both the thermal stability of the 1,2,4-oxadiazole linkage that results from the reaction of TPNO and an arylnitrile group as well as certain synthetic considerations suggest that a pendent aryl-nitrile group be incorporated as a crosslinking site for TPNO in the predominantly poly(perfluoroether) oxadiazole chain.

Aromatic nitriles undergo 1,3-cycloaddition reactions with nitrile oxides, whereas aliphatic nitriles react readily only when they bear electron-withdrawing substituents.[7] These results suggest that an arylnitrile bearing additional electron-withdrawing nitrile groups should be more reactive to TPNO than the parent mononitrile. In order to successfully incorporate an aromatic trinitrile into the growing EDAF dinitrile/TPNO polymer chain, two of the three nitrile groups must possess reactivity (toward a nitrile oxide group) comparable to that of the EDAF dinitrile. The third nitrile group, however, must be considerably less reactive to a nitrile oxide group than the other two nitrile groups in order to prevent crosslinking or gelling during the polymerization.

The termonomer, 1,3,5-tricyanobenzene, meets these requirements. Presumably, the first nitrile group of 1,3,5-tricyanobenzene, being strongly activated by the electron withdrawing effect of the two other nitrile groups, competes favorably with the EDAF dinitrile oligomer for reaction with TPNO at ambient temperatures. In a stepwise addition process, the second nitrile group, still activated by one free nitrile group, also reacts with TPNO and the EDAF dinitrile oligomer at ambient temperature to form 4:
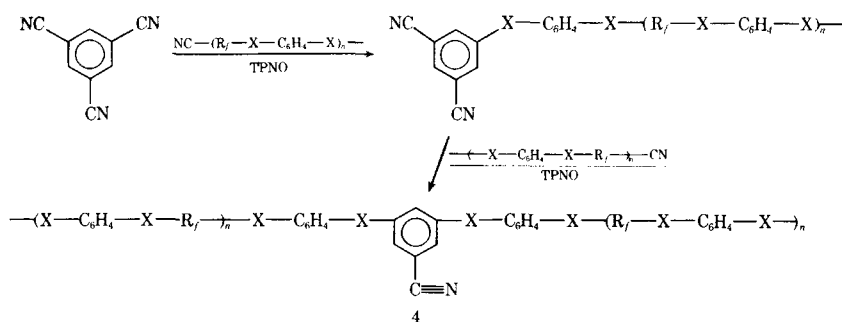


$R_f$ = perfluoroether linkage

$X$ = 1,2,4-oxadiazole linkage

This process effectively chain extends the growing EDAF dinitrile/TPNO polymer chain and, simultaneously, inserts a pendent arylnitrile group into the polymer for subsequent crosslinking with TPNO. The lower reactivity of the third nitrile group toward TPNO or the growing EDAF dinitrile/TPNO polymer is due presumably to the fact that the two oxadiazole rings on the ar-ylnitrile (4) do not sufficiently activate the nitrile to undergo the 1,3-addition reaction to any appreciable extent at ambient temperature. When the poly-

TABLE III
Moisture Stability at 165°F, 100% Relative Humidity[a]

| Elapsed time, days | Ultimate tensile strength, psi | % Elongation | Tensile strength at 200% elongation, psi | Set at break, % | Shore A hardness |
|---|---|---|---|---|---|
| 0 | 1025 (1350) | 490 (680) | — | 0 (10) | 55–60 (45) |
| 3 | 1060 (1168) | 516 (560) | 136 (148) | 27 (29) | 56 (58) |
| 7 | 776 (1270) | 414 (612) | 148 (168) | 25 (28) | 43 (45) |
| 18 | 720 (—) | 532 (—) | 148 (—) | 26 (—) | 44 (—) |
| 30 | 712 (1052) | 440 (520) | 308 (288) | 27 (27) | 43 (46) |
| 60 | 840 (—) | 460 (—) | 316 (—) | 26 (—) | 48 (46) |

[a] Test specimens (two per determination averaged) were cut from gum prepared in run F cured with 3% TPNO. Specimens were postcured 24 hr at 400°F. Values in parentheses are test values for unpostcured samples.

TABLE IV
Thermal Stability at 400°F in Air[a]

| Elapsed time, days | Ultimate tensile, psi | % Elongation | Shore A hardness | Set at break, % | Cumulative weight loss, % |
|---|---|---|---|---|---|
| 0 | 1025 | 490 | 55–60 | 0 | — |
| 3 | 810 | 390 | 60 | 10 | 0.544 |
| 7 | 575 | 320 | 40–45 | 0 | 0.987 |
| 14 | 490 | 340 | 40 | 0 | 1.322 |
| 30 | 344 | 255 | 35 | 0 | 2.27 |
| 60 | 340 | 155 | 45 | 0 | 5.66 |

[a] Two specimens (two per determination averaged) were cut from unfilled gum prepared in run F cured with 3% TPNO. Specimens were postcured 24 hours @ 400°F prior to testing.

merization is carried out at ambient temperatures, it is therefore possible to prevent gelling of the polymer and to prepare high yields of Freon TF-soluble polymer gum. The polymerization forms, in most cases, a tough, crepe gum. However, some branching of the polymer chain is probably occurring.

The polymerization is carried out in a two-step, two-phase reaction whereby a solution of the EDAF dinitrile in Freon TF solvent (trichlorotrifluoroethane) containing suspended TPNO and 1,3,5-tricyanobenzene is initially stirred at ambient temperature for several days. During this oligomerization stage, the EDAF dinitrile polymerizes with the TPNO and builds up molecular weight. The 1,3,5-tricyanobenzene is essentially insoluble in this reaction medium and is not incorporated into the polymer to any great extent (oligomerizations run with and without the 1,3,5-tricyanobenzene give polymers of qualitatively similar viscosities). During the oligomerization reaction, the greater solubility of the EDAF dinitrile over the TPNO in the Freon TF would result in a much greater concentration of EDAF dinitrile over that of TPNO in solution. This difference in concentration should result in a nitrile-end-capped oligomer. The fact that the final polymer gum (run B, Table II) failed to cure without adding TPNO suggests that the oligomers are not end capped in nitrile oxide groups.

The second step or chain extension step of the polymerization is effected

by addition of methylene chloride to the Freon TF suspension. The methylene chloride is miscible with the Freon TF and brings the 1,3,5-tricyanobenzene into solution. By bringing the trinitrile into solution, its concentration is increased and two of the three nitrile groups may add TPNO followed by the EDAF dinitrile oligomer. The chain extension reaction is allowed to proceed for several days at ambient temperature. The suspension is then filtered and the clear polymer solution is treated with additional methylene chloride to precipitate the polymer. If the chain extension reaction is run at temperatures higher than ambient or is run at ambient temperature for periods of time exceeding four days, some gellation usually occurs, making the filtration exceedingly difficult.

The precipitated polymer is then redissolved in fresh Freon TF and reprecipitated with methylene chloride. The fractionated polymer is obtained in 60–70% yield (based on the EDAF dinitrile taken) after drying at 110°C.

The two-step, heterogeneous nature of the reaction medium offers certain advantages over more conventional solution polymerizations. First, the EDAF dinitrile/TPNO oligomerization time may be varied before the trinitrile is brought into solution. This should, in theory, modify the density of crosslinking sites in the resulting elastomer gum. Second, the heterogeneous nature of the reaction makes exact stoichiometry of the ingredients unnecessary. A disadvantage of the procedure lies in the fact that TPNO homopolymerizes to form a polyfuroxan (5) or polyoxazoxime (6) in competition with the EDAF dinitrile/TPNO oligomerization. It is reported that the homopolymerization of TPNO at ambient temperature and in solution is most likely to form 5[8]:



5



6
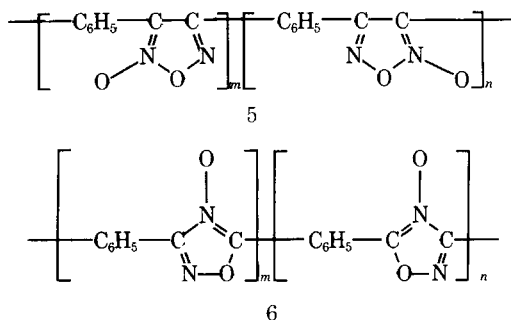
Undoubtedly, blocks of the TPNO homopolymer are incorporated into the polymer chain to some extent. The TPNO homopolymer (5) has been shown to be stable to 260°C and stable to alcoholic potassium hydroxide at reflux temperature.[8]

It is evident from runs E through G that a variation in the length of the perfluoroether chain (5-EDAF through 9-EDAF) results in significant differences, both in the appearance of the polymer gum and in the physical properties of the cured elastomers. The polymer from the 5-EDAF dinitrile is a solid, parafin-like material which, when cured, exhibits a high degree of strength and also a high tensile set (plastic deformation). The 8-EDAF dinitrile polymer gives, in most cases, a tough elastomeric gum which, when cured, results in a tough elastomer possessing a low tensile set. The 9-EDAF dinitrile polymer is initially a tacky gum which solidifies upon standing long

periods of time. When cured, the 9-EDAF dinitrile polymer is rather weak but possesses a low tensile set. The wide variation in physical properties of these three polymers as well as the low TR-10 measurement[9] (temperature at which a stretched frozen sample of rubber retracts 10% when warmed) of −73°F observed for the 8-EDAF dinitrile elastomer demonstrates the flexibility that the perfluoroether chain imparts to the backbone of the polymer.

An important variable in the polymerization reaction appears to be the purity of the TPNO used. High-purity TPNO made from high-purity terephthalhydroximoyl chloride appears to be less reactive (more stable) than TPNO of lower purity. The greater stability of pure TPNO over impure TPNO has been recognized in other work at these laboratories.[4a] In polymerization runs A through K, TPNO of lower purity was used. This TPNO was prepared from terephthalhydroximoyl chloride which was purified by precipitation from ether solution by hexane. In polymerization runs L through R, the TPNO used was quite pure and was prepared from terephthalhydroximoyl chloride recrystallized from toluene. However, both the quality of the polymers prepared with this pure TPNO and the physical properties of the cured elastomers from these polymers were definitely inferior to those of polymers and elastomers prepared with a less pure variety of TPNO (runs A through K). Since several batches of both the pure and impure terephthalhydroximoyl chloride were prepared and converted to TPNO, it appears that this is not merely a spurious observation. Moreover, increasing the reaction time from a total of seven days to a total of ten days to counteract the lack of reactivity of the pure TPNO does not appear to improve the quality of polymer.

The 1,3,5-tricyanobenzene incorporated into the polymer appears to decrease when the amount charged is decreased. In comparing runs G and H (Table I), it is apparent that decreasing the trinitrile concentration from 24 mole-% to 7 mole-% produces a much more "soupy" polymer. However, in runs Q and R, where the trinitrile was increased from the normally charged 24 mole-% to 42 mole-%, low yields of high molecular weight polymer were obtained. When compared to other runs with 8-EDAF dinitrile, little difference in properties of the cured elastomer from runs Q and R was observed.

In the case where a small amount of methylene chloride was initially present in the polymerization suspension (run N) to effect a gradual incorporation of the trinitrile during oligomerization, the polymer crosslinked in the pot. Other solvents or mixed solvent systems for the polymerization were not investigated.

Increasing the amount of TPNO curing agent from 3% to 5% or 6% appeared to offer little advantage in terms of better physical properties and it increased the tendency for scorching (premature curing).

The cured elastomer held up quite well to the 60-day humidity test (Table III). Most of the degradation in physical properties occurred in the first few days of the test with a leveling off of the degradation thereafter. The unpostcured samples appeared to hold up better than the postcured samples.

The cured elastomer did not hold up well to long-term aging at 400°F in air (Table IV) considering that the cured elastomer showed no weight loss up to 270°C (517°F) on TGA analysis. It has been reported that 3,5-bis(perfluoroalkyl ether) 1,2,4-oxadiazole model compounds derived from TPNO ther-

maily degrade to form large amounts of perfluoronitrile compounds in either an air or a nitrogen atmosphere. These results led to the conclusion that degradation was occurring by thermal decomposition of the oxadiazole units rather than by oxidative attack on the aromatic ring.[10]

The cured elastomer derived from 8-EDAF dinitrile exhibited high compression set values (see Table II) at 325°F, 350°F, and 400°F, even when the samples were postcured at these temperatures prior to the testing. The poor compression set resistancemay be due to the mobility under pressure of the long, linear, highly flexible perfluoroether chains located between the cross-linking sites.

## EXPERIMENTAL

### General

The poly(perfluoroether) diacid fluorides (EDAF's) were prepared by PCR, Inc., Gainesville, Florida, from tetrafluoroethylene oxide[11] according to pbublished procedures.[1,2] The EDAF dinitriles were prepared in high yield from the diacid flrides by amidation and dehydration with phosphorus pentoxide.[3] The 5-EDAF, 8-EDAF, and 9-EDAF dinitriles (2; Y = F; $m + n = 3$, 6, and 7, respectively) used in this study were prepared and characterized by PCR, Inc.

Melting points were obtained on a Büchi melting point apparatus (oil bath) and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 337 infrared spectrophotometer. The mass spectrum of 1,3,5-tricyanobenzene was obtained on a du Pont Model 21-490 mass spectrometer modified with a chemical ionization source. Microanalyses were performed by the Air Force Materials Laboratory Analytical Branch, Wright-Patterson AFB, Ohio.

The Freon TF (du Pont trichlorotrifluoroethane) and methylene chloride solvents used for the polymerizations were dried over anhydrous magnesium sulfate prior to use.

### Terephthalhydroximoyl Chloride

The terephthalhydroximoyl chloride, precursor to TPNO, was prepared according to the procedure of LaRochelle.[12]

It is necessary to run the reaction in an efficient fume hood. Terephthaldioxime (13.2 g, 0.08 mole, mp 226–229°C) and 675 ml 8N HCl were placed in a 2-liter, three-neck flask equipped with an efficient mechanical stirrer, thermometer, fritted glass gas inlet tube leading well below the surface of the liquid, and a gas outlet tube leading to a bubbler. With stirring and with nitrogen gas being bubbled slowly through the suspension, the reaction mixture was cooled to 0°C in an ice/salt bath. Chlorine gas was then bubbled slowly through the vigorously stirring suspension for 6 hr. Foaming can be controlled, if necessary, by addition of several milliliters of ether. At the end of the 6-hr chlorination, the ice-salt bath was removed and nitrogen was again bubbled through the suspension while it was allowed to warm to ambient temperature. The crude material was filtered, washed with water, and air

dried overnight.  The material was then taken up in 200 ml ether and dried with anhydrous magnesium sulfate.  After filtering and evaporating the ether solution to dryness, there remained 16.7 g of slightly off-white solid, mp 174–177°C.  The solid was again taken up in ether and precipitated with hexane to yield 14.8 g (80%) of crude, off-white terephthalhydroximoyl chloride, mp 178–180°C.  Material prepared in this manner was converted to TPNO and used in polymer runs A through K.

Much purer terephthalhydroximoyl chloride (mp 188–190°C) was prepared by recrystallizing the crude material from toluene (1 g/100 ml).  The white terephthalhydroximoyl chloride purified in this manner was converted to TPNO and was used in polymer runs L through R.

ANAL.  Calcd for $C_8H_6N_2O_2Cl_2$:  C, 41.23; H, 2.60; N, 12.02; Cl, 30.43.  Found:  C, 41.24; H, 2.52; N, 12.02; Cl, 30.38.

## N,N'-Terephthalonitrile Dioxide (TPNO)[12]

To a 300-ml, three-neck, round-bottom flask equipped with a magnetic stirrer, a thermometer, and a 125-ml dropping funnel topped with a drying tube were added triethylamine (6.1 g, 60 mmoles) and ether (150 ml).  The solution was cooled to −5°C in an ice/salt bath, and a solution of terephthalhydroximoyl chloride (4.7 g, 20 mmoles) in ether (75 ml) was added dropwise at −5°C with rapid stirring over a period of 20 min.  The resulting white suspension was stirred an additional 40 minutes at −5°C.  Cold distilled water (30 ml) was then added, and the suspension was stirred an additional 20 min at 0° to −5°C and was then filtered on a sintered glass filter.  The nearly white solid was washed thoroughly on the filter with cold distilled water (3 × 25 ml) and cold ether (3 × 25 ml) and was then dried in a vacuum desiccator for 2¼ hr (0.7 mm) to yield 3.1 g (95%) of nearly white, fluffy terephthalonitrile oxide (TPNO).  Caution!  The dry material decomposed explosively when heated to 155°C in air, as reported elsewhere.[8]

Infrared spectrum (CHCl₃): $\nu_{max}$ 2300(s), 1360(s), 1105(s), 1015(w), 830(w) cm⁻¹.  The infrared spectrum exhibited no absorption attributable to polymeric forms of TPNO.[8]

ANAL.  Calcd for $C_8H_4N_2O_2$:  C, 60.00; H, 2.53; N, 17.48.  Found:  C, 59.70; H, 2.38; N, 17.41.

## 1,3,5-Tricyanobenzene

The 1,3,5-tricyanobenzene, mp 257.5–258.5°C (lit.[13] 254–258°C) was prepared by treating trimesamide[14] with thionyl chloride in DMF according to the procedure of Bailey et al.[13]  Infrared spectrum (mixed mull): $\nu_{max}$ 3075(m), 2250(m), 910(s), 720(w), 670(s) cm⁻¹.  Mass spectrum:  parent peak $m/e$ 153.

ANAL.  Calcd for $C_9H_3N_3$:  C, 70.59; H, 1.96; N, 27.45.  Found:  C, 70.20; H, 1.71; N, 27.42.

## Poly(perfluoroether) Oxadiazole Elastomer Gum

The procedure listed is for run I in Tables I and II.  Runs C through P used this same general procedure with variations as listed in Table I.

To a dry 250-ml indented, single-neck, round-bottom flask equipped with a magnetic stirring bar were added N,N'-terephthalonitrile oxide (TPNO, 2.36

g, 14.7 mmoles) and 1,3,5-tricyanobenzene (0.551 g, 3.6 mmoles) along with Freon TF solvent (50 ml). A solution of 8-EDAF dinitrile [NC-$CF_2(OCF_2CF_2)_m$-O-$(CF_2)_5$-O-$(CF_2CF_2O)_n$-$CF_2CN$, $m + n = 6$, 12.84 g, 11.35 mmoles] in Freon TF solvent (20 ml) was added all at once to the TPNO/trinitrile suspension. The flask was capped with a vacuum adapter, and, with stirring, the flask was alternately evacuated (to 300 mm) and flushed with dry nitrogen. The flask was then sealed off, disconnected from the nitrogen line, and then allowed to stir at ambient temperature for four days. Forty milliliters methylene chloride was then added to the suspension and stirring was continued for an additional three days. Freon TF, 30 ml, was then added and the suspension was filtered on a Büchner funnel, giving a clear polymer solution. The clear solution was concentrated at ambient temperature *in vacuo* and the polymer was precipitated by the addition of methylene chloride. The supernatant liquid was decanted and the precipitated polymer was redissolved in Freon TF solvent (50 ml) and reprecipitated with methylene chloride (110 ml). After again decanting the supernatant liquid, the polymer was dried for 20 min at 120° in an air oven and for 1½ hr at 115°/1.0 mm. The tough, pale-yellow gum (10.8 g, 70%) showed an inherent viscosity of 0.22 dl/g in hexafluoroisopropanol at 25.0°C (gum from run J gave an inherent viscosity value of 0.29 dl/g) and is proposed to be of the following general structure:



where $R_f =$

$$—CF_2(OCF_2CF_2)_{\overline{m}}—O—(CF_2)_5—O—(CF_2CF_2O)_{\overline{n}}—CF_2—, \quad m + n = 6$$

and $X =$
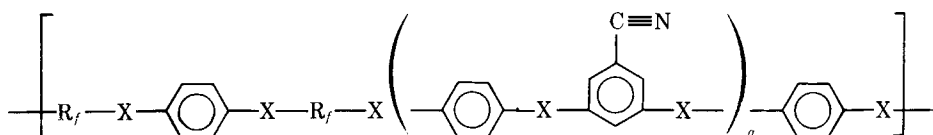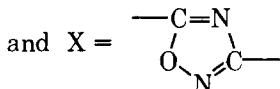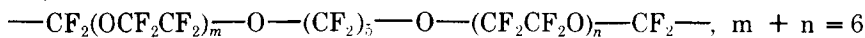


and $a =$ a small proportion of polymer chain.

The infrared spectrum (film cast from Freon TF) shows $\nu_{max}$ 1610, 1550, 1460, 1330, 1250–1110, 990, 960, 900, 880, and 860 cm$^{-1}$. A portion of the gum was further dried at 180°C/0.1 mm for 6 hr to provide a sample for $T_g$ determination and elemental analysis. The polymer gum shows a $T_g$ of −64°C with a possible $T_m$ at 33°C (polymer gum from run J shows a $T_g$ of −57°C and no $T_m$). The calculated values for the following elemental analysis are based on the incorporation of one trinitrile group for every seven 8-EDAF dinitrile groups in the polymer chain.

ANAL. Calcd for 7:1:8 EDAF dinitrile:trinitrile:TPNO polymer composition: C, 28.28; H, 0.38; N, 4.95. Found (run I): C, 27.99; H, 0.41; N, 4.54. Found (run J): C, 27.74; H, 0.35; N, 5.43. Found (run L): C, 27.36; H, 0.19; N, 4.81.

The gum prepared in run I was blended with 3% (w/w) TPNO on a laboratory micromill and then press cured 20 min at 200°F to give the physical properties shown in Table II. A sample of the cured sheet of elastomer was suspended in the following hydraulic fluids at the indicated temperatures for

72 hr with the following volume change being measured:   275°F in MIL-H-5606, volume change +5.6%; 350°F in MIL-H-83282, volume change −1.6%.

A TGA analysis (3°C/min in air) of a cured sample of gum from run C showed no weight loss up to 270°C and 6% weight loss at 300°C.

## References

1. J. L. Warnell, U.S. Pat. 3,250,806 (1966).

2. C. G. Fritz and E. P. Moore, U.S. Pat. 3,250,807 (1966).

3. C. G. Fritz and J. L. Warnell, U.S. Pat. 3,347,901 (1967).

4. (a) R. W. LaRochelle, Air Force Materials Laboratory, unpublished work; (b) R. W. Rosser, J. A. Parker, R. J. Pasquale, and E. C. Stump, *Polym. Prepr.*, 15 (1), 216 (1974).

5. D. S. Breslow, U.S. Pat. 3,390,204 (1968).

6. J. W. Collette and J. E. Nottke, U.S. Pat. 3,840,506 (1974).

7. R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 575 (1963).

8. C. G. Overberger and S. Fujimoto, *J. Polym. Sci. Part C*, 16, 4161 (1968).

9. ASTM Designation:  D 1329-58T, ASTM Standards 1958, Part 9, American Society for Testing Materials, Philadelphia, Pa., 1958, pp. 1423–1426.

10. K. L. Paciorek, private communication, 1975.

11. H. H. Biggs and J. L. Warnell (to du Pont), Brit. Pat. 931,587 (1963).

12. R. W. La Rochelle, Synthesis of Nitrile Oxide Curing Agents for Perfluoroalkyl s-Triazine Elastomers, Technical Report AFML-TR-72-239, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio, May 1973.

13. A. S. Bailey, B. R. Henn, and J. M. Langdon, *Tetrahedron*, 19, 161 (1963).

14. A. V. Kirsanor and E. A. Abrazhanova, *Sbornik Statei Obshchei Khim.*, 2, 865 (1953); *C. A.*, 49, 6820e (1955).