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Polyfluoroalkyl Derivatives of Nitrogen. XLI [1], Cross-linking of a Nitroso Rubber Using Perfluoro-2,5-diazahexane-2,5-dioxyl and Its Derivatives

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Polyfluoroalkyl Derivatives of Nitrogen. XLI [1]. Cross-linking of a Nitroso Rubber Using Perfluoro-2,5-diazahexane-2,5-dioxyl and Its Derivatives

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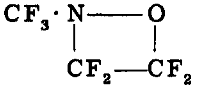
ABSTRACT

Perfluoro-2,5-diazahexane-2,5-dioxyl and a polymeric product resulting from its reaction with trifluoronitrosomethane have been used to cross-link elastomeric copolymers prepared from trifluoronitrosomethane, tetrafluoroethylene, and hexafluorobuta-1,3-diene. The dioxyl, a diradical, is an effective vulcanizing agent at room temperature, and its polymeric derivative is similarly useful at elevated temperatures, presumably via in situ formation of diradicals which effect cross-linking. The thermal stabilities of the vulcanizates obtained are very similar to those of the raw elastomers.

INTRODUCTION



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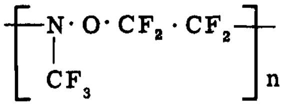
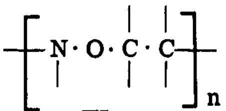


$$\left[\underset{CF_3}{N} \cdot O \cdot CF_2 \cdot CF_2 \right]_n$$

II



$$\left[\underset{|}{N} \cdot O \cdot \overset{|}{\underset{|}{C}} \cdot \overset{|}{\underset{|}{C}} \right]_n$$

III

During the early 1950s it was discovered [2, 3] that trifluoronitrosomethane ($CF_3 \cdot N{=}O$) reacts readily with tetrafluoroethylene in the dark at room temperature to give two major products, perfluoro-(2-methyl-1,2-oxazetidine) (I) and an alternating copolymer (II). Subsequent work [4] showed that high-molecular-weight samples of the copolymer are elastomeric, that alternating copolymers can be prepared from other fluorinated nitroso compounds and/or fluoroolefins, and that both I and II are highly resistant to chemical attack. Other workers reported [5, 6] that copolymer II is completely nonflammable, has excellent resistance to chemical reagents including powerful oxidizing agents, is soluble only in highly fluorinated solvents, and has good low-temperature flexibility. Not unexpectedly, this work attracted the interest of the aerospace industry, with the result that a range of fluorinated alternating copolymers having the general structure III became available and the class name *nitroso rubbers* was coined. Details of the synthesis and properties of *nitroso rubbers* can be found in a recent review [7].

No elastomer serves a useful purpose unless it can be vulcanized. In this respect the excellent chemical stability of the simple nitroso rubber II is a serious handicap, and the only successful cures reported were effected by reaction of the raw elastomer with triethylenetetramine and hexamethylenediamine carbamate, either singly or in admixture, in a two-stage cycle requiring extended periods of heating at temperatures up to 150° C [5-7]. The precise mechanism of the cross-linking reaction is not known, but since amines degrade nitroso rubbers [8], it seems likely that cross-linking and degradation occur simultaneously during the curing cycle. The tensile properties of the vulcanizates are poor [7], and their resistance to chemical attack and their thermal stabilities are markedly inferior to those of the raw elastomer [7, 9]. Irradiation with gamma rays or UV light causes degradation of nitroso rubbers but not cross-linking [10].

To overcome these cross-linking difficulties, attention was turned to the development of copolymers containing a small amount of a third monomer unit carrying a functional group to serve as a cross-linking site. Many termonomer systems were investigated [7], and the most useful outcome was the introduction of the so-called carboxy nitroso rubbers. These contain units derived from $CF_3 \cdot N{=}O$, $CF_2{=}CF_2$, and a nitroso-acid $HO_2C \cdot [CF_2]_x \cdot NO$ (x = 2, 3), and the pendant carboxy-functions provided by the last monomer enable such rubbers to be cured by treatment with, for example, chromium(III) trifluoroacetate [11] or the bisepoxide of dicyclopentadiene [12] Although many of the desirable properties of the raw nitroso rubbers, e.g., nonflammability in pure oxygen and resistance to degradation by N_2O_4, are retained by cross-linked carboxy nitroso rubbers, deterioration is caused by reagents which react with the cross-links, e.g., ClF_3 and aqueous alkali [11], but which leave the polymer backbone unchanged. Similarly, solvents which interact with the cross-links, e.g., methyl ethyl ketone, cause swelling of the vulcanizates, although they do not interact with raw rubbers.

Cross-links in a vulcanized rubber should have the same chemical structure as the main polymer chains if the chemical and thermal stabilities of raw polymer and vulcanizate are to be identical. Unfortunately, this is rarely possible in practice, and the cross-linking sites or the cross-links themselves may provide opportunities for the onset of chemical or thermal degradation; this is particularly so for fluoroelastomers in general. Following the discovery [13] that trifluoronitrosomethane copolymerizes with hexafluorobuta-1,3-diene to yield a nitroso rubber built up from the units $-N(CF_3) \cdot O \cdot CF_2 \cdot CF(CF{=}CF_2)-$ and $-N(CF_3) \cdot O \cdot CF_2 \cdot CF{=}CF \cdot CF_2-$, we embarked on a study of the preparation and vulcanization of unsaturated copolymers based on the $CF_3 \cdot N{=}O/CF_2{=}CF_2/CF_2{=}CF \cdot CF{=}CF_2$ termonomer system, the ultimate goal being to introduce cross-links of the same type as the backbone, i.e., to produce a perfect nitroso rubber network. Our initial work with a cross-linking agent based on perfluoro-NN'-difluoropiperazine has been described recently [14]; the present paper describes results obtained with the novel diradical $\cdot O \cdot N(CF_3) \cdot CF_2 \cdot CF_2 \cdot N(CF_3) \cdot O \cdot$ or derived material as vulcanizing agent [15].

EXPERIMENTAL

General

A conventional Pyrex vacuum system was used for the manipulation of volatile materials to prevent contamination by air and moisture and to minimize toxicity hazards. Infrared, ^{19}F NMR, and mass spectra were obtained with a Perkin-Elmer spectrophotometer model 137, Perkin-Elmer R10 and Perkin-Elmer-Hitachi R20A instruments (56.46 MHz), and an A.E.I. MS-902 spectrometer, respectively. Thermogravimetric and differential thermal analyses were carried out using a Du Pont model 900/950 instrument.

Monomers

Trifluoronitrosomethane was prepared by pyrolysis of trifluoroacetyl nitrite in boiling perfluorotributylamine [7, 16, 17] and purified by precise low-temperature distillation in a semiautomatic still [18]. Commercial tetrafluoroethylene was purified by passing it through a tube packed with silica gel, followed by trap-to-trap distillation in vacuo. Hexafluorobuta-1,3-diene was prepared by the route [19-21]

$$CF_2{=}CFCl + ICl \xrightarrow[0\text{-}20^\circ C]{CH_2Cl_2} CF_2Cl\cdot CFClI \xrightarrow[CH_2Cl_2,\ 25^\circ C]{Zn/Ac_2O}$$

$$CF_2Cl\cdot CFCl\cdot CFCl\cdot CF_2Cl \xrightarrow{Zn/EtOH} CF_2{=}CF\cdot CF{=}CF_2$$

and purified by precise low-temperature distillation. The purities of all three monomers were checked by gas-liquid chromatography and IR analysis and molecular weight determination (Regnault's method).

Polymerization

Copolymer samples were prepared by suspension polymerization in a 1-liter stainless steel autoclave fitted with a high-speed magnetic stirrer; the polymerizations are self-initiating [22]. Lithium bromide (400 g) (freezing point depressant) was dissolved in deoxygenated, deionized water (780 cm^3), and the filtered solution was charged into the autoclave together with anhydrous magnesium carbonate (22 g) (suspending agent). The autoclave and its contents were then outgassed in freeze-thaw cycles using liquid nitrogen as the coolant. Previously purified and outgassed monomers, CF_3NO (35.6 g, 0.36 mole), C_2F_4 (28.8 g, 0.288 mole), and C_4F_6 (11.7 g, 0.072 mole) were condensed successively in vacuo into the cold (-196°C) autoclave, which was sealed and kept at -30°C ($CaCl_2$-ice bath) for 20 hr (stirring rate 1200 to 1500 rpm). Volatile product was transferred to the vacuum system and the aqueous content of the autoclave was treated with concentrated hydrochloric acid to destroy magnesium carbonate and coagulate the copolymer. The gummy polymer was washed with water, dried in vacuo at 20°C, and then dissolved in 1,1,2-trichlorotrifluoroethane. The solution was shaken successively with 2 M hydrochloric acid and water to remove residual magnesium carbonate and lithium bromide, then evaporated in vacuo; the polymer thus isolated was kept in a vacuum desiccator over P_2O_5 for several days to ensure complete removal of solvent and moisture.

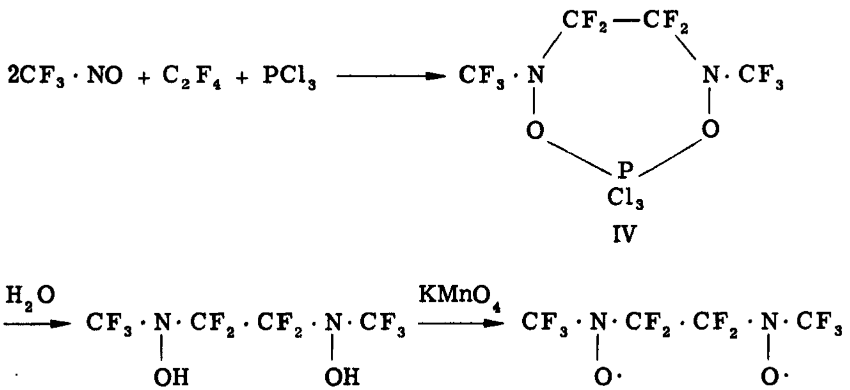
Two batches of polymer, A and B, were prepared; in each case the yield was 30 g. The intrinsic viscosity of Copolymer A in perfluorotributylamine at 25°C was 0.19 dl/g, while that of Copolymer B was 0.21 dl/g. The IR spectra of both copolymers showed absorptions at 5.6 ($-CF{=}CF_2$) and 5.8 μm ($-CF{=}CF-$), indicating [13] the occurrence of both 1,2-and 1,4-addition of the diene to the growing chains. The integrated ^{19}F NMR spectra obtained from solutions of the copolymers in 1,1,2-trichlorotrifluoroethane coupled with microanalysis (C, N, and F) showed that the molar ratios of the monomers in both copolymers were $CF_3NO:C_2F_4:C_4F_6$ = 4:3:1.

Copolymer A was used directly in cross-linking experiments since its gummy consistency made it easy to prepare small quantitites of mixtures with vulcanizing agents simply by manual stirring. Copolymer B was roughly fractionated and only the fraction of highest molecular weight was used in cross-linking experiments. The fractionation was carried out by precipitation. A 2-liter flask with a tapered bottom, fitted with a mechanical stirrer, a condenser, and a burette, and containing 27.5 g of Copolymer B in 720 cm^3 of 1,1,2-trichlorotrifluoroethane, was placed in a thermostat at 25°C. Acetone (55 cm^3) was slowly added from the burette to the stirred solution and some copolymer was precipitated. The temperature of the thermostat was then raised to 30°C to redissolve any coprecipitated copolymer of low molecular weight, and then lowered again to 25°C. The system was then allowed to stand for 12 hr, after which the supernatant solution was decanted and the precipitated copolymer was removed and freed from solvent under reduced pressure. A second fraction of copolymer was precipitated and isolated after addition of a further 60 cm^3 of acetone. The low molecular weight copolymer which remained in solution was isolated by removal of the solvent under reduced pressure. The first fraction of copolymer (6.0 g) was an elastomeric solid having an intrinsic viscosity of 0.52 dl/g in perfluorotributylamine at 25°C; the second fraction (2.6 g), intrinsic viscosity 0.31 dl/g, was an elastomeric solid which flowed on standing; and the third fraction, intrinsic viscosity 0.009 dl/g, was a viscous liquid.

Cross-linking Agents

Hexamethylenediamine carbamate (Diak No. 1; E. I. du Pont de Nemours and Co.) was used as supplied.

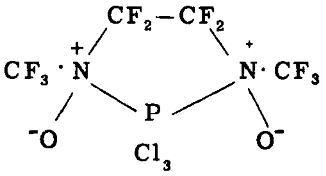
Perfluoro-2,5-diazahexane-2,5-dioxyl was prepared according to the scheme



IV

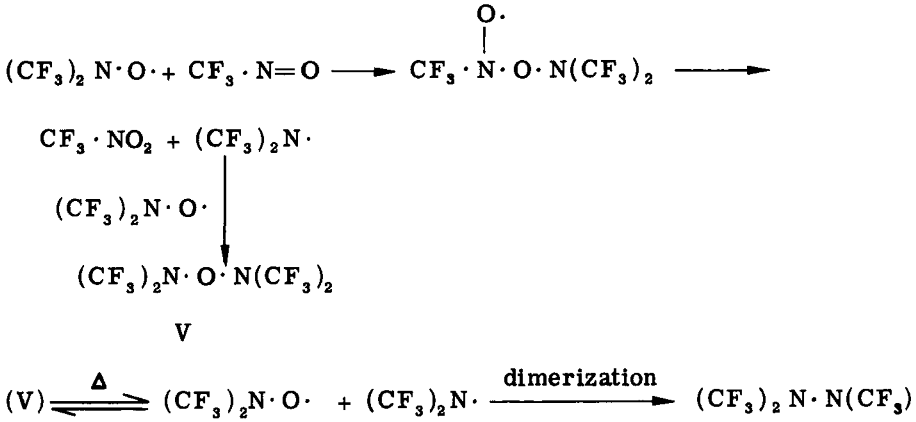
$$2CF_3\cdot NO + C_2F_4 + PCl_3 \longrightarrow \text{IV} \xrightarrow{H_2O} CF_3\cdot N(OH)\cdot CF_2\cdot CF_2\cdot N(OH)\cdot CF_3 \xrightarrow{KMnO_4} CF_3\cdot N(O\cdot)\cdot CF_2\cdot CF_2\cdot N(O\cdot)\cdot CF_3$$

Structure IV [23] for the heterocycle obtained from trifluoronitrosomethane, tetrafluoroethylene, and phosphorus trichloride has been challenged [24], the alternative proposal being



A mixture of trifluoronitrosomethane (24.96 g, 252.1 mmoles), tetrafluoroethylene (12.61 g, 126.1 mmoles), and phosphorus trichloride (21.43 g, 157.6 mmoles) was stored in a cold (-32°C) evacuated Pyrex flask (1150 cm^3) for 19 days. The involatile liquid product (43.46 g) was added dropwise, with stirring, to cold (0°C) water during a 3-hr period; the solution produced was filtered to remove traces of white solid, then treated with saturated silver nitrate solution (61 cm^3) to remove chloride ion (failure to do so can result in the formation of an explosive by-product [15]). Silver chloride was removed by filtration, and the filtrate was added slowly to a hot (90°C) stirred solution of potassium permangante (100 g) in 10% aqueous sulfuric acid (200 cm^3) contained in a 3-liter round-bottomed Pyrex flask equipped with an air bleed and a water-cooled reflux condenser leading to a train of five cold (-196°C) traps and thence to a vacuum pump. The pressure in the apparatus was reduced to ~20 cm Hg so that volatile product was carried continuously into the traps by a stream of air. Trap-to-trap fractional distillation, in vacuo, of the material that collected in the cold traps provided perfluoro-2,5-diazahexane-2,5-dioxyl (18.26 g, 61.27 mmoles; 49%) (Found: C, 16.4; N, 9.5%; M [Regnault's method], 296. $C_4F_{10}N_2O_2$ requires C, 16.1; N, 9.4%; M, 298) as a deep purple liquid, bp 55°C at 769 Torrs. The dioxyl attacks hydrocarbon stopcock grease, giving the hydroxylamine $CF_3\cdot N(OH)\cdot CF_2\cdot CF_2\cdot N(OH)\cdot CF_3$, which is probably toxic like the monohydroxylamine $(CF_3)_2N\cdot OH$; it is best stored at low temperatures (0°C) in the dark in ampules fitted with glass-polytetrafluoroethylene needle valves.

Polymeric N—O—N Compound. The monoradical bistrifluoromethyl nitroxide combines readily with trifluoronitrosomethane to give the monomeric N—O—N compound perfluoro-(2,4-dimethyl-3-oxa-2,4-diazapentane) (V), [25], which dissociates into the parent nitroxide and bistrifluoromethylamino radical at 65°C [26]:



$$(CF_3)_2N\cdot O\cdot + CF_3\cdot N{=}O \longrightarrow CF_3\cdot \overset{O\cdot}{\overset{|}{N}}\cdot O\cdot N(CF_3)_2 \longrightarrow$$

$$CF_3\cdot NO_2 + (CF_3)_2N\cdot \quad (CF_3)_2N\cdot O\cdot \longrightarrow (CF_3)_2N\cdot O\cdot N(CF_3)_2$$

V

$$(V) \overset{\Delta}{\rightleftharpoons} (CF_3)_2N\cdot O\cdot + (CF_3)_2N\cdot \xrightarrow{\text{dimerization}} (CF_3)_2N\cdot N(CF_3)$$

This reaction was applied to the bisnitroxide $\cdot O\cdot N(CF_3)\cdot CF_2\cdot CF_2\cdot N(CF_3)\cdot O\cdot$ in an attempt to prepare the polymeric N—O—N compound $+N(CF_3)\cdot CF_2\cdot CF_2\cdot N(CF_3)\cdot O+_n$ for use as a relatively involatile thermal source of diradicals capable of cross-linking $CF_3\cdot NO/C_2F_4/C_4F_6$ copolymers.

Perfluoro-2,5-diazahexane-2,5-dioxyl (3.81 g, 12.8 mmoles) and trifluoronitrosomethane (2.52 g, 25.6 mmoles) were condensed in vacuo in a 300-cm^3 Pyrex tube, which was sealed and shaken for 3 days in the dark at room temperature. The volatile product (a mixture of $CF_3\cdot NO$, $CF_3\cdot NO_2$, and $CF_3\cdot N{:}CF_2$, identified by IR spectroscopy) was transferred to the vacuum system, leaving an involatile pale purple liquid (1.6 g) in the reaction vessel. The ESR spectrum of a solution of the liquid in perfluorotributylamine was not well resolved and showed variation in line width, but the 8-line signal was consistent with the presence of nitroxide radicals. The mass spectrum of volatile material obtained by heating the liquid at 150°C in the inlet of the spectrometer showed a series of peaks at masses n × 149 and 50 + (n × 149) which could be attributed to $\left[CF_2 \cdot N(CF_3) \cdot O \right]_x$ and $-CF_2\left[CF_2 \cdot N(CF_3) \cdot O \right]_x$ units, respectively. Mass peaks corresponding to values of x up to 5 were observed. From these considerations, it has been tentatively concluded that the liquid product is a copolymer containing units of the type

$$\left[N(CF_3) \cdot CF_2 \cdot CF_2 \cdot N(CF_3) \cdot O \right] \quad \text{and} \quad \left[CF_2 \cdot N(CF_3) \cdot O \right]$$

Microanalysis showed that the liquid contained 16.9 C, 63.2 F, and 9.7% N compared with expected values 17.0 C, 67.4 F, and 9.9% N for the first structural unit and 16.1 C, 63.7 F, and 9.4% N for the second.

Cross-linking

The gummy Copolymer A was compounded with the cross-linking agent simply by mixing the weighed components in a small weighing bottle using a spatula. This operation was carried out in a fume cupboard when the dioxyl was used as the vulcanizing agent, owing to its volatility and potential toxicity. Only the polymeric derivative of the dioxyl was used in cross-linking experiments with the high molecular weight fraction of Copolymer B; the latter was an elastomeric solid and compounding was carried out by mixing the weighed components in the presence of 1,1,2-trichlorotrifluoroethane until a homogeneous dough was obtained, after which the solvent was pumped off.

Cross-linking was carried out in a small hydraulic press, the platens of which were equipped with thermostatically controlled electrical heaters. Compounded samples were placed in a small rectangular steel mold (2 × 0.5 × 0.01 in.) between PTFE sheets (thickness ~0.05 in.) and molded and cured in the press at a pressure of 1000 psi. The use of PTFE sheets overcame difficulties caused by adhesion of samples to metal plates; it did, of course, increase the time taken for a sample to reach platen temperature.

A qualitative indication of the degree of cross-linking in a sample of cured copolymer was obtained by determining its V_r value, i.e., the ratio of the volume of the "dry" rubber to that of the swollen network formed in the presence of a solvent for the linear copolymer. An accurately weighed, thin strip (0.1 to 0.2 g) of cured copolymer was immersed in 1,1,2-trichlorotrifluoroethane contained in a stoppered vessel which was kept in a thermostat at 28°C. After 72 hr the swollen strip was taken from the solvent, quickly freed from surface liquid by gently wiping it with filter paper, and weighed in a stoppered vessel. The rubber was "dried" to constant weight by evaporation of the solvent at 30°C. From the differences in weights and the densities of elastomer (1.86 g/cm^3 at 25°C) and solvent, the V_r and gel content were calculated. When a filler was incorporated in the rubber, the necessary modification was made in the calculations.

RESULTS

Cross-linking with Hexamethylenediamine Carbamate

The results of experiments with Copolymer A are shown in Table 1; curing times are molding periods, and the temperatures are those of the press platens.

Cross-linking with Perfluoro-2,5-diazahexane-2,5-dioxyl

The results of experiments conducted with Copolymer A are shown in Table 2. Note that the dioxyl contents are based on the final weights

TABLE 1. Cross-linking of Copolymer A with HMDC

Sample	Compounding, parts (wt) per 100 parts copolymer		Curing cycle	V_r	Gel (%)
1	HMDC MgO	16 5	10 minutes at 150°C	0.38	71.2
2	HMDC MgO Silica (Aerosil)	8 5 8	As 1	0.39	69.0
3	As 2		As 1 + 30 min at 175°C in air	0.35	73.4

TABLE 2. Cross-linking of Copolymer A with Perfluoro-2,5-diazahexane-2,5-dioxyl

Sample	Dioxyl content pph copolymer	Curing temperature (°C)	Curing time (hr)	V_r	Gel (%)
4	10	20	0.5	0.10	33.0
5	10	20	1.5	0.20	40.4
6	10	20	4	0.29	51.0
7	10	20	24	0.29	58.2
8	10	20	48	0.32	64.6
9	10	20	72	0.29	59.0
10	10	20	168	0.33	60.9
11	10	50	2	0.32	63.0
12	10	80	1	0.30	63.2
13	10	125	0.5	0.35	68.0
14	0.5	125	0.5	0.05	-
15	3.5	125	0.5	0.25	59.0
16	7	125	0.5	0.34	67.1
17	11	125	0.5	0.35	68.2

of the compounded mixtures prepared in weighing bottles, and that some losses were likely owing to volatilization during transfer to the mold. In all cases the purple color of the dioxyl, seen in freshly compounded samples, had disappeared after molding.

The relative intensities of the C═C stretch absorptions at 5.8 and 5.6 μm in the IR spectra of raw Copolymer A and the cured Samples 14, 15, 16, and 17 are shown in Fig. 1.

Cross-linking with the Polymeric N—O—N Compound

In a preliminary experiment it was found, by visual observation, that the polymeric N–O–N derivative of the dioxyl decomposed at ~150°C when heated in a sealed evacuated tube. The results of experiments in which Copolymer A was cross-linked by means of this polymeric derivative at 155°C are given in Table 3. Two samples

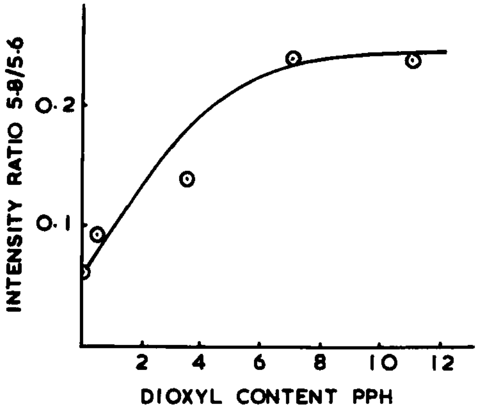


FIG. 1. Relative intensities of the C=C absorptions at 5.8 and 5.6 μm in the IR spectra of raw Copolymer A and samples of this copolymer cured using the dioxyl.

TABLE 3. Cross-linking of Copolymer A with the Polymeric N—O—N Derivative of the Dioxyl at 155°C

Sample	Content of polymeric derivative pph copolymer	Curing time (hr)	V_r	Gel (%)
18	2	4	0.07	-
19	5	4	0.15	-
20	10	4	0.30	65.8
21	15	4	0.33	71.2
22	20	4	0.35	72.8
23	10	0.5	0.21	32.5
24	10	1.5	0.28	65.7
25	10	2.5	0.29	66.8

of the highest molecular weight fraction of Copolymer B were cross-linked using the polymeric N—O—N derivative of the dioxyl; the results are given in Table 4.

TABLE 4. Cross-linking of Copolymer B with the Polymeric N—O—N Derivative of the dioxyl at 155 °C

Sample	Compounding pph copolymer		Curing time (hr)	V_r	Gel (%)
26	Polymeric derivative of dioxyl	10	3	0.45	94.0
27	Polymeric derivative of dioxyl Silica (Aerosil)	10 15	3	0.49	92.3

Thermal Analysis

Differential thermal analysis showed that the glass transition temperature of raw Copolymer A was -46° C. The glass transition temperatures of samples of cross-linked Copolymer A were all slightly higher than that of the raw copolymer, Sample 22 having the highest T_g (-41° C). All analyses were carried out under nitrogen with a heating rate of 15° C/min.

Samples were subjected to thermogravimetric analysis at a heating rate of 15° C/min under a slow current of oxygen-free nitrogen. The results obtained for raw Copolymer B and for the three fractions of this material are shown in Fig. 2. The onset of weight-loss occurred at 70° C for Copolymer B and at 65, 185, and 200° C for Fractions 3, 2, and 1, respectively. All samples degraded completely, leaving no residue. Fractions 1 and 2 gave almost identical overall results.

The results obtained in thermogravimetric analyses of cross-linked samples of Copolymer A are given in Fig. 3. The onset of weight loss occurred at 80° C for the gel content (i.e., the residue from V_r determination) of Sample 1 (HMDC cure). This sample contained involatile compounding material, and allowance has been made for this in calculating the weight of polymer in the sample at each temperature. For the gel contents of Samples 17 and 20 (dioxyl cure and polymeric derivative cure, respectively) the onset of weight loss occurred at about 210° C, whereas for the unextracted (i.e., gel + sol) samples the onset temperature was 100° C.

The results obtained for a sample of Copolymer B, Fraction 1, cross-linked with the polymeric derivative of the dioxyl, are compared in Fig. 4 with those obtained with the raw copolymer fraction. The onset of weight loss in the unextracted cross-linked material occurred

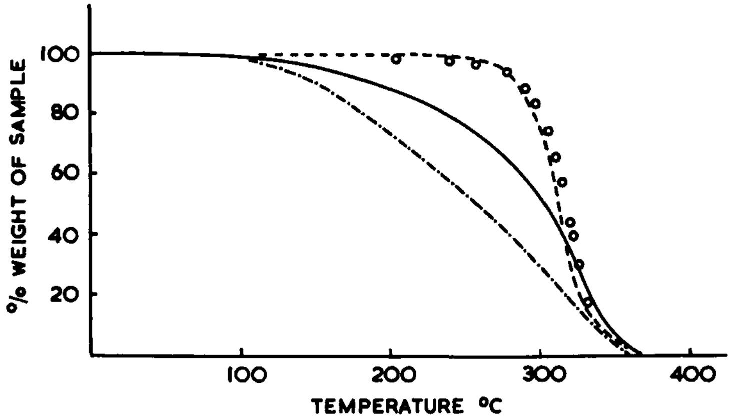


FIG. 2. Thermogravimetric analysis of raw Copolymer B. (—) Copolymer B; (--) Copolymer B, Fraction 1; (○) Copolymer B, Fraction 2; (-·) Copolymer B, Fraction. 3.

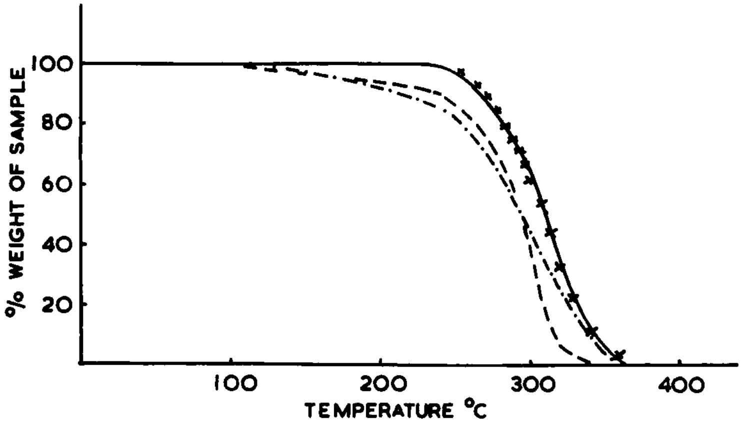


FIG. 3. Thermogravimetric analysis of cured samples of Copolymer A. (--) Gel fraction, Sample 1; (—) gel fraction, Sample 17; (×) gel fraction, Sample 20; (-·) Sample 17 before V_r determination.

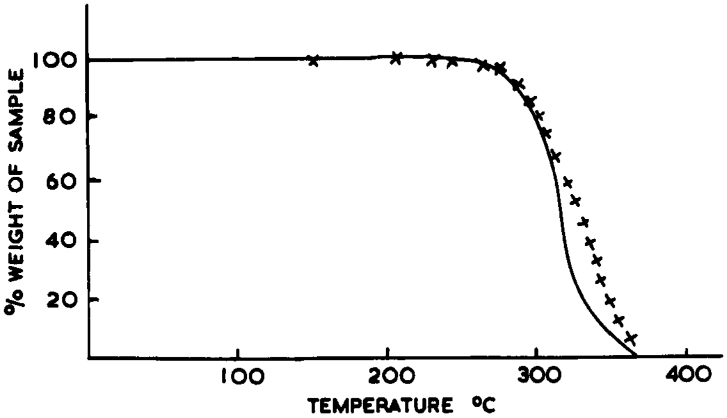


FIG. 4. Thermogravimetric analysis of Copolymer B, Fraction 1, cured with the polymeric N—O—N derivative of the dioxyl. (—) Raw Copolymer B, Fraction 1; (×) Sample 26.

at 150°C, but the overall results for the two samples are almost identical over the first 40% of degradation.

DISCUSSION

Fractionation of $CF_3 \cdot NO/CF_2{=}CF_2/CF_2{=}CF \cdot CF{=}CF_2$, Copolymer B, showed that the yield of high-molecular-weight material present was low; this seems to be characteristic of nitroso copolymerization systems. Morneau et al. [27] have reported similar results from their more extensive work on the fractionation of $CF_3 \cdot NO/CF_2{=}CF_2$ copolymers, and they also determined the constants K (= 8.77×10^{-5} dl/g) and α (= 0.66) in the Mark-Houwink equation, $[\eta] = K\overline{M}_w^{\alpha}$, relating the intrinsic viscosity of a solution of a $CF_3 \cdot NO/C_2F_4$ copolymer in perfluorotributylamine at 25°C with the weight-average molecular weight of the copolymer. If these data are assumed to be valid for solutions of the copolymers prepared in the present work, then $\overline{M}_w$ of Copolymer B was of the order 1.3×10^5, while for Fractions 1, 2, and 3 of this material the averages were of the order 5.2×10^5, 2.4×10^5, and 1.1×10^3, respectively.

The presence of low molecular weight material explains the lower gel contents and V_r values of the products obtained by cross-linking unfractionated Copolymer A as compared with those of cross-linked Fraction 1 of Copolymer B. Evidently a considerable proportion of the unfractionated copolymer either had too low a molecular weight to be incorporated into the network or did not contain a hexafluorobutadiene structural unit. The unfractionated gummy copolymer was, nevertheless, used in much of the present work in order to conserve material and because it was much easier to compound in small-scale testing of the efficacy of curing agents.

The effect of low-molecular-weight materials can also be seen in the results of thermogravimetric analyses. True thermal degradation of the raw high-molecular-weight fractions of Copolymer B and of the gel fractions of copolymers cured with cross-linking agents other than hexamethylenediamine did not commence until temperatures in the range of 200 to 220° C had been reached. Unfractionated raw Copolymer B, the low-molecular-weight fraction of this raw copolymer, and cured copolymers not treated with solvent all began to lose weight at temperatures below 200°C, owing to volatilization of low-molecular-weight material. Similar effects have been observed [10] in thermogravimetric analyses of copolymers of $CF_3 \cdot NO$ with C_2F_4.

Hexamethylenediamine carbamate has been used as a cross-linking agent for $CF_3 \cdot NO/C_2F_4/C_4F_6$ copolymers (Table 1) and for polyhexafluorobutadiene [28]. It seems likely that, in both cases, cross-linking occurs by reaction of the diamine with backbone and pendant unsaturation, successive addition and HF-elimination reactions taking place, as suggested to explain the postdehydrofluorination steps in the cross-linking of Viton with diamines [29]. The thermal stabilities of the gel fractions of the diamine-cured copolymers were significantly lower than that of the raw high-molecular-weight fraction of Copolymer B (Figs. 2 and 3). In this respect the amine-cured copolymers are similar to the amine-cured $CF_3 \cdot NO/C_2F_4$ copolymers.

The results presented in Table 2 show that the diradical perfluoro-2,5-diazahexane-2,5-dioxyl is an effective cross-linking agent for $CF_3 \cdot NO/C_2F_4/C_4F_6$ copolymers at temperatures ranging from 20 to 125° C, a result of clear technological potential which provides a room-temperature cure. Diradical contents of the order of 7 to 8 parts per hundred of copolymer are necessary for an optimum cure, and amounts in excess of this do not cause significant changes in V_r and gel content. Thermogravimetric analyses show that the thermal stabilities of copolymers cross-linked with the dioxyl (or with its polymeric N—O—N derivative) are identical with that of the raw copolymer; this is to be expected if the chemical structure of the cross-links is closely similar to that of the main polymer chains.

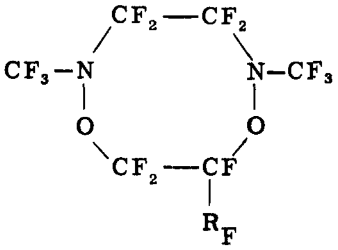
Cross-linking Mechanism

Bistrifluoromethyl nitroxide, the monofunctional analog of perfluoro-2,5-diazahexane-2,5-dioxyl, readily attacks C=C bonds in fluorinated olefins to yield 2:1 adducts, e.g.,

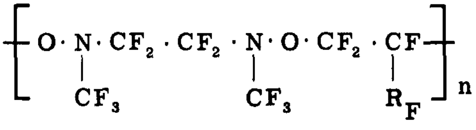
$$(CF_3)_2N\cdot O\cdot \; + \; CF_2{=}CF_2 \longrightarrow \underset{\text{VI}}{[(CF_3)_2NO\cdot CF_2\cdot CF_2\cdot]} \xrightarrow{(CF_3)_2N\cdot O\cdot}$$

$$\underset{\text{VII}}{(CF_3)_2N\cdot O\cdot CF_2\cdot CF_2\cdot O\cdot N(CF_3)_2}$$

Scavenging of intermediate radicals such as VI by the nitroxide is so efficient that even in experiments designed to produce telomeric material, a 2:1 adduct (e.g., VII) is the predominant or even exclusive product [25]. Such scavenging is believed to lie behind the failure to cross-link $CF_3\cdot NO/C_2F_4/C_4F_6$ copolymers effectively with bistrifluoromethyl nitroxide [30].



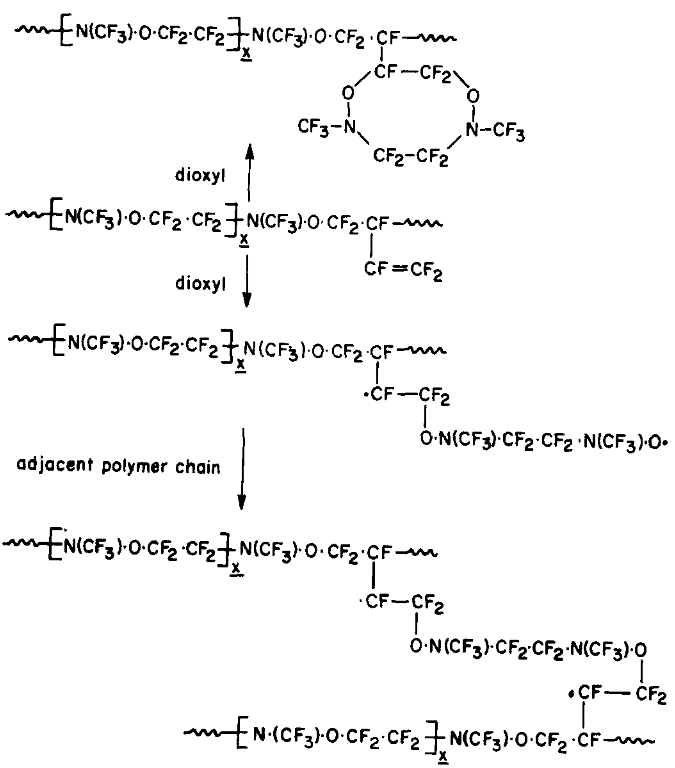
VIII



$$\left[O\cdot \underset{CF_3}{N}\cdot CF_2\cdot CF_2\cdot \underset{CF_3}{N}\cdot O\cdot CF_2\cdot \underset{R_F}{CF} \right]_n$$

IX

Perfluoro-2,5-diazahexane-2,5-dioxyl readily attacks the perfluoroolefins $CF_2{=}CFR_F$ (R_F = F or CF_3) to yield eight-membered heterocycles (VIII) and nitroso rubbers (IX), the relative proportion of each product depending on conditions, production of the latter being much favored by use of low temperatures and condensed phase systems [15]. Attack of the dioxyl on $CF_3\cdot NO/C_2F_4/C_4F_6$ copolymers is thus readily envisaged to involve both the formation of cross-links via a "polymerization" sequence and noncure consumption of the diradical through cyclization reactions. These proposals are exemplified in Scheme 1; similar reactions involving the backbone



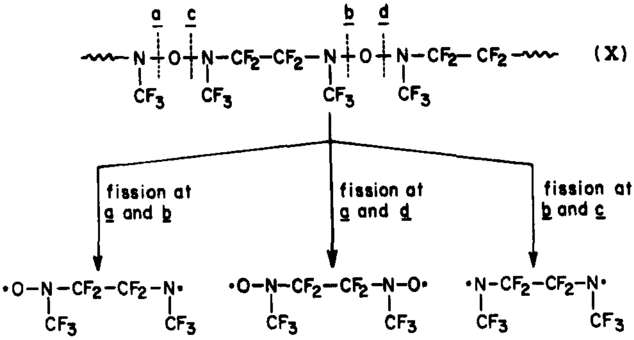
SCHEME 1

—CF=CF— sites are also possible, but the IR data (see Fig. 1) reveal that attack at the less hindered pendant olefinic sites is preferred. IR analysis also revealed the presence of residual unsaturation, as expected, since the amount of dioxyl necessary for optimum cure (7 to 8 parts per hundred of copolymer) corresponded to approximately one diradical molecule for every five C=C sites. The presence of residual unsaturation, and hence sites for chemical attack, may be undesirable in such a special purpose rubber; work now in progress may eliminate this feature of the cure.

The high volatility of the dioxyl (bp 55°C at 769 Torrs) requires that care must be taken during compounding, but the polymeric N—O—N derivative

$$\left[N(CF_3)\cdot CF_2\cdot CF_2\cdot N(CF_3)\cdot O \right]_n$$

is easily mixed with nitroso rubbers and provides diradicals during a thermal cure procedure (see Scheme 2). As explained earlier, the product of the reaction of perfluoro-2,5-diazahexane-2,5-dioxyl with



SCHEME 2

trifluoronitrosomethane at room temperature was not the "pure" N—O—N polymer X, and appears to possess a hybrid structure incorporating the $-N(CF_3)\cdot O\cdot CF_2-$ unit. The success of this copolymer as a cross-linking agent for unsaturated nitroso rubbers can be ascribed to homolysis of the N—O linkages in the N—O—N structures present; the part, if any, played by the N—O—C— units present may be revealed by work on the synthesis of the homopolymer $\mathrm{+N(CF_3)\cdot O\cdot CF_2+_n}$ currently in progress.

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