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π-BIS(BENZENE)CHROMIUM(0) CATALYZED COOLIGOMERIZATION OF PERFLUOROPROPYLENE AND PERFLUOROBUT-2-YNE

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SUMMARY

Perfluoropropylene and perfluorobut-2-yne can be polymerized in the presence of π-bis(benzene)chromium(0) in pyridine solution. The liquid products are separated by preparative gas chromatography showing that they are homooligomers, cooligomers, and the HF addition products. The structures of the compounds 1, 2, 3, 4, 5, 6, 7 are identified with MS and NMR, and the probable structures of 8, 9, 10 and 11 are deduced by GC-MS.

INTRODUCTION

In our previous publications, we reported that π-bis-(arene)chromium(0) could catalyze oligomerization of perfluoropropylene in benzene or THF solution to give two dimers, two trimers and two defluorotrimers[1]. The formation of the latter was attributed to the hydrogenation of one of the trimers followed by dehydrofluorination, and HF evolved added to perfluoropropylene to give 2-hydroheptafluoropropane. The hydrogen source for

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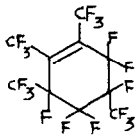
hydrogenation was found to arise from the ligand of the catalyst, presumably through π-σ rearrangement [2]. The same catalyst could catalyze perfluorobut-2-yne in benzene solution to give an insoluble white polymer [3] while in pyridine solution it gave soluble black polymers [4]. It could also catalyze perfluoro-2-alkynenitriles in benzene/pyridine solution to give soluble black polymer [5]. Both soluble polyperfluorobut-2-yne and soluble polyperfluoroalkynenitriles are linear in structures and possess weak electric conductivity.

As for the copolymerization of perfluoropropylene and perfluorobut-2-yne, Jackson et al. reported that it was unobtainable by potassium fluoride catalyst [6]. However, we found that π-bis(benzene)chromium(O) in benzene solution was able to catalyze the copolymerization of these two monomers to give solid copolymer, characterized by the presence of characteristic band CF_3-$\overset{|}{C}F$ in IR [7] and Chambers et al.[8]. achieved the cooligomerization by CsF catalyst, and identified two of their products as



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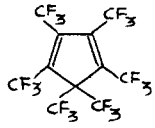


RESULTS AND DISCUSSION

We would like to report in this paper the results of the oligomerization and cooligomerization of perfluoropropylene and perfluorobut-2-yne catalyzed by π-bis(benzene)chromium(O) in pyridine solution. Besides a large amount of a brown solid copolymer, the liquid obtained was found to be a mixture of homooligomers, cooligomers and their HF addition products. Figure 1 shows the chromatogram of the liquid products.

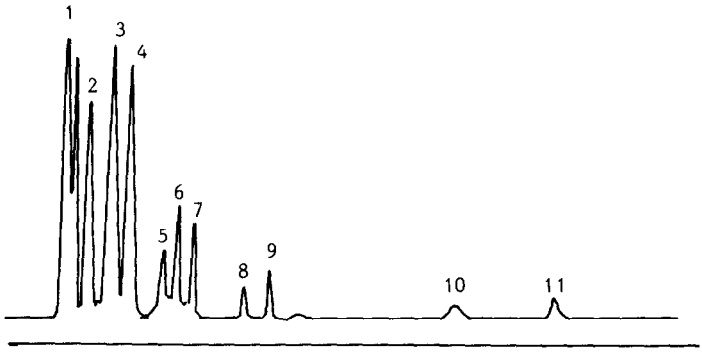


Fig. 1. Gas chromatogram of liquid products formed from oligomerization and cooligomerization of perfluoropropylene and perfluorobut-2-yne catalyzed by π-bis-(benzene)chromium(0) in pyridine solution. Stationary phase: 16% Perfluorotriazine on 102 white support. Column Length, 4M; Temp. of vaporization, 150°C. Flow rate of N_2, 20ml/min. Detector, thermoconductor.

Products of peaks 1, 2, 3, 4, 6, 7 were separated by preparative gas chromatography, their MS, NMR data and structures are shown in Table 1.

The product 1 isolated from peak 1 is identified as a mixture of dimers of perfluoropropylene which we had reported previously, and 2 isolated from peak 2 is the HF addition product of 1a. Product 3 isolated from peak 3 is the dimer of perfluorobut-2-yne while 4 is one mole more HF addition product of 3. Product of peak 5 is identified as cooligomer of 2 moles of perfluoropropylen and 1 mole of perfluorobut-2-yne by GC-MS. The MS data of the product of peak 5, M^+=462, is in complete coincidence with that found by Chambers et.al., and the retention time of gas chromatography was found to be identical with the sample prepared by Chambers's method. Product 7 isolated from peak 7, M=474, is identified as cooligomer of 1 mole of perfluoroprpopylene and 2 moles of perfluorobut-2-yne, while from peak 6 is its isomerized product.

TABLE 1

Structures, MS, and NMR of the Compound Isolated from Each Peak

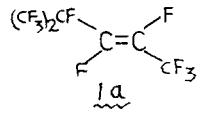
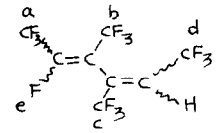
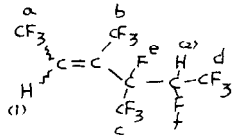
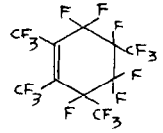
Peak	Structure	M/E	^{19}F NMR(TFA,external) ^{1}H NMR(TMS,external) δ ppm
1	 1a $(CF_3)_2C=CFCF_2CF_3$ 1b	M^+=300(C_6F_{12})	^{19}F NMR was found in coincidence with that reported in the lit.[1]
2	$(CF_3)_2CH-CF_2CF_2CF_3$	M^+-19=301($C_6F_{12}H$), 213(C_5F_8H), 201(C_4F_8H), 169(C_3F_7), 119(C_2F_5), 100(C_2F_4), 93(C_3F_3), 69(CF_3)	F(a) -14.3(6F); F(b) +49.5(2F); F(c) +35.9 (2F); F(d) +4.6(3F);
3		M^+=344($C_8F_{13}H$), 325($C_8F_{12}H$), 275($C_7F_{10}H$), 255(C_7F_9), 237 (C_7F_8H), 187(C_6F_6H), 113(C_3F_4 H), 93(C_3F_3), 69(CF_3)	F(a),(b),(c),(d): -15.7 (3F), -13.8(3F), -7.6 (3F), -6.1(3F); F(e) +28.5(1F), H 6.63
4		M^+-19=345($C_8F_{13}H_2$), 325(C_8F_{12} H), 295($C_7F_{11}H_2$), 275($C_7F_{10}H$), 225(C_6F_8H), 207($C_6F_7H_2$), 163 (C_6F_4H), 119(C_2F_5), 113(C_3F_4H) 69(CF_3)	F(a),(b),(c),(d): -17.6 (3F), -13.4(3F), -10.0 (3F), -6.9(3F); F(e) +31.9(1F); F(f) 38.0 (1F); H(1) 6.64(1H); H(2) 3.79(1H)
5		M^+=462($C_{10}F_{18}$), 443($C_{10}F_{17}$), 393(C_9F_{15}), 355(C_9F_{13}), 343 (C_8F_{13}), 293(C_7F_{11}), 243(C_6F_9), 205(C_6F_7), 162(C_4F_6), 150(C_3F_6), 119(C_2F_5), 93(C_3F_3), 69 (CF_3)	^{19}F NMR was found in coincidence with that reported in the lit. [8]

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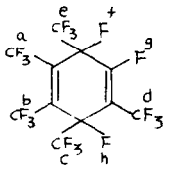
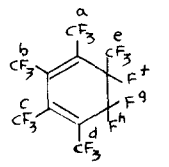
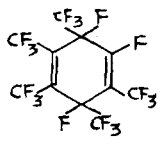
TABLE 1 (cont.)

Peak	Structure	M/E	^{19}F NMR(TFA, external) ^{1}H NMR(TMS, external) δ ppm
6		M^+=474($C_{11}F_{18}$), 455($C_{11}F_{17}$), 405($C_{10}F_{15}$), 355(C_9F_{13}), 317 (C_9F_{11}), 267(C_8F_9), 217(C_7F_7), 179(C_7F_5), 148(C_6F_4), 129(C_6F_3), 79(C_5F).	F(a),(b),(d), -2.9(9F); F(c),(e): -12.3(6F); F(g) +3.1(1F); F(f) +95.6(1F); F(h) 93.4(1F).
7		M^+=474($C_{11}F_{18}$), 455($C_{11}F_{17}$), 405($C_{10}F_{15}$), 355(C_9F_{13}), 317 (C_9F_{11}), 267(C_8F_9), 217(C_7F_7), 179(C_7F_5), 148(C_6F_4), 129(C_6F_3), 79(C_5F).	F(a),(b),(c): -6.1(9F); F(d) -18.6(3F); F(e) -20.1(3F); F(f) +83.0 (1F); F(g),(h): +11.5 (1F), +16.2(1F).



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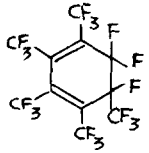

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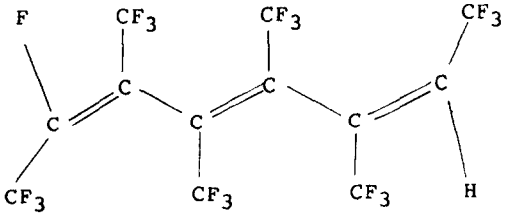
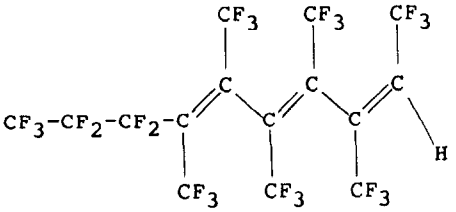
The amounts of the products 8, 9, 10, 11 of peaks 8, 9, 10, 11 are too small to be isolated by preparative gas chromatography. The GC-MS shows that 8, 9, M^+-19=487, are most likely to be a couple of isomers formed from trimer of perfluorobut-2-yne followed by addition of HF. Product 10, M^+-20=636, is a compound formed from one molecule of perfluoropropylene, three molecules of perfluorobut-2-yne followed by addition of one moledcule of HF. Product 11 is the HF addition product of tetramer of perfluorobut-2-yne.



8 and 9

M^+-19(F)=487($C_{12}F_{18}H$), 437($C_{11}F_{16}H$), 399($C_{11}F_{14}H$), 387 ($C_{10}F_{14}H$), 349($C_{10}F_{12}H$), 299($C_9F_{10}H$), 249(C_8F_8H), 119 (C_2F_5), 93(C_3F_3), 69(CF_3).



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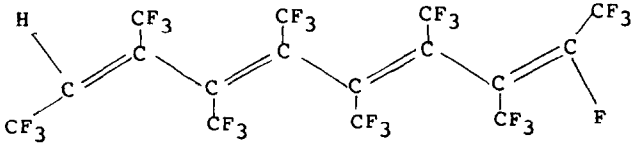
M^+-20(HF)=636($C_{15}F_{24}$), 617($C_{15}F_{23}$), 567($C_{14}F_{21}$), 529 ($C_{14}F_{19}$), 479($C_{13}F_{17}$), 429($C_{12}F_{15}$), 379($C_{11}F_{13}$), 341 ($C_{11}F_{11}$), 291($C_{10}F_9$), 241(C_9F_7), 169(C_3F_7), 93(C_3F_3), 69 (CF_3).



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M^+-19(F)=649($C_{16}F_{24}H$), 599($C_{15}F_{22}H$), 561($C_{15}F_{20}$), 511 ($C_{14}F_{18}H$), 461($C_{13}F_{16}H$), 442($C_{13}F_{15}H$), 373($C_{12}F_{12}H$), 323 ($C_{11}F_{10}H$), 299($C_9F_{10}H$), 265($C_{11}F_7$), 223(C_9F_6H), 181 (C_4F_7), 163(C_4F_6H), 119(C_2F_5), 93(C_3F_3), 69(CF_3).

The residual solid has absorption band $CF_3\overset{|}{C}F$ 980 cm^{-1} in IR, showing it is a copolymer of perfluoropropylene and perfluorobut-2-yne.

EXPERIMENTAL

^{19}F and ^{1}H NMR was determined with Varian EL-360, and GC-MS was determined with Finnigan-4021, IR with Perkin-Elmer 559, GC with Shanghai Factory of Analysis Instrument G-102.

A 80 ml sealed tube, flushed with O_2-free N_2, was charged with 25 ml of pyridine solution of π-bis-(benzene)chromium(0)(0.24 mmol). After cooling in a solid CO_2 / acetone bath, the sealed tube was evacuated, filled with N_2 and the process repeated several times. Into the tube was then charged 6g of perfluorobut-2-yne. and 10g of perfluoropropylene. After sealing, the sealed tube was taken out from the cooling bath and allowed to stand for 72 hr. The product was distilled and 5.4 g of liquid was obtaind. The residue was boiled with 6N of HCl for 2hr. then washed with water till the aqueous solution was neutral and dried. 7.6 g of black-brown solid was obtained.

ACKNOWLEDGEMENTS

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