Cotrimerization of mono- and dinitriles of perfluorocarboxylic acids under high pressures

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Cotrimerization of mono- and dinitriles of perfluorocarboxylic acids under high pressures affords oligoperfluoroalkylenetriazines. These oligomers are highly efficient stabilizers of thermooxidative destruction of perfluoropolyethers, when they are contacting with metals at elevated temperatures.

Key words: nitriles of perfluorocarboxylic acids, cotrimerization; perfluoropolyethers; stabilizers of thermal destruction; high pressure.

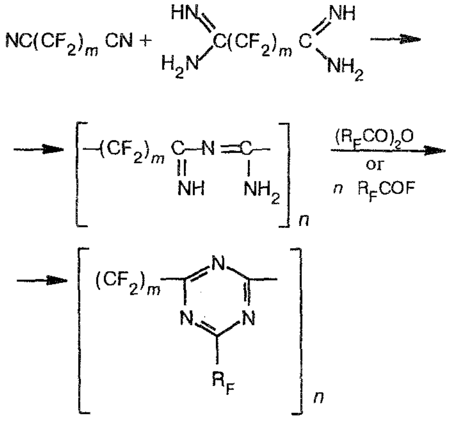
Oligo- and polyperfluoroalkylenetriazines are usually prepared by reactions of dinitriles of perfluorocarboxylic acids with their diamidines in a solvent. The intermediate oligo- and polyperfluoroalkyleneimidoylamidines produced in these reactions are converted into the corresponding triazine derivatives by acylation—cyclodehydration with anhydrides of perfluorocarboxylic acids or perfluoroacyl fluorides[1,2] (Scheme 1).

The process yields perfluorocarboxylic acids as by-products, and these should be thoroughly separated from triazines.

Previously[3] we have shown that at 110—124 °C under high pressures (300—1400 MPa), in the presence of amidines of perfluorocarboxylic acids as catalysts, mononitriles of perfluorocarboxylic acids are converted into tris(perfluoroalkyltriazines) in quantitative yields.

In the present work we have found that cotrimerization of mono- and dinitriles of perfluorocarboxylic acids in the presence of amidines and imidoylamidines of perfluorocarboxylic acids under high pressures (300—1400 MPa) allows one to obtain soluble oligoperfluoroalkylenetriazines (Scheme 2, Tables 1 and 2) that contain no cyanoperfluoroalkyl groups, according to NMR and IR spectroscopy data.

Scheme 1



Perfluoropolyethers, which are used at present as the base of nonfreezing aggressive-resistant lubricants, undergo thermal destruction at elevated temperatures in

Table 1. Some characteristics of oligoperfluoroalkylenetriazines prepared by cotrimerization of $NC(CF_2)_6CN$ with mononitriles of perfluorocarboxylic acids under high pressure

Specimen of the oligomer	Mononitrile	Ratio between di- and mononitriles (mol. %)	Molecular weight of the oligomer* (M)	Degree of polymerization (*n*)	T_g /°C
1	$CF_3O(CF_2CF_2O)_3CF_2CN$	1 : 2.34	3030	0.37	−85
2	$CF_3O(CF_2CF_2O)_3CF_2CN$	1 : 1.75	3220	0.48	−82
3	$CF_3O(CF_2CF_2O)_3CF_2CN$	1 : 1.60	3500	0.65	−80
4	$CF_3O(CF_2CF_2O)_3CF_2CN$	1 : 1.40	5170	1.50	−80
5	$CF_3O(CF_2O)_4CF_2CN$	1 : 1.40	9090	2.64	−94

* Determined by ebullioscopy in C_6F_6.

[†] Deceased.

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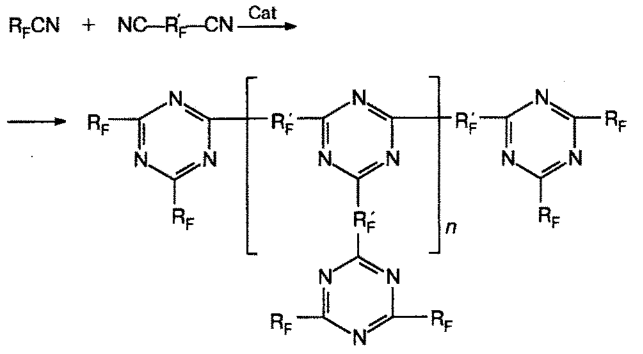
Table 2. Some characteristics of oligoperfluoroalkylenetriazines prepared by cotrimerization of di- and mononitriles of perfluorocarboxylic acids under high pressure

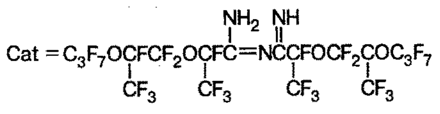
Specimen of the oligomer	Reactants*	Ratio between di- and mononitriles (mol. %)	Molecular weight of the oligomer** (M)	Average degree of polymerization (*n*)	T_g /°C
6	$NCCF_2O(CF_2CF_2O)_{5.48}CF_2CN$, $CF_3O(CF_2CF_2O)_{4.85}CF_2CN$	1 : 2	3400	0	−112
7	$NCCF_2O(CF_2CF_2O)_{5.48}CF_2CN$, $CF_3O(CF_2CF_2O)_{4.85}CF_2CN$	1 : 1.6	3430	0	−108
8	$NCCF_2O(CF_2CF_2O)_{5.48}CF_2CN$, $CF_3O(CF_2CF_2O)_{4.85}CF_2CN$	1 : 1.3	10000	2	−107
9	$NCCF_2O(CF_2CF_2O)_4CF_2CN$, $CF_3O(CF_2O)_4CF_2CN$	1 : 1.3	6670	2	−129
10	$NCCF_2O(CF_2CF_2O)_4 CF_2CN$, $CF_3O(CF_2CF_2O)_6CF_2CN$	1 : 1.3	6900	1	−112

* The average compositions of the compounds were determined from the ^{19}F NMR spectra. ** Determined by ebullioscopy in C_6F_6.

Scheme 2



$R_F = CF_3O(CF_2O)_3CF_2, CF_3O(CF_2CF_2O)_3CF_2, CF_3O(CF_2CF_2O)_{4.85}CF_2;$
$R'_F = CF_2O(CF_2CF_2O)_4CF_2;$



$$\mathrm{Cat} = C_3F_7O\underset{CF_3}{\underset{|}{C}}FCF_2O\underset{CF_3}{\underset{|}{C}}F\overset{NH_2}{\overset{|}{C}}{=}N\overset{NH}{\overset{\|}{C}}\underset{CF_3}{\underset{|}{C}}FOCF_2\underset{CF_3}{\underset{|}{C}}OC_3F_7$$

the presence of metals or their oxides. In addition, under the action of the products of their decomposition, corrosion of the metal occurs. We found that the addition of 5 % (w/w) oligoperfluoroalkylenetriazines to a perfluoropolyether not only dramatically decreases its thermal destruction (Fig. 1), but also prevents the metal corrosion.

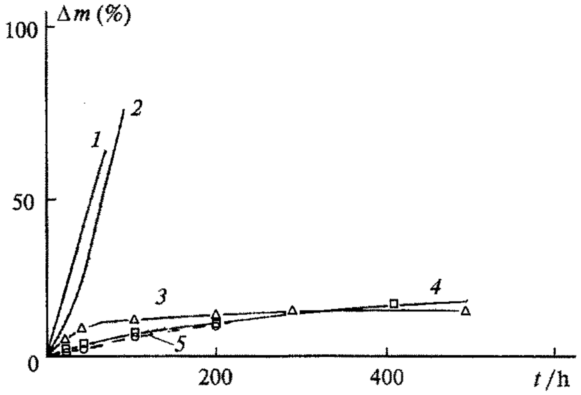


Fig. 1. Losses of the mass (Δ*m*) of perfluoropolyethers in the presence of steel-45 at 200 °C:
$CF_3O(CF_2O)_{42}(CF_2CF_2O)_{7.4}CF_3$ without the stabilizer (*1*);
$CF_3O(CF_2O)_{44}(CF_2CF_2O)_2CF_3$ without the stabilizer (*2*);
$CF_3O(CF_2O)_{42}(CF_2CF_2O)_{7.4}CF_3$ in the presence of 5 % (w/w) oligomer (specimen *2*, see Table 1) (*3*);
$CF_3O(CF_2O)_{44}(CF_2CF_2O)_2CF_3$ in the presence of 5 % (w/w) oligomer (specimen *2*, see Table 1) (*4*);
$CF_3O(CF_2O)_{44}(CF_2CF_2O)_2CF_3$ without the stabilizer and the metal (*5*).

Experimental

Cotrimerization of mono- and dinitriles of perfluorocarboxylic acids was carried out according to a procedure similar to that reported previously[3] using a high-pressure unit[4] in a Teflon reactor in the presence of 3 % (w/w) of the catalyst (see Scheme 2). Volatile products were evaporated from the reaction mixture at 150 °C (0.01 Torr) to give the light-yellow oligomer (in 90 % yield). The oligomer (100 mg) was placed in a glass tube; the tube was evacuated, sealed, and heated at the desired temperature for 1 h. Then the tube was connected to a manometer and an LKhM-8 MD chromatograph, and the gaseous products of destruction were analyzed. The temperature of the beginning of decomposition, detected by the appearance of gaseous destruction products, was 430—450 °C.

Steel-45 plates 20×20×2 mm in size (the purity achieved by the surface treatment corresponded to grade 7), 5 g of perfluoropolyether, $CF_3O(CF_2O)_{42}(CF_2CF_2O)_{7.4}CF_3$ (M = 3870) or $CF_3O(CF_2O)_{44}(CF_2CF_2O)_2CF_3$ (M = 4000), and 5 % (w/w) oligoperfluoroalkylenetriazine (specimen *2*, see Table 1) were placed in glass beakers with a diameter of 30 mm and a height of 50 mm. The beakers were kept in a thermostat at 200 °C and weighed at regular intervals. In two reference beakers with perfluoropolyethers, no oligoperfluorotriazines were added (see Fig. 1, curves *1* and *2*). Similar results were obtained, when other oligoperfluorotriazines were added to perfluoropolyethers.

The steel plates placed in the reference beakers corroded, while with oligoperfluorotriazines present only bluing of the surface occurred.

References

1. V. A. Ponomarenko, S. P. Krukovskii, and A. Yu. Alybina, in *Ftorsoderzhashchie geterotsepnye polimery* [*Fluorine-Containing Heterogeneous-Chain Polymers*], Nauka, Moscow, 1973, 230 (in Russian).
2. *Fluoropolymers*, Ed. L. Wall, New York, 1972.
3. V. A. Ponomarenko, T. N. Redina, A. A. Yarosh, A. A. Zharov, V. M. Zhulin, and A. V. Ignatenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1893 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **34**, 1755 (Engl. Transl.)].
4. G. I. Nikishin, S. S. Spektor, N. I. Kapustina, and E. P. Kaplan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1664 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25**, No. 7 (Engl. Transl.)].

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