Synthesis and characterization of fluorinated polyetheric amides

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Abstract

Di- and tetra-amides have been synthesized from the esters of perfluoropolyetheric mono- and di-carboxylic acids and ethylenediamine, hexamethylenediamine and piperazine, and characterized by viscosimetric and osmometric determinations, FT-IR, ^{1}H NMR and ^{19}F NMR spectra. They were also submitted to stability tests in acidic and basic media, by UV irradiation and heating.

The properties shown by the amides make them eligible as protective materials for stone exposed to atmospheric agents. Preliminary tests on the efficacy of these products on a bioclastic limestone (Pietra di Lecce) have provided very promising results.

Introduction

Perfluorinated organic molecules are chemically and thermally very stable due to the high energy of the C–F bond and to the deactivation induced by the electronegative fluorine atoms. They have been available for many years and, because of their unique properties, have found profitable uses for special technological applications. Perfluoropolyethers are being used as high-vacuum fluids, lubricants for electronic equipment, in the separation of oxygen from air, in the aeronautic and astronautic industries, and in the protection of stone [1, 2].

This last novel application requires products of good adhesion to stone, besides the properties normally conferred by perfluoropolyethers.

Several perfluoropolyethers are available, having somewhat different structures due to the different starting materials and procedures used for their preparation [3–7]. These products, Krytox, Fomblin, Demnum (Scheme 1), have average molecular weights in the range 1500–15 000, and chemical and physical properties which are not very different from each other [7].

Perfluoropolyethers are liquid materials having approximately the same chemical stability as polytetrafluoroethylene. Their properties make them eligible as protective agents for stone [8, 9]. The protection of stone exposed to atmospheric agents is carried out by applying to its surface products acting as water repellents which, as a result, reduce the contact and penetration of rain carrying contaminants.

$$CF_3CF{-}CF_2 \xrightarrow{\text{F}^-}$$

(epoxide O bridge)

$$CF_3CF_2CF_2O{-}(\underset{\underset{CF_3}{|}}{CF}{-}CF_2{-}O)_n{-}\underset{\underset{CF_3}{|}}{CF}COF \quad \text{(Krytox)}$$

$$CF_3CF{=}CF_2 + O_2 \xrightarrow{h\nu}$$

$$CF_3O{-}(\underset{\underset{CF_3}{|}}{CF}{-}CF_2{-}O)_m{-}(CF_2{-}O)_n{-}CF_3$$

$$\text{(Fomblin Y (YR))}$$

$$CF_2{=}CF_2 + O_2 \xrightarrow{h\nu}$$

$$CF_3O{-}(CF_2{-}CF_2{-}O)_m{-}(CF_2{-}O)_n{-}CF_3$$

$$\text{(Fomblin Z)}$$

$$\underset{\underset{CH_2{-}O}{|}}{CF_2}{-}\underset{|}{CF_2} \xrightarrow[F_2]{\text{F}^-}$$

$$F{-}(CF_2{-}CF_2{-}CF_2{-}O)_n{-}CF_2CF_3 \quad \text{(Demnum)}$$

Scheme 1.

The lone pair of electrons on the oxygen atoms, although deactivated by the fluorine present in the molecule, is responsible for the adhesion of these molecules to a supporting material. Such interaction, when the support is stone, is not very strong and not sufficient to keep this material in place: the fluorinated oil tends to flow slowly and to be absorbed by the porous structure, thus leaving its surface impoverished.

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As a consequence, the protective treatment loses its efficiency with time [10]. In response to the requirements of this application, we planned to synthesize new fluorinated products having similar chemical and thermal stability to those cited before, but bearing polar groups capable of 'fixing' them to the stone.

Photo-oxidation of hexafluoropropene leads to a poly(hexafluoropropan-ether) containing $-C_3F_6-$ units bound, head to tail, to oxygen atoms, with $-CF_2-$ and $-CF(CF_3)-$ groups statistically interposed. The polymeric chain is terminated by $-CF_3$ and $-COF$ groups in a 1:1 ratio [4, 6]. The $-COF$ group may be either $-CF_2COF$, acyl fluoride or $-OCOF$, fluoroformate.

The crude product from the photo-oxidation generally undergoes thermal (250 °C) treatment which leads to the destruction of all peroxidic derivatives and fluoroformates. After this treatment, the residue consists mainly of perfluoropolyetheric molecules terminated by the original $-CF_3$ groups, ketonic groups $-COCF_3$ and a few acyl fluorides. Subsequent treatment with KOH at 250 °C leads to a stabilized perfluorinated oil. When the temperature used for this treatment is limited to 100 °C, only the ketonic groups are eliminated and potassium salts of the perfluoropolyetheric monocarboxylic acids are obtained.

$$-OCF_2COCF_3 \begin{cases} \nearrow -OCF_2H + CF_3COOK \\ \searrow -OCF_2COOK + CF_3H \end{cases}$$
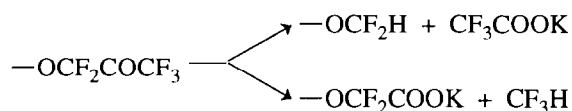
Perfluoropolyetheric carboxylic acids are very interesting products in the area of stone conservation because of the possibility that they offer, through their functional group, of binding these molecules to the stone support. The carboxylic acid cannot be used as such in the conservation of stone of artistic and historical relevance because it would react with the carbonates usually present, and would therefore lead to an irreversible transformation which is not desirable. Even the esters of these carboxylic acids cannot be used in this field for the same reason: once on the surface of the stone, exposed to atmospheric humidity, they hydrolyze with the formation of the free acid, thus creating all the problems mentioned above. The amide derivative of the carboxylic acid, on the other hand, seems to fulfil the necessary requirements. It does not hydrolyze when exposed on a stone surface to atmospheric agents and seems to possess all the other stability characteristics expected for this class of products. The polarity of the amide group, especially in the case of the monoalkyl amides, suggests good binding ability to the stone via hydrogen bonds.

In the present paper, we report the synthesis and characterization of several mono-, di- and tetra-amides of perfluoropolyetheric acids, together with the first results obtained in preliminary tests on their activity as protective materials for stone.

Procedures

Monoamides

Two series of monoamides have been synthesized: diethylamides (DET) and isobutylamides (IBA) (Table 1).

The isobutyl ester of the perfluoropolyetheric monocarboxylic acids was reacted in 1,1,2-trichlorotrifluoroethane (A113) solution with the amine in a 1:1 molar ratio at room temperature under nitrogen.

The acids used were R_fCOOH, where $R_f = CF_3O-[CF_2-CF(CF_3)-O]_m-(CF_2-O)_n-CF_2-$, and had an average molecular weight of 425 (G440), 880 (G900) and 2380 (G2200).

Reaction times necessary to prepare IBA derivatives were in the range of 4–8 h, and increased as the average molecular weight of the ester increased. For DET derivatives, reaction times were much longer (in the range of 40 h) while conversions did not exceed 95%.

Diamides

Three series of diamides $[R_fCONH(CH_2)_y-NHCOR_f]$ have been synthesized (Table 1) having $y = 2$,

TABLE 1. Physical properties of perfluoropolyetheric amides

| Amide	$d_{25 °C}^4$	Molecular weight		Viscosity at 20 °C[a] (cSt)
		Calculated	Found	
Monoamides				
DETG440	1.520	480	430	6
DETG900	1.681	935	765	15
DETG2200	1.820	2435	2960	426
IBAG440	1.499	480	410	32
IBAG900	1.661	935	745	77
IBAG2200	1.822	2435	2280	1008
Diamides				
DC2G440	1.738	875	845	5940
DC2G900	1.807	1785	1610	7838
DC2G2200	1.880	4785	4485	43362
DC6G440	1.635	930	790	1566
DC6G900	1.751	1840	1350	1566
DC6G2200	1.830	4840	4560	29997
DpipG440		900	711	352
Tetra-amides				
TC2G440	1.800	3460	2585	22090
TC2G900	1.810	4370	3895	44716
TC2G2200	1.820	7370	9995	109718
TC6C440		3570	2760	6139
TC6G900	1.770	4480	3091	6213
TC6G2200	1.830	7480	5907	26800

[a]Neat.

6 and 4, i.e. ethylenediamides (DC2), hexamethyle-nediamides (DC6) and piperazinediamides (Dpip). The synthesis of the diamides was analogous to that of the monoamides, the only difference being the ester/amine molar ratio which in this case was 2:1. The ester was added slowly under nitrogen, while stirring at room temperature, to the suspension of the amine in A113.

Reaction times were in the range of 4–12 h for the DC2 and DC6 derivatives. A much longer time (48 h) and a temperature of 50 °C was necessary for the piperazine derivative (DpipG440).

Tetra-amides

Tetra-amides [$R_fCONH(CH_2)_y-NHCO-R_{fz}-CO-NH(CH_2)_y-NHCOR_f$], where $R_{fz} = -(CF_2CF_2O)_n - (CF_2O)_m$, with an average molecular weight of 2560 (Z2000) and R_fCOOH as mentioned before, were prepared from ethylenediamine (TC2) and hexamethyl-enediamine (TC6).

The synthesis involved two subsequent stages: (a) synthesis of the hemiamide of the monocarboxylic acid

$$R_fCOOBu^i + H_2N(CH_2)_y-NH_2 \longrightarrow$$

$$R_fCONH(CH_2)_y-NH_2 + Bu^iOH$$
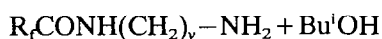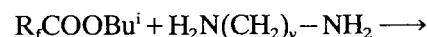
and (b) reaction of the above hemiamide with the dimethyl ester of the dicarboxylic acid HOOC−R_{fz}−COOH:

$$2R_fCONH(CH_2)_y-NH_2 + H_3COOC-R_{fz}-COOCH_3$$
$$\downarrow$$
$$R_fCONH(CH_2)_y-NHCO-R_{fz}-CONH(CH_2)_y-NHCOR_f + 2CH_3OH$$
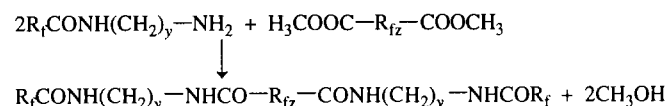
The hemiamide was synthesized by adding, under nitrogen while stirring at room temperature, the isobutyl ester in A113 solution to the diamine in a 1:1 molar ratio. After a few hours when the hemiamide had formed, the dimethyl ester of the Z2000 acid was added to the above solution in a 1:2 molar ratio of diester/hemiamide. After 8–10 h, the reaction was complete (Table 1).

All products were purified by column chromatography on an Al₂O₃/C (3:1) mixture. Yields always exceeded 90%. Infrared, ¹H NMR and ¹⁹F NMR spectral data are reported in Tables 2, 3 and 4.

Experimental

IR spectra were recorded on an FT-IR Perkin-Elmer model 1760X spectrometer, pure products being examined between KBr windows and solutions in 50 or 100 μm cells equipped with KBr windows. ¹H NMR spectra were recorded on a Varian VXR-300 spectrometer operating at 299.949 MHz using TMS as external standard in A113 solutions. ¹⁹F NMR spectra

were recorded using the same instrument at 282.203 MHz using CFCl₃ as external standard, either on the pure products or in difluorotetrachloroethane (A112) or in A113 solution.

Viscosity determinations were made using a Cannon–Fenske capillary osmometer on the pure products with capillaries having different diameters at temperatures between 20 °C and 45 °C. Molecular weights were determined using a Wescan osmometer model 233 on A113 solutions of the mono- and di-amides and on 2,2,3,3,3-pentafluoropropan-1-ol solutions of the tetra-amides.

UV stability tests were made using HPK 125 W Philips UV lamps placed in a thermostatic chamber. Chromatic determinations were made using a reflecting colorimeter (Chroma–Meter Minolta CR 200) on both treated and untreated samples.

Materials

Monocarboxylic perfluoropolyetheric acids R_fCOOH were Ausimont products; R_fCOOH, av.mol.wt. 425 (G440) and av.mol.wt. 880 (G900) were supplied in pure form and used as such. In contrast, R_fCOOH, av.mol.wt. 2380 (G2200) was supplied as a 40% solution in a non-functionalized perfluoropolyether (YR). The acid was separated from the YR diluent by neutralization with excess CaCO₃ extraction of YR by A113, followed by acidification of the salt by stirring with excess concentrated hydrochloric acid. The fluorinated acid was recovered by extraction with A113.

Isobutyl esters of G440, G900 and G2200 acids were prepared by heating the acids with the alcohol in 1:1.5, 1:1.5 and 1:25 molar ratios, removing the water produced in the condensation process continuously by rectification.

The dimethyl ester of the dicarboxylic perfluoro-polyetheric acid, HOOC−R_{fz}−COOH, av.mol.wt. 2250 (Z2000) was prepared by heating the acid, as supplied by Ausimont, with methyl alcohol in excess. Other reagents were as follows: isobutylamine, C. Erba reagent grade; diethylamine, Aldrich–Chemie reagent grade; ethylenediamine, C. Erba reagent grade, distilled under nitrogen before use; hexamethylenediamine, Janssen C, distilled over KOH under nitrogen at reduced pressure; and piperazine, C. Erba reagent grade.

Synthesis of amides

The same procedure was used for all amides. Longer reaction times were necessary for those of higher molecular weight. The synthesis of the G440 ethylenediamide is given as a typical example.

In a two-necked 100 ml flask, equipped with a reflux condenser and a dropping funnel, a solution consisting of 0.478 g (7.958 mmol) of ethylenediamine in 6 ml of A113 was placed under nitrogen. The isobutyl ester

TABLE 2. FT-IR spectra of perfluoropolyetheric amides $(cm^{-1})^a$

Amide	ν_{NH}			ν_{CH}	ν_{CO}	δ_{NH}
	free	ass.asym	ass.sym			
DETG440			2985 (m); 2946 (m); 2915 (ww); 2885 (w)	1696 (s)		
DETG900			2987 (m); 2947 (w); 2916 (ww); 2886 (ww)	1699 (s)		
DETG2200			2988(w); 2948 (ww); 2916 (ww); 2887 (ww)	1707 (s); 1699 (s)		
IBAG440	3461 (w)	3324 (m)	3098 (w)	2970 (m); 2941 (w); 2880 (w)	1709 (s)	1552 (m)
IBAG900	3462 (w)	3322 (m)	3102 (w)	2970 (m); 2942 (w); 2881 (w)	1709 (s)	1552 (m)
IBAG2200	3462 (w)	3326 (m)	3098 (w)	2970 (m); 2940 (w); 2881 (w)	1709 (s)	1551 (m)
DC2G440	3463 (ww)	3315 (m)	3107 (w)	2955 (w); 2890 (ww)	1707 (s)	1555 (m)
DC2G900	3462 (ww)	3315 (m)	3107 (w)	2956 (w); 2881 (w)	1707 (s)	1553 (m)
DC2G2200	–	3315 (m)	3110 (w)	2954 (ww); 2857 (w)	1705 (s)	1554 (m)
DC6G440	3457 (w)	3315 (m)	3097 (w)	2944 (m); 2866 (w)	1709 (s)	1553 (m)
DC6G900	3459 (w)	3315 (m)	3102 (w)	2944 (m); 2866 (w)	1708 (s)	1553 (m)
DC6G2200	3462 (w)	3320 (m)	3096 (w)	2943 (w); 2866 (w)	1707 (s)	1551 (m)
DpipG440				3012 (ww); 2949 (w); 2883 (w)	1701 (s)	
TC2G440	3462 (ww)	3315 (m)	3111 (w)	2958 (w); 2895 (ww)	1707 (s)	1557 (m)
TC2G900	3461 (ww)	3315 (m)	3111 (w)	2957 (w); 2896 (ww)	1708 (s)	1556 (m)
TC2G2200	–	3316 (m)	3110 (w)	2957 (w); 2895 (ww)	1706 (s)	1556 (m)
TC6G440	3460 (w)	3312 (m)	3099 (w)	2944 (m); 2866 (w)	1708 (s)	1555 (m)
TC6G900	3459 (w)	3318 (m)	3103 (w)	2943 (m); 2866 (w)	1709 (s)	1553 (m)
TC6G2200	3462 (w)	3316 (m)	3098 (w)	2944 (m); 2865 (w)	1708 (s)	1559 (m)

^{a}Neat; ν = stretching frequency; δ = bending frequency; ass.sym = associated asymmetrical NH stretching; ass.sym = associated symmetrical NH stretching; ww = very weak; w = weak; m = medium; s = strong.

of the G440 acid, (7.894 g, 15.916 mmol), was then added slowly through the funnel and allowed to react at room temperature for 4 h. The product recovered after elimination of the solvent was purified by elution through an Al_2O_3/C chromatography column using A113 as solvent. The yield was 95%.

All the amides are colourless transparent fluids.

Stability tests

The stability test for hydrolysis was performed by applying 1 ml of a 10% solution of the amide in A113 on the surface of 2×4×0.2 cm samples of the stone (Pietra di Lecce). After evaporation of the solvent, the samples were kept under distilled water at room temperature for 15 d, then dried and the organic material which was still present on the sample extracted using an A113/acetone (87.5:12.5 w/w) mixture. The product recovered was in all cases the unaltered amide. Similar tests on the isobutyl ester of the G2200 acid showed rapid hydrolysis of the ester under the above conditions with the formation of the calcium salt of the acid. This salt, which was soluble in the A113/acetone mixture,

could be identified via its FT-IR spectrum because of the C=O stretching absorption band of the carboxylate group at 1658 cm^{-1}.

Stability tests on the amides in acidic or basic solutions were performed by mixing 0.2 g of the amide either with 15 ml of HCl (36 vol.%) or 15 ml of 1 N NaOH and storing the suspension at room temperature for 9 d under strong stirring. The product recovered by extraction with the A113/acetone (87.5:12.5 w/w) mixture was always the unaltered original product.

The stability of the amides towards heating was determined by applying these products on the surface of marble samples and keeping the samples at 75 °C for 3 d and then at 100 °C for 7 d. No colour changes were observed after this treatment.

UV stability tests were performed by exposing the samples of marble treated with the amide, placed in a climatic chamber maintained at 25 °C and 50% RH, to irradiation from two HPK Philips UV lamps placed at 25 cm distance for 48 h. Again the samples were not affected by this treatment. Control was effected both by colorimetry and by FT-IR techniques on the liquid recovered by extraction.

TABLE 3. ^{1}H NMR chemical shifts of perfluoropolyetheric amides (A113 solutions)

Diethylamides

	$R_f-CO-N(CH_2-CH_3)_2$ $-N(\underline{CH}_2-CH_3)_2$	$-N(CH_2-\underline{CH}_3)_2$
DETG440	3.46 (m)	1.20 (m)
DETG900	3.42 (m)	1.20 (m)
DETG2200	3.33 (m)	1.09 (m)

Isobutylamides

	$R_f-CO-NH-CH_2-CH(CH_3)_2$ $-CO-\underline{NH}-$	$-NH-\underline{CH}_2-CH-$	$-CH_2-\underline{CH}-(CH_3)_2$	$-CH_2-CH-(\underline{CH}_3)_2$
IBAG440	8.29 (sl)	3.15 (t) $^3J=7.3$ Hz	1.91 (m)	0.92 (d) $^2J=7.5$ Hz
IBAG900	8.01 (sl)	3.16 (t) $^3J=6.4$ Hz	1.92 (m)	0.95 (d) $^2J=7.8$ Hz
IBAG2200	8.00 (sl)	3.18 (t) $^3J=6.7$ Hz	1.94 (m)	0.97 (d) $^2J=7.3$ Hz

Ethylenediamides

	$R_f-CO-NH-(CH_2)_2-NH-CO-R_f$ $-CO-\underline{NH}-$	$-NH-(\underline{CH}_2)_2-NH-$
DC2G440[a]	8.72 (sl) 8.42 (s)	3.55 (sl)
DC2G900	8.39 (sl)	3.58 (s)
DC2G2200	8.15 (sl)	3.48 (sl)

Hexamethylenediamides

	$R_f-CO-NH-CH_2{}^\alpha-CH_2{}^\beta-CH_2{}^\gamma-CH_2{}^\gamma-CH_2{}^\beta-CH_2{}^\alpha-NH-CO-R_f$ $-CO-\underline{NH}-$	$-CH_2{}^\alpha-$	$-CH_2{}^\beta-$	$-CH_2{}^\gamma-$
DC6G440	7.64 (sl) 7.75 (sl)	3.37 (s) 3.34 (s)	1.62 (s)	1.40 (s)
DC6G900	7.51 (sl)	3.36 (s)	1.61 (s) 3.34 (s)	1.40 (s)
DC6G2200	7.03 (sl) 8.31 (sl)[a]	3.37 (s) 3.35 (m)[a]	1.63 (s) 1.63 (m)[a]	1.43 (s) 1.42 (m)[a]

Piperazinediamide

	$R_f-CO-N(CH_2-CH_2)_2N-CO-R_f$ $-N(\underline{CH}_2-CH_2)_2N-$
DpipG440	3.63 (s)

Ethylenetetra-amides

	$R_f-CO-NH-(CH_2)_2-NH-CO-R_{f_2}-CO-NH-(CH_2)_2-NH-CO-R_f$ $-CO-\underline{NH}-$	$-NH-(\underline{CH}_2)_2-NH-$
TC2G440[a]	8.46 (sl) 8.39 (sl)	3.56 (s)
TC2G900[a]	8.35 (s) 8.45 (sl)	3.57 (s)
TC2G2200[a]	8.43 (sl) 8.30 (sl)	3.58 (s)

Hexamethylenetetra-amides

	$R_f-CO-NH-(CH_2)_6-NH-CO-R_{f_2}-CO-NH-(CH_2)_6-NH-CO-R_f$ $-CO-\underline{NH}-$	$-CH_2{}^\alpha-$	$-CH_2{}^\beta-$	$-CH_2{}^\gamma-$
TC6G440[b]	9.00 (sl) 9.14 (sl)	3.37 (t) $^3J=8.6$ Hz	1.67 (m)	1.47 (s)
TC6G900[b]	8.72 (sl) 8.92 (sl)	3.32 (t) $^3J=7.7$ Hz	1.62 (s)	1.41 (s)
TC6G2200[b]		3.36 (t) $^3J=6.2$ Hz	1.67 (s)	1.47 (s)

s = singlet; sl = broad singlet; d = doublet; t = triplet; m = multiplet.
[a]Solvent = A113/acetone-d_6.
[b]Solvent = A113 + CD$_3$OD.

TABLE 4. ^{19}F NMR chemical shifts of perfluoropolyetheric amides[a]

Amide	$-O-CF_2-CONH-$	$-O-CF-CONH-$ CF_3	$-CF_2-O-CF_2-CONH-$	$-O-CF_2-CF_2-O-$	$-O-CF-CO-NH-$ CF_3	$-O-CF_2-CF-O-$ CF_3
DETG440	-69.6 (sl)	-82.7 (sl)	-84.7 (m)		-131.5 (m)	-145.0 (m)
DETG900	-69.8 (sl)	-82.9 (sl)	-85.4 (m)		-131.5 (m)	-145.0 (m)
DETG2200	-70.0 (sl)	-82.9 (sl)	-85.5 (m)			-145.0 (m)
IBAG440	-76.0 (s)	-82.4 (s)	-85.0 (m)		-131.6 (m)	-145.0 (m)
IBAG900[c]	-75.8 (s)	-82.6 (sl)	-85.5 (m)		-131.2 (m)	-145.0 (m)
IBAG2200[b]	-76.0 (s)	-82.7 (sl)	-85.7 (m)		-131.6 (m)	-145.0 (m)
DC2G440[c]	-75.4 (s)	-82.5 (s)	-85.0 (m)		-132.5 (m)	-145.0 (m)
DC2G900[c]	-75.6 (sl)	-82.6 (sl)	-85.5 (m)		-132.2 (m)	-145.0 (m)
DC2G2200[b]	-75.8 (sl)	-82.8 (sl)	-85.5 (m)		-132.5 (m)	-145.0 (m)
DC6G440[b]	-75.5 (s)	-82.3 (s)	-84.3 (m)		-132.0 (m)	-145.0 (m)
DC6G900[c]	-75.8 (s)	-82.6 (sl)	-85.1 (m)		-132.3 (m)	-145.0 (m)
DC6G2200[b]	-75.9 (sl)	-82.9 (s)	-85.7 (m)		-132.5 (m)	-145.0 (m)
DpipG440	-69.3 (sl)	-82.5 (sl)	-85.0 (m)		-131.5 (m)	-145.0 (m)
TC2G440	-76.0 (sl)	-83.0 (sl)	-85.7 (m)	-89.3 (s), -90.7 (s)	-130.0 (m)	-145.0 (m)
TC2G900	-76.2 (s)	-82.9 (sl)	-85.6 (m)	-88.9 (s), -90.5 (s)	-130.0 (sl)	-145.0 (sl)
TC2G2200	-76.5 (s)	-82.8 (sl)	-85.8 (m)	-89.1 (s), -90.8 (s)	-130.0 (sl)	-145.0 (m)
TC6G440	-76.0 (s)	-82.9 (sl)	-85.1 (m)	-89.2 (s), -90.8 (s)	-130.0 (m)	-145.0 (m)
TC6G900	-75.9 (s)	-83.1 (sl)	-85.4 (m)	-89.0 (s), -90.8 (s)	-130.2 (m)	-145.0 (m)
TC6G2200	-76.3 (sl)	-82.9 (sl)	-85.9 (m)	-89.2 (s), -90.9 (s)	-130.0 (sl)	-145.0 (m)

[a]Neat.
[b]Solvent = A113/acetone-d_6.
[c]Solvent = A112/acetone d_6.
s = singlet; sl = broad singlet; m = multiplet.

Results and discussion

All the prepared amides were stable to both acidic and basic hydrolysis, to UV irradiation and to heating up to 100 °C.

Molecular weight determinations in trichlorotrifluoroethane (A113) on DET, IBA, DC2, DC6 and Dpip, and in 2,2,3,3,3-pentafluoropropan-1-ol on TC2 and TC6, did not provide very accurate results but were in broad agreement with the formulations suggested (Table 1). The uncertainty in these results was due to the very low concentration of the solutions used. Our products were not very soluble in the solvents appropriate for this determination. In some cases, the apparent molecular weights found increase with the concentration of the solution (Table 5). Such increases in molecular weight were higher for the di- than for the mono-functional derivatives, and more for the ethylenediamides than for the hexamethylenediamides. Determinations made on G440 derivatives gave results which were nearer to the expected values than those on higher molecular weight materials, owing to the greater solubility of these products and therefore to the higher concentration of the solutions used for these determinations; hence, the greater accuracy of the determination.

The FT-IR spectra of the fluorinated amides show absorptions in the 3500–3000 cm^{-1} region due to N–H stretching: that at 3500–3400 cm^{-1} may be ascribed to free N–H stretching, whilst others in the 3400–3300 and 3165–3000 cm^{-1} regions may be attributed to associated N–H asymmetric and symmetric stretching modes. The degree of association of the amide groups which is proportional to the A_2/A_1 ratio (see Table 6), was small in the monofunctional derivatives, but increased considerably in the di- and tetra-ethylenediamides, being lower in the hexamethylenediamides. The association phenomena involving the N–H groups are due to the formation of inter- and intra-molecular hydrogen bonds. Dilution of the solutions causes a decrease in such association down to zero in the case of isobutyl monoamides whilst the association is retained to a certain extent in the diamides under the same conditions (Table 6). Surprisingly, in the case of the hexamethylenediamides, the modest association noticed with 10% solution does not decrease as rapidly with dilution (Table 6) as for the monoamides. Hydrogen-

TABLE 5. Molecular weights by osmometry of some perfluoropolyetheric amides[a]

IBAG440			IBAG900			IBAG2200		
Conc.[b]	$MW_{calc.}$	MW_{found}	Conc.[b]	$MW_{calc.}$	MW_{found}	Conc.[b]	$MW_{calc.}$	MW_{found}
1.7976	480	404	1.7805	935	761	1.7345	2435	2282
1.8117		412	2.2524		756	2.4397		2280
2.3601		406	6.4827		711	6.4622		2308
6.4623		414	8.9267		743	8.7636		2362
						8.7828		2356
						14.3676		2375

DC2G440			DC2G900			DC2G2200		
Conc.[b]	$MW_{calc.}$	MW_{found}	Conc.[b]	$MW_{calc.}$	MW_{found}	Conc.[b]	$MW_{calc.}$	MW_{found}
1.7472	875	824	1.8052	1785	1612	2.3792	4785	4489
2.4029		864	6.3631		1603	2.4664		4484
6.3281		1106	8.8795		1698	6.3912		4699
8.8342		1244	14.4205		1863	6.4394		4770
14.3912		1510				8.8197		4873
						8.7330		4948
						14.4104		5240

DC6G440			DC6G900			DC6G2200		
Conc.[b]	$MW_{calc.}$	MW_{found}	Conc.[b]	$MW_{calc.}$	MW_{found}	Conc.[b]	$MW_{calc.}$	MW_{found}
1.8190	930	789	2.4264	1840	1341	2.6458	4840	4562
2.3413		791	6.4598		1354	6.3979		5202
6.4724		851				8.8050		5469
6.3661		848				14.4312		5749
8.8014		855						
14.3204		943						

[a]A113 solution.
[b]Conc. as mg ml^{-1}.

TABLE 6. Frequency and intensity of FT-IR, NH stretching bands of some perfluoropolyetheric amides[a]

Amide	NH_free		NH_ass				A_2/A_1
	ν	A_1	ν_{asym}	A_2	ν_{sym}	A_3	
IBAG440[b]	3461	0.450	3324	20.315	3100	1.485	45
10%[c]	3461	2.527	3349	8.457	3103	0.437	3
5%[c]	3462	1.670	3359	3.300	3101	0.157	2
1%[c]	3464	1.112	–	–	–	–	0
DC2G440[b]	3463	0.010	3315	38.030	3108	3.667	3803
10%[c]	3457	0.099	3319	29.544	3108	1.912	298
5%[c]	3458	0.152	3320	17.059	3107	1.038	112
1%[c]	3460	0.248	3330	4.608	3105	0.294	19
DC6G440[b]	3456	0.709	3315	30.419	3097	2.826	43
10%[c]	3456	1.414	3331	16.419	3101	0.969	12
5%[c]	3457	1.007	3334	8.623	3099	0.477	8
1%[c]	3458	0.768	3362	1.508	3093	0.096	2
TC2G440[b]	3467 (sp)	0.013	3315	32.678	3110	3.068	2513
TC6G440[b]	3460	0.142	3312	8.291	3100	0.763	58

[a]A113 solutions at different concentrations; ν = frequency of absorbance in cm^{-1}; A_1, A_2, A_3 = area of absorption bands from 3490–3450 cm^{-1} (A_1), 3450–3170 cm^{-1} (A_2) and 3165–3030 cm^{-1} (A_3) at indicated frequency.
[b]Neat sample.
[c]A113 solutions at 10%, 5% or 1%, respectively.

bond interaction between different molecules of aliphatic amides affects the viscosity of their solutions [11, 12]. Fluorinated amides also show the same behaviour which may be connected with intermolecular hydrogen-bond formation (Table 7).

Viscosity determinations are relevant in order to establish the eventual connection between this parameter, the mobility of the product on its support and the associative phenomena. By comparing the behaviour of diethyl and isobutyl-amides, it is clearly apparent that when all other factors are kept constant the viscosity increases when hydrogen-bond formation is possible. The viscosity increased by at least an order of magnitude in passing from the mono- to the di-amides.

As shown by the data obtained from di- and tetra-amides, a further increase in the number of functional groups per molecule caused a further, almost proportional, increase in the viscosity of the ethylenediamine derivatives. The viscosity of the amides from hexamethylenediamine was of the same order of magnitude but lower than that of the corresponding diethylamine derivatives. This particular behaviour appears to be in line with that already noted both from the molecular weight determinations and association phenomena, as well as with the N–H stretching bands in the FT-IR spectra. It is worth noting that the piperazine diamide (DpipG440) which cannot associate by hydrogen bridging had a much lower viscosity than the other alkyldiamides (DC2G440, DC6G440) but higher than that

of the corresponding monoamide (IBAG440). In all cases the viscosity of these products decreased by c. 10 ± 2 times as the temperature was increased from 20 °C to 45 °C.

The increase in molecular weight of the ethylenediamides of the G440 acid as the concentration of the solution was increased is obviously due to intermolecular association phenomena over the concentration range explored. A lower degree of association noted in the case of the corresponding hexamethylenediamine derivatives may be ascribed to lower intermolecular interaction due to competing intramolecular interaction arising from the greater distance between the two amidic groups in the same molecule. The correctness of this interpretation has been confirmed by studying the associative phenomena via the N–H stretching association bands in the FT-IR spectra. Associative phenomena decreased as the concentration of the solution decreased.

With the ethylenediamine derivatives, association phenomena decreased as the concentration was decreased, but never reached zero even at high dilution. In the case of the hexamethylenediamine derivatives, the association phenomena (which are not so relevant as in the previous case even at fairly high concentrations) decreased much more slowly as the concentration was decreased but again never reached zero even at high dilution.

This latter behaviour is in good agreement with that of molecules showing mainly intramolecular associative phenomena which are only slightly affected by the concentration of the solution. The viscosity determinations gave results in keeping with the above observations: the viscosity increased in each class of product as the average molecular weight increased, being higher for derivatives capable of association via hydrogen bridges for products of equal molecular weight.

The hexamethylenediamine derivatives gave anomalous results as far as the viscosity determinations were concerned, their viscosity being lower than that of the ethylenediamine derivatives. The interpretation given above explains these results satisfactorily.

Conclusions

All three parameters observed, average molecular weight, viscosity and FT-IR associative bands, conform to the same picture regarding the interactions and interaction activity of the molecules synthesized: the greater the number of polar groups per molecule, the greater the association phenomena. First tests on the efficacy of these products as protective materials for stone have indicated them as very efficient materials, especially the hexamethylenediamine derivatives (Table 8). Molecules in which intramolecular association

TABLE 7. Viscosities of some perfluoropolyetheric amides at various temperatures[a]

Amide	Viscosity (cSt) at						Viscosity ratio 20 °C/45 °C
	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	
DETG440	6						
DETG900	15						
DETG2200	426						
IBAG440	32	23	18	14	11	9	3.56
IBAG900	77	53	39	29	23	18	4.28
IBAG2200	1008	661	447	307	226	162	6.22
DC2G440	5940	3710	2314	1434	896	575	10.33
DC2G900	7838	4921	3272	2072	1323	836	9.38
DC2G2200	43362	24051	13621	7857	4676	2861	15.16
DC6G440	1566	988	636	420	282	193	8.11
DC6G900	1566	986	626	415	274	188	8.33
DC6G2200	29997	15571	8497	6149	2904	1815	16.53
DpipG440	352	231	156	107	76	55	6.40
YR(6-7000)	1597	1122	803	590	438	337	4.74
TC2G440	22090	12970	8486	5759	3894	2754	8.02
TC2G900	44716	31513	19117	12398	8519	5386	8.30
TC2G2200	109718	–	37936	23061	14176	8724	12.58
TC6C440	6139	4013	2682	1832	1278	905	6.78
TC6G900	6213	3935	2545	1701	1123	769	8.07
TC6G2200	26800	14740	8985	5629	3617	2391	11.21

[a]Neat.

TABLE 8. Protective efficacy ($E\%$)[a] of some perfluoropolyetheric compounds on a bioclastic limestone (Pietra di Lecce, 46% porosity) on ageing

Protective agent	g m^{-2}	Protective efficacy months after treatment								
		1	5	6	7	8	15	16	19	21
YR	159	33					23			
IBAG2200	158	68					65			
DC2G2200	142	92		82		79		77		75
DC6G2200	154	99	100		100		100		100	

[a]The protective efficacy is: $E\% = (A_0 - A_1)/A_0 \times 100$, where A_0 and A_1 are the amounts of absorbed water (ml cm^{-3}) before and after treatment, respectively. The water absorbed (A) was determined by measuring via the 'pipette method' [8] the amount of water absorbed in 25 min by stone per unit of surface at room temperature at atmospheric pressure.

phenomena are relevant not only bind to the stone support like those showing intermolecular associative phenomena to the same extent, but do so more readily because the binding sites are evidently more prone to interaction.

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