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Polyperfluoroether–silica hybrids

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A hydroxyl terminated perfluoroether oligomer was reacted with chlorendic anhydride in bulk. Further telechelic chain extension reactions were carried out with ε-caprolactone (CL). Both products were then functionalised through reactions with γ-glycidyloxypropyltrimethoxysilane, using primarily infrared spectroscopy and proton-nuclear magnetic resonance (NMR) to analyse the structure of the end-group as a means of monitoring the progress of the reaction. Scanning electron microscopy was used to examine the morphology of the corresponding silica hybrids. Functionalisation of the modified perfluoroether oligomer was found to be essential to control the morphology of hybrids in order to obtain transparent systems. The compatibility of the components for the preparation of the hybrids was further improved when less than five CL units were present at the end of each modified perfluoroether chain.

The use of higher amounts of CL brings about the formation of crystallisable units at the chain ends and as discrete homopolymers. The presence of the silica phase in the corresponding hybrid material inhibits, however, the crystallisation of the polycaprolactone phase and restricts the growth of spherulites. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: perfluoroethers; fluoroalkane oligomers; organic–inorganic hybrids)

INTRODUCTION

Due to the strength of the carbon-fluorine (CF) bond fluorinated polymers are generally chemically resistant and thermally stable, while their strong hydrophobic character confers to them a very low surface energy.

Perfluoroethers are attractive raw materials for the synthesis of macromolecular products because of the intrinsically high chain flexibility which results in products with a very low glass transition temperature. Polymeric perfluoroether alkane oxides have in fact a glass transition temperature in the region of $-120°C$[1].

Although these systems are available as oligomers with functional end-groups[2], their very low solubility in common solvents imposes considerable limitations on their use for the production of polymeric materials. It has recently been found, however, that certain hydroxyl terminated perfluoroether oligomers can be telechelically extended to render them soluble in aprotic polar solvents[3–5]. There are indications from their behaviour that solutions of chain extended perfluoroethers contain micelle types of molecular aggregates which induce readily phase separation into nanoscale domains during polymerisation or formation of tridimensional networks[5]. The characteristics of such oligomers are interesting for the production of organic–inorganic hybrids (known also as ceramers), in so far as they possess functional end-groups which can react with other functional groups attached to the siloxane network, creating at the same time favourable conditions for the formation of a very large number of nuclei, which lead to the precipitation of very fine domains of a desolubilised organic phase prior to the gelation of the alkoxysilane solution. This is the opposite of what normally occurs in the production of ceramers and it provides, therefore, an additional degree of freedom in engineering the morphology of these materials.

Although there are several approaches for the production of organic–inorganic hybrids[6], one of the most widely used methods involves two steps:

(a) The reaction of an α-ω hydroxyl terminated oligomer with an isocyanate functionalised trialkoxysilane to introduce terminal alkoxysilane groups in the oligomer chains[7–9].
(b) Hydrolysis and polycondensation of mixtures of silane functionalised oligomers and a tetralkoxysilane[10–13].

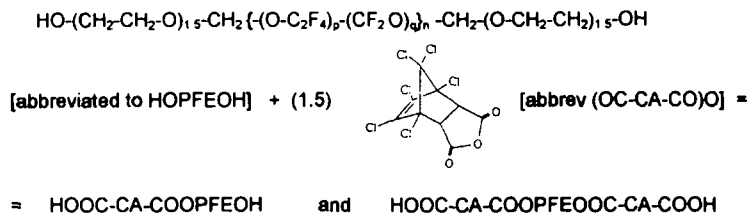When a polymeric, rather than oligomeric, organic component is used the chemical linking of the two phases is often induced by adding the alkoxysilane 'coupling agent' directly to the mixture[11–14]. It is possible that the chemical reactions between the organofunctional groups of the trialkoxysilane in the outer layers of the silica phase and the organic component take place in subsequent 'curing' reactions at higher temperatures. There is no real need, however, to chemically link the two phases provided that the phase separation process is controlled in such a manner that a co-continuous morphology results from the spinodal decomposition of the solution mixture, during the condensation reactions within the siloxane chains. This can be achieved through strong H-bonds between the outer hydroxyl groups of the silica phase and the repeating units of the polymer chains when appropriate components are used[15–17].

The purpose of this study is to produce and characterise silica hybrids based on chain extended perfluoroethers through functionalisation reactions with γ-glycidoxy-propyltrimethoxysilane (GOTMS), followed by reactions with tetraethoxysilane by the sol-gel process. Moreover this work seeks to clarify the structure and reaction yields for the preparation of chain extended perfluoroether oligomers reported previously[3–5].
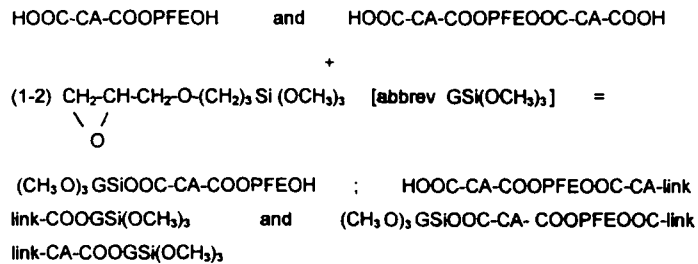
The various types of reactions involved are, thus, according to the scheme shown below:

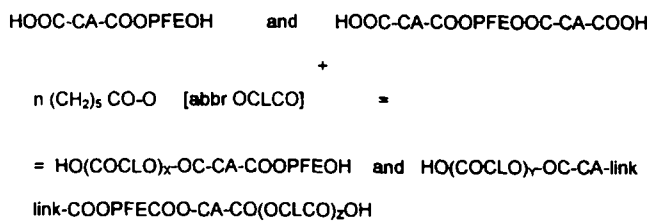---

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REACTION 1. Reaction of perfluoroether oligomer with chlorendic anhydride (CA) in bulk:
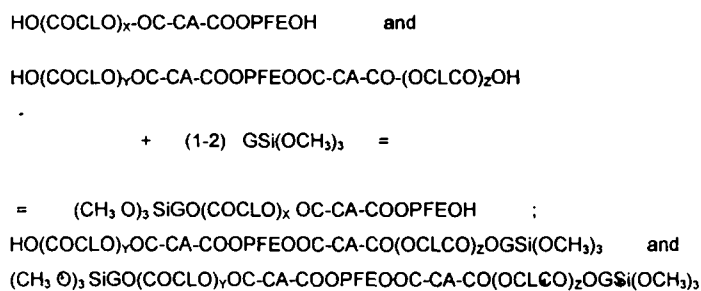
HO-(CH₂-CH₂-O)₁.₅-CH₂{-(O-C₂F₄)ₚ-(CF₂O)₄}ₙ-CH₂-(O-CH₂-CH₂)₁.₅-OH

[abbreviated to HOPFEOH] + (1.5) [abbrev (OC-CA-CO)O] =

= HOOC-CA-COOPFEOH   and   HOOC-CA-COOPFEOOC-CA-COOH

REACTION 2. Functionalisation of CA-perfluoroether adduct:

HOOC-CA-COOPFEOH   and   HOOC-CA-COOPFEOOC-CA-COOH

+

(1-2) CH₂-CH-CH₂-O-(CH₂)₃ Si (OCH₃)₃ [abbrev GSi(OCH₃)₃] =
         \ /
          O

(CH₃O)₃GSiOOC-CA-COOPFEOH   ;   HOOC-CA-COOPFEOOC-CA-link
link-COOGSi(OCH₃)₃   and   (CH₃O)₃GSiOOC-CA- COOPFEOOC-link
link-CA-COOGSi(OCH₃)₃

REACTION 3. Extension of CA-perfluoroether adduct with CL:

HOOC-CA-COOPFEOH   and   HOOC-CA-COOPFEOOC-CA-COOH

+

n (CH₂)₅ CO-O [abbr OCLCO]   =

= HO(COCLO)ₓ-OC-CA-COOPFEOH and HO(COCLO)ᵧ-OC-CA-link

link-COOPFECOO-CA-CO(OCLCO)₂OH

REACTION 4. Functionalisation of CL chain extended CA-perfluoroether adduct:

HO(COCLO)ₓ-OC-CA-COOPFEOH   and

HO(COCLO)ᵧ-OC-CA-COOPFEOOC-CA-CO-(OCLCO)₂OH

+   (1-2) GSi(OCH₃)₃   =

=   (CH₃O)₃SiGO(COCLO)ₓ OC-CA-COOPFEOH   ;
HO(COCLO)ᵧOC-CA-COOPFEOOC-CA-CO(OCLCO)₂OGSi(OCH₃)₃   and
(CH₃O)₃SiGO(COCLO)ᵧOC-CA-COOPFEOOC-CA-CO(OCLCO)₂OGSi(OCH₃)₃

REACTION 5. Sol-gel reactions for the production of perfluoroether–silica hybrids:

(CH₃O)₃SiGOC-CA-COOPFEOH   and
(CH₃O)₃SiGOOC-CA-COOPFEOOC-CA-COOGSi(OCH₃)₃

or

(CH₃O)₃SiGO(COCLO)ₓ OC-CA-COOPFEOH   and

(CH₃O)₃SiGO(COCLO)ᵧOC-CA-COOPFEOOC-CA- (COCLO)₂OGSi(OCH₃)₃

+

n   (CH₃CH₂O)₄Si   + (3-4) H₂O   =

supramolecular
siloxane network.. O O O
aggregate............SiOSiOSiOSi(OH)₃₋ₓGOOC-CA-COOPFEOH
                        O O O

and

supramolecular
siloxane network....O O O
aggregate............SiOSiOSiOSi(OH)₃₋ₓGOOC-CA-COOPFEOOC-CA-link
                        O O O

                        O O O
link COOGSi(OH)₃₋ₓ OSiOSiOSiO............supramolecular siloxane
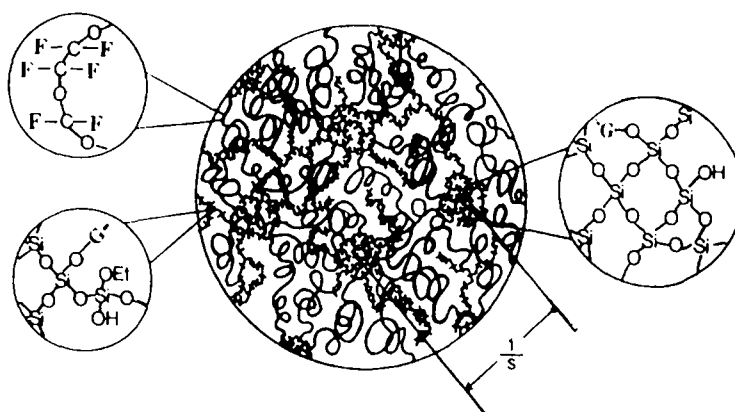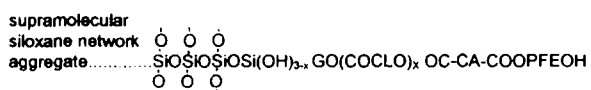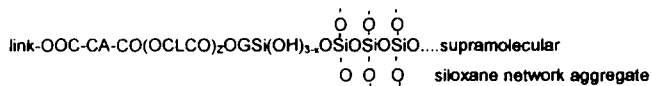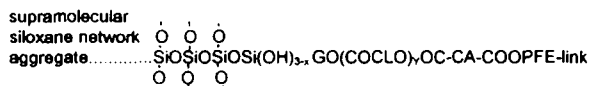   O O O   network aggregate

Figure 1 Schematic representation of the morphological structure of perfluoroether–silica hybrids (adapted from Wilkes *et al.*[18,19], copyright American Chemical Society): 1/s corresponds to the average distance between periodic fluctuations of cross-linking density

Similar structures for hybrids based on CL extended perfluoroether adducts:

supramolecular
siloxane network   O   O   O
aggregate............SiOSiOSiOSi(OH)₃.,GO(COCLO)ₓ OC-CA-COOPFEOH
                    O   O   O

and

supramolecular
siloxane network   O   O   O
aggregate............SiOSiOSiOSi(OH)₃.,GO(COCLO)ᵧOC-CA-COOPFE-link
                    O   O   O

                         O   O   O
link-OOC-CA-CO(OCLCO)zOGSi(OH)₃.,OSiOSiOSiO....supramolecular
                         O   O   O   siloxane network aggregate

The supramolecular structure of the hybrid so produced can be schematically represented by the model put forward by Wilkes and his group[18,19], as shown in *Figure 1*.

The expected advantages arising from the use of fluoroligomers for the production of hybrids, over alkaneoxide oligomers, such as tetramethyleneoxide types, and caprolactone oligomers previously used for the production of ceramers[7-10], are with respect to the very low surface energy and high thermal oxidative stability. The latter is particularly important if ceramers have to be regarded as materials with properties that are intermediate between polymers and ceramics. The very low surface energy, on the other hand, will confer to these materials characteristics that cannot be achieved with conventional ceramics.
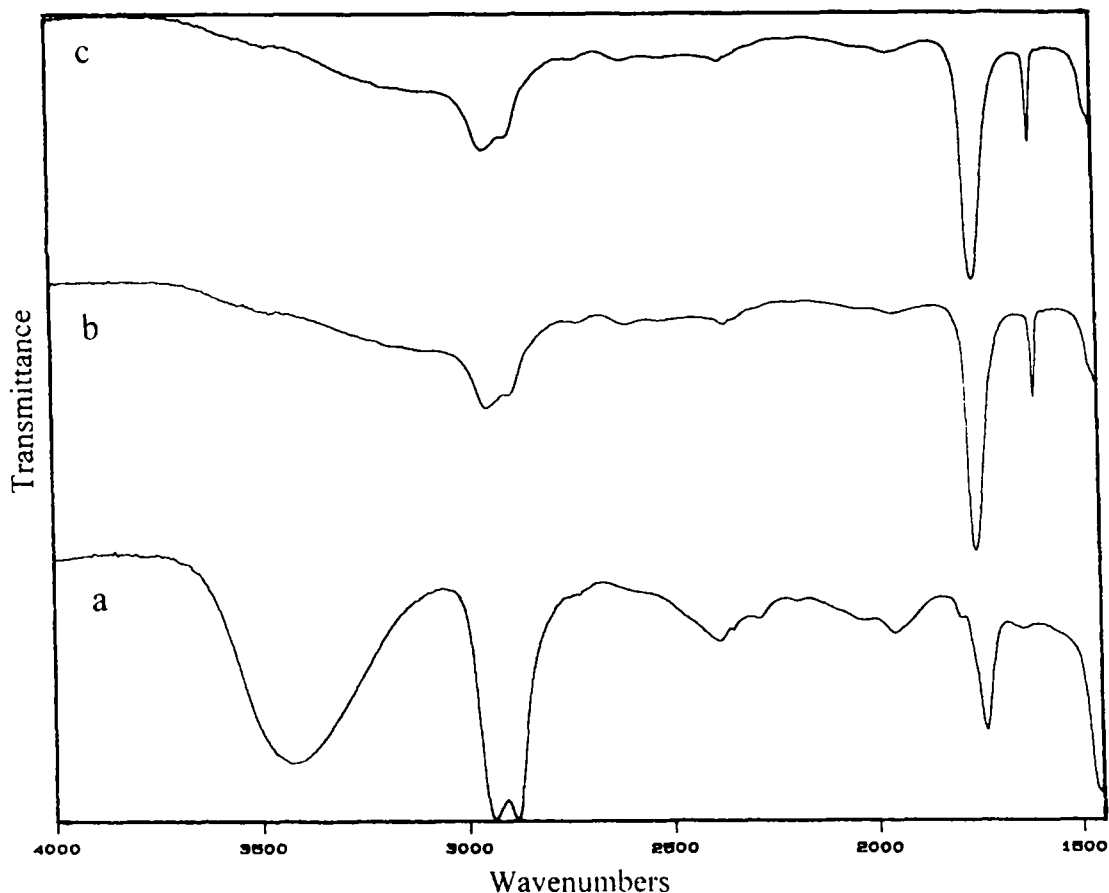

Figure 2 Infrared spectra of CA-perfluoroether adducts (FCM-x) obtained from reactions in bulk at 150°C: a, original perfluoroether oligomer; b, CA-perfluoroether adduct (1.5:1 molar ratio); reaction time: 0.25 hours; c, CA-perfluoroether adduct (1.5:1 molar ratio); reaction time: 6 hours
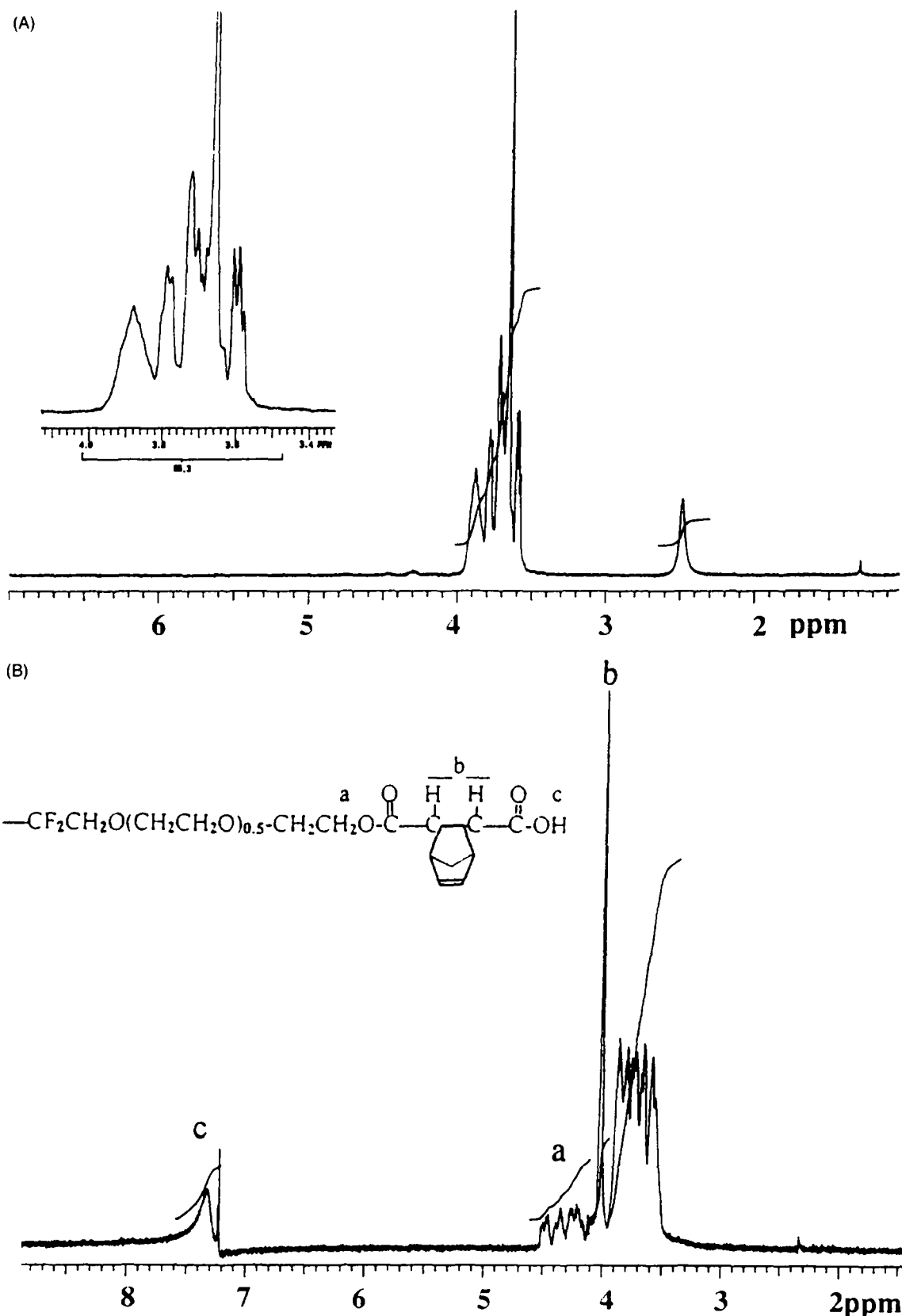
Figure 3 ^{1}H-n.m.r. spectra CA-perfluoroether adducts (FCM-x) obtained from reactions in bulk at 150°C: a, original perfluoroether oligomer;b, CA-perfluoroether adduct (1.5:1 molar ratio); reaction time: 0.25 hours; c, CA-perfluoroether adduct (1.5:1 molar ratio); reaction time: 6 hours

EXPERIMENTAL

Materials

(a) A functionalised fluoroalkeneoxide oligomer, Fomblin ZDOL-TX, from Ausimont SpA. Its chemical structure can be represented by the following formula:
$$HO-(CH_2-CH_2-O)_{1.5}-CH_2[-(OC_2F_4)_p-(CF_2O)_q]_n-CH_2-(O-CH_2-CH_2)_{1.5}-OH$$
where p/q molar ratio is approximately unity; n is in the region of 10–12, giving a number average molecular weight of approximately 2200.

(C)

—CF₂CH₂O(CH₂CH₂O)₀.₅-CH₂CH₂O-C—C—C—C-OH

c

b

a

9   8   7   6   5   4   3ppm
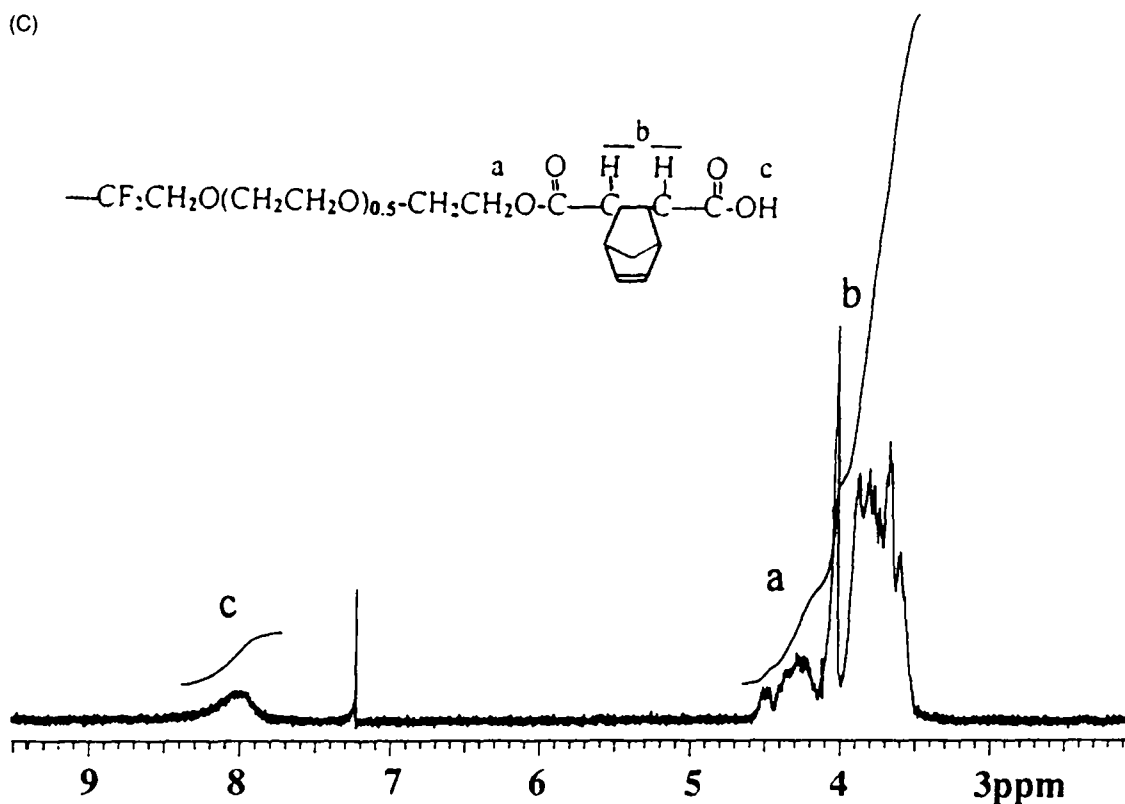
(b) Hexachloro endomethylene tetrahydrophthalic anhydride, known also as chlorendic anhydride (CA), was obtained as a white powder from Aldrich Chemical Co. with purity of 96%.

(c) caprolactone (CL), from Aldrich Chemical Co., is an internal ester of ε-hydroxyl caproic acid with a boiling point of 97°C. Purity was 99%.

(d) High purity grades of tetraethoxysilane (TEOS) and GOTMS were obtained from Fluka Co.

(e) Distilled water, a 32 wt% HCl (catalyst) solution and dimethyl formamide (DMF), standard analytical grades, were used to induce the hydrolytic reactions in the alkoxysilane components.

Telechelic modifications of the perfluoroether oligomer

The procedure used and the reactants molar ratio for the telechelic extension of the perfluoroether oligomeric chains were the same as that described in previous work[3–5].

c

b

a

Heat Flow(w/g)

10
5
0
-5
-10
-15

-140 -120 -100 -80 -60 -40 -20 0 20 40 60 80
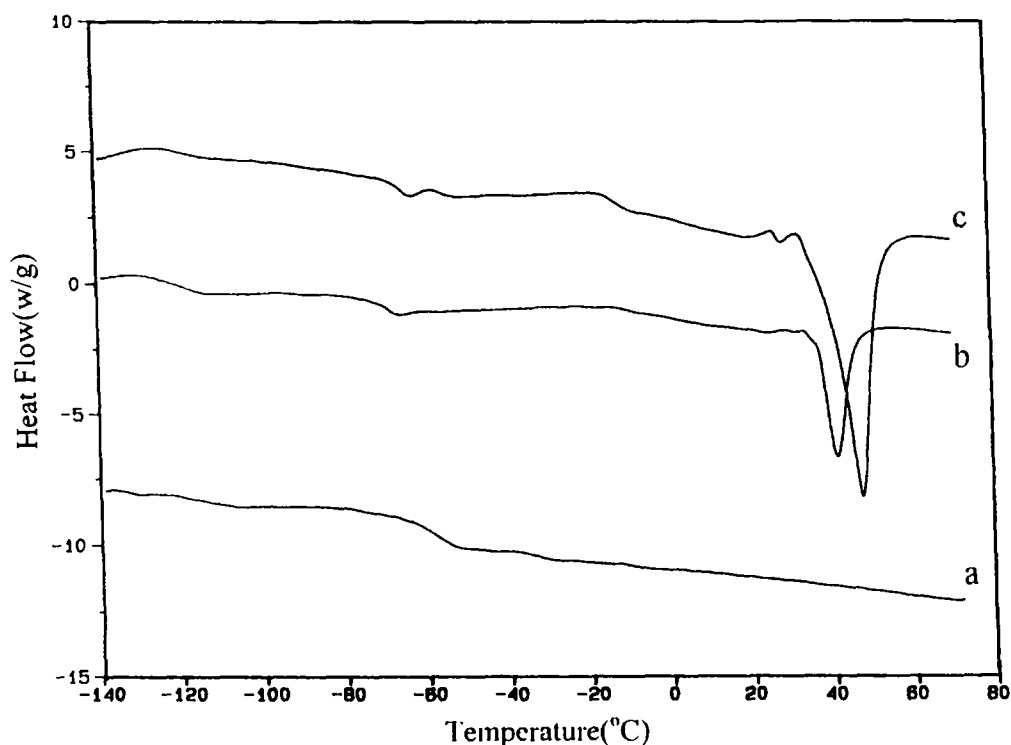
Temperature(°C)

Figure 4 DSC thermograms of caprolactone extended CA-perfluoroether adducts (FCM) functionalised with GOTMS; molar ratio of CA-perfluoroether to CL: a, 1:2; b, 1:5; c, 1:10
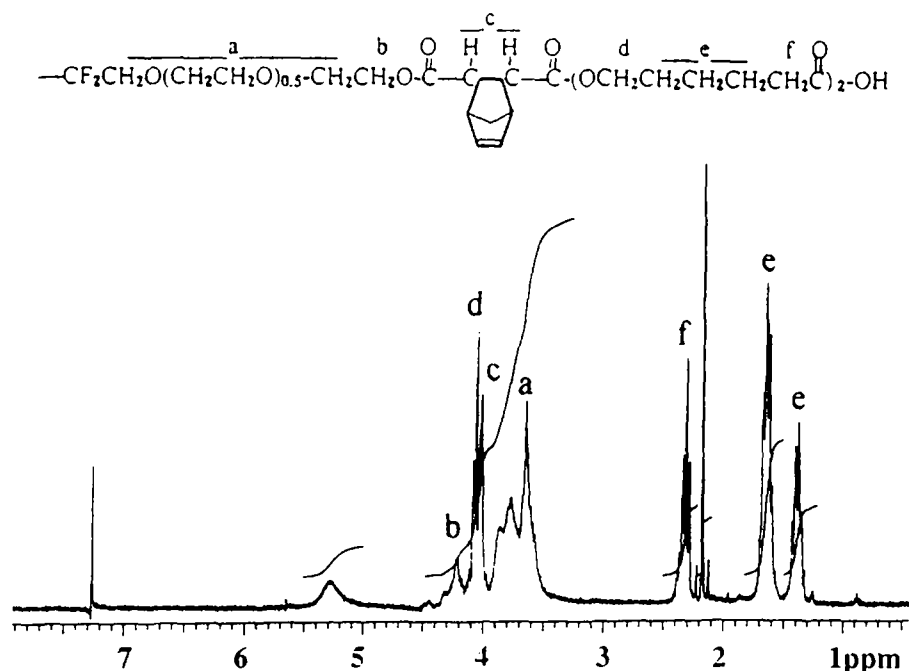
Figure 5 ¹H-n.m.r. spectra of caprolactone extended CA-perfluoroether adduct (FCMC-1)

Amounts of fluoroalkane oxide oligomer and CA powder at a molar ratio of 1:1.5 were placed in a round-bottom flask and stirred at 150°C until all the unreacted powder had vanished and a clear solution was obtained. (It is recalled that a lower amount of CA did not enhance sufficiently the solubility of the fluoroligomer in aprotic

Table 1 Effect of reaction time at 90°C on the acid number[a] of the products of the reaction of the perfluoroether oligomer with finely ground chlorendic anhydride

Sample	Reaction time (hours)	Acid number
FCM-1	0.25	50.5
FCM-2	1.00	51.5
FCM-3	3.00	48.1
FCM-4	6.00	48.2

[a] Amount of KOH (mg) required to neutralise 1 g of oligomer

Table 2 NMR chemical shifts of specific hydrogens in the CA-perfluoro-ether adducts

Sample	FCM-1 (ppm)	FCM-4 (ppm)
COOH	7.30–7.50 3.95–4.05	7.80–8.20 4.00–4.10
CH₂–O–C	4.05–4.55	4.10–4.55

polar solvents. The use of larger amounts of CA, on the other hand, resulted in the formation of products of high molecular weight which also displayed insufficient solubility in ordinary solvents.) Heating was continued for different lengths of time and the extent of reaction monitored by chemical analysis of the reaction mixture. This product was coded FCM-x, referred to also as the CA-perfluoroether adduct, and was further reacted with CL for 2 hours at 140°C. This product was coded FCMC-x and is referred to also as caprolactone extended CA-perfluoroether adduct.

End group functionalisation of FCM-x and FCMC-x with trialkoxysilanes

The telechelically modified perfluoroether oligomers, FCM-x and FCMC-x, described earlier, were subsequently reacted with GOTMS at 90°C for different times of up to 2 hours and the progress of the reaction was monitored by *FT*i.r.

Table 3 Effects of GOTMS content in the functionalised CA-perfluoro-ether adducts (FCMG-x) on the visual appearance of resulting ceramers with 40 wt% silica

Sample	FCM-x:GOTMS (molar ratio)	Appearance of ceramer
FC-4	1:0.0	Opaque
FC-10	1:0.4	Hazy
FC-3	1:1.0	Transparent

Table 4 Effects of CL content in the CA-perfluoroether adduct (FCM) on the physical state of resulting ceramers

FCM:CL(molar ratio)	Functionalised[a] perfluoroether:SiO₂ (weight ratio)		
	2:3	3:2	2:1
1:0.0	Transparent	Transparent	Hazy
1:2.0	Transparent	Transparent	Transparent
1:5.0	Hazy	Cloudy	Cloudy
1:10.0	Cloudy	Opaque	Opaque (powdery film)

[a] Extent of silane functionalisation corresponds to FCM:GOTMS = 1:1 (molar ratio) at 85% conversion
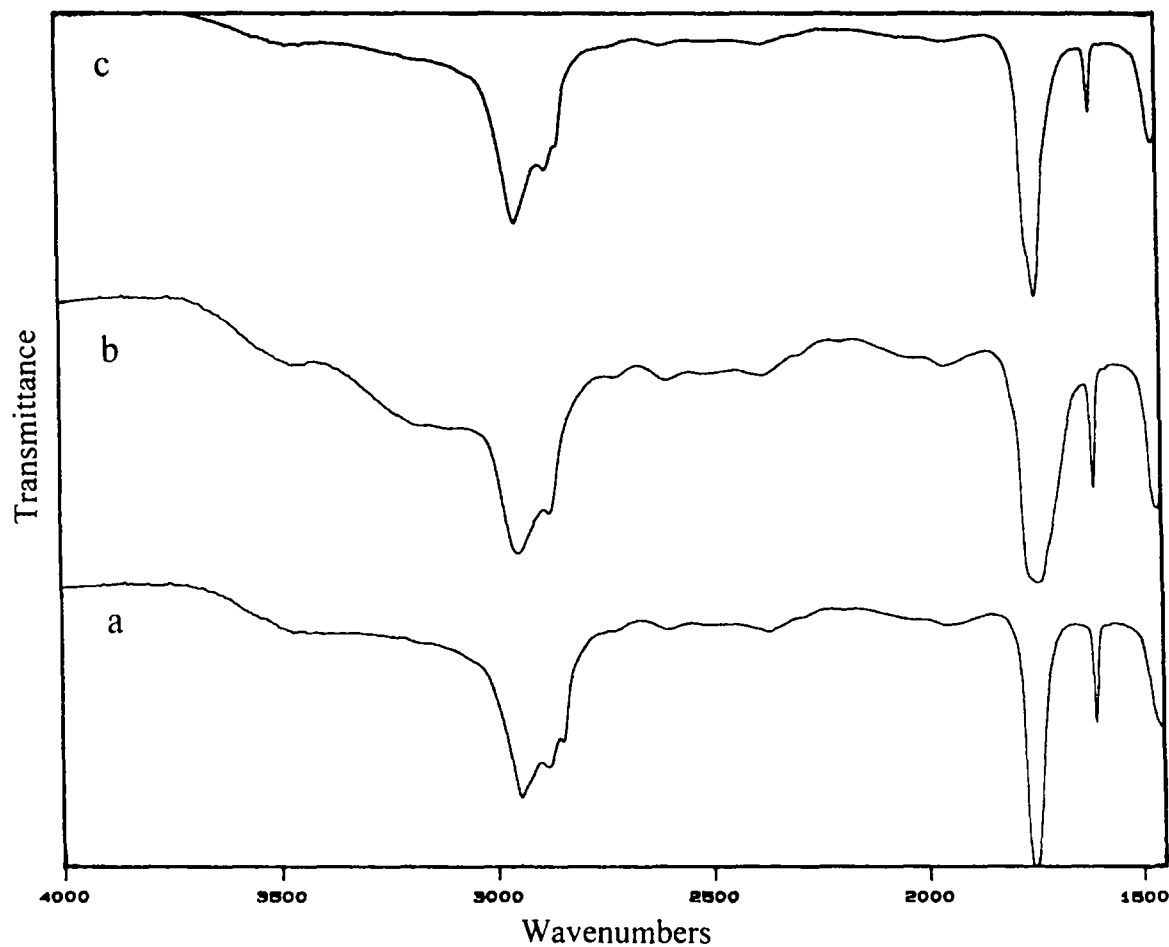
Figure 6 Infrared spectra of CA-perfluoroether precursors: a, CA-adduct functionalised with GOTMS; b, CA-perfluoroether adduct extended with caprolactone; c, caprolactone extended CA-perfluoroether adduct functionalised with GOTMS
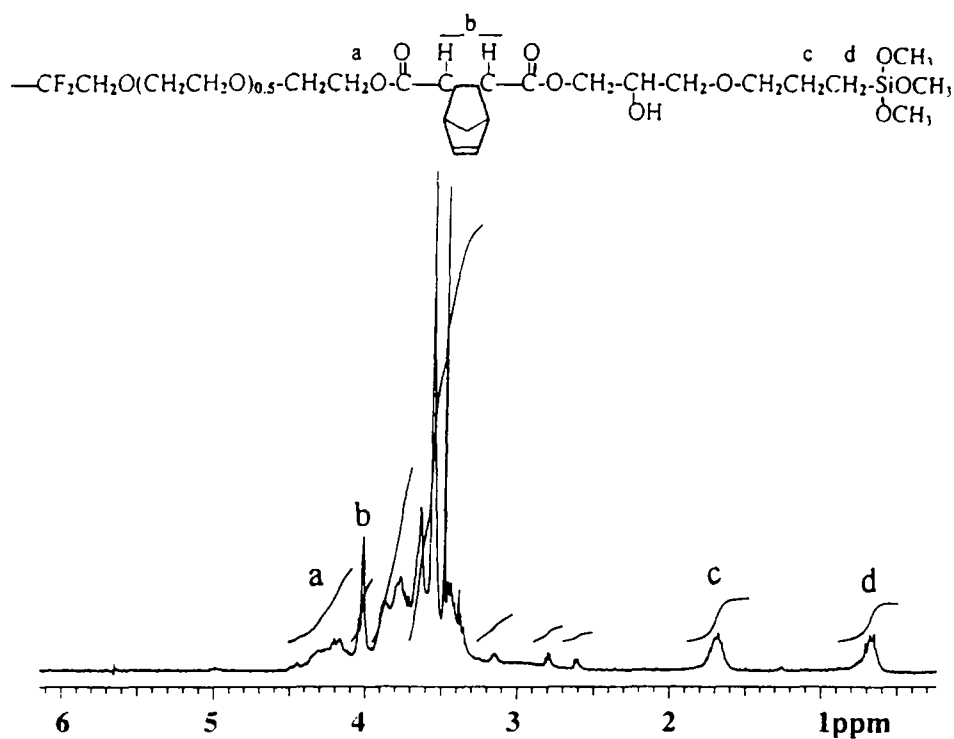

Figure 7 ^{1}H-NMR spectra of CA-perfluoroether adduct functionalised with GOTMS

analysis. These products were coded FCMG-x and FCMCG-x respectively, following the previous coding rationale.

No attempt was made to purify the reaction products since any unreacted GOTMS would be expected to enter the siloxane network and, possibly, react further with the oligomer in subsequent curing reactions, even though it may affect the morphology of the ceramer. This is presently being investigated in a separate study.

Preparation of polyperfluoroether–silica hybrid films

The general procedure used for preparing the poly-perfluoroether–silica hybrids was to dissolve the alkoxy-silane functionalised perfluoroether oligomers in DMF at a concentration of about 25 wt%. Measured amounts of water and TEOS at molar ratios of 3.0–3.5:1 were mixed and a catalytic amount of HCl was added to adjust the pH to 2–3. A homogeneous solution was obtained after stirring for 1 hour and was then placed in an oven at 80°C for 4–5 hours to increase the viscosity of the solution. This was then cast at room temperature onto glass slides to produce films about 0.2 mm thick. The resulting films were further dried under vacuum for 72 hours at 40°C. Thick specimens were produced by casting the solution in PTFE moulds, 40 × 12 × 3 mm, dried at room temperature and cured for 48 hours at 80°C under vacuum condition.

Characterisation of modified perfluoroethers and corresponding hybrids

The telechelic modification and functionalised perfluoro-ethers were analysed by FTi.r. and proton n.m.r.. For the FTi.r. analysis samples were prepared by smearing a drop of the solution of the pure liquid product in THF between NaCl discs. The ^{1}H-n.m.r. spectra were registered at 300 MHz in a mixture of deuterated trichloromethane (Cl_3CD)/trichloro-trifluoroethane $1/1(v/v)$ using a Varian Unity 300 instrument with the following conditions: flip angle 90°, acquisition time 4 s, pulse delay 8 s and 500 scans. The content of COOH end-groups on the telechelic modified perfluoroether was determined by chemical titration with a 0.01 M KOH solution in ethanol. The component compatibility of the hybrids was assessed by visually inspecting the cast films to provide qualitative information about the relative sizes of the dispersed domains. Visually revealed cloudiness or opacity was taken to be indicative of a heterogeneous structure of the order of 0.5 μm and larger. The final

Table 5 Thermal data for polyperfluoroether ceramers at different molar ratio of CA-perfluoroether adduct to caprolactone and as function of the silica content in the final hybrid

FCMCG-x:SiO$_2$	T_m (°C)	ΔH_m (J g^{-1})
For CA-perfluoroether:Cl = 1:5		
100:0	41.4	26.4
66.7:33.3	—	—
60:40	—	—
For CA-perfluoroether:Cl = 1:10		
100:0	42.7	81.2
66.7:33.3	44.3	24.2
60:40	44.2	12.3

Figure 8 Effect of GOTMS content in the functionalised CA-perfluoro-ether adduct (FCMG-x) on the morphology of ceramers containing 40 wt% silica: molar ratio of CA-perfluoroether to GOTMS: a, 1:0; b, 1:0.4; c, 1:1

morphology was examined on fractured surfaces of the films using both a Cambridge (360 model) stereoscan electron microscope (SEM) and an optical microscope (Zeiss).

The development of crystallinity in the CA-perfluoro-ether adduct extended with varying amounts of CL, and in the corresponding silica hybrid was evaluated by thermal analysis using a DuPont DSC 9000 apparatus.

RESULTS AND DISCUSSION

Telechelic extension reactions of perfluoroether oligomers

The reaction between CA and the perfluoroether oligomer, Fomblin ZDOL-TX, takes place in a heterogeneous phase.

Table 6 Effect of silica content on free oligomer present in the ceramer for systems based on CL extended CA-perfluoroether adducts at molar ratio of 1:2

Silica content	(wt%)	25	40	60	75
	(vol%)^a	30	46	66	79
Extracted matter in THF^b	(wt%)	23.5	13.0	0.0	0.0

^{a} Estimated from relative densities, i.e. 1.7 for the fluoroligomer component and 1.3 for the silica (xerogel) component
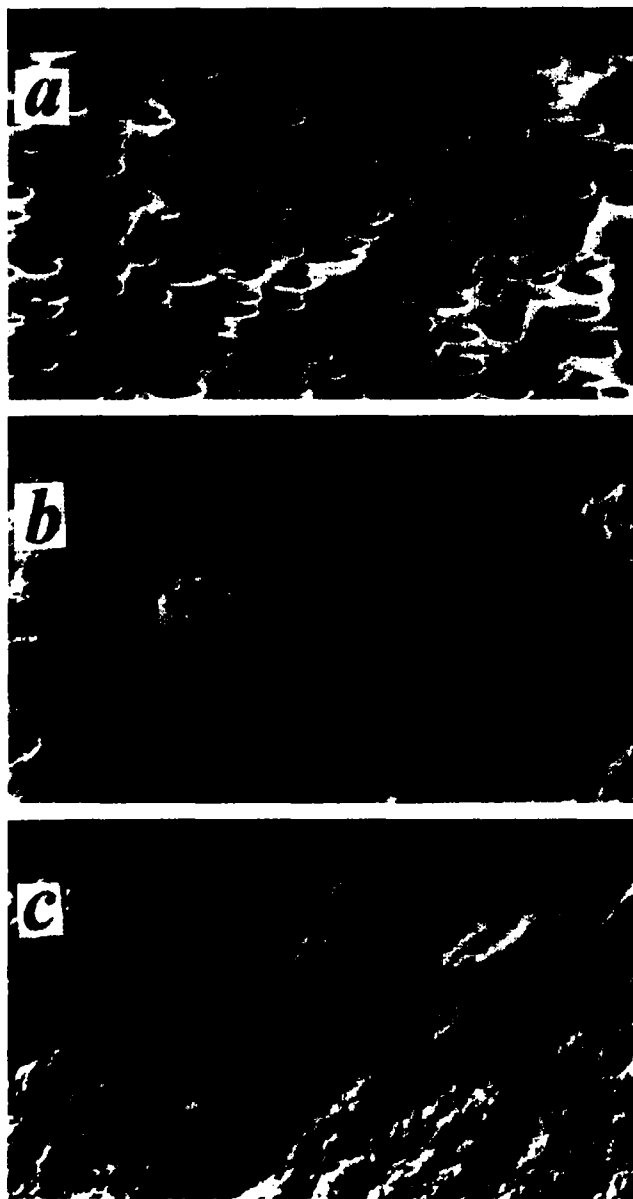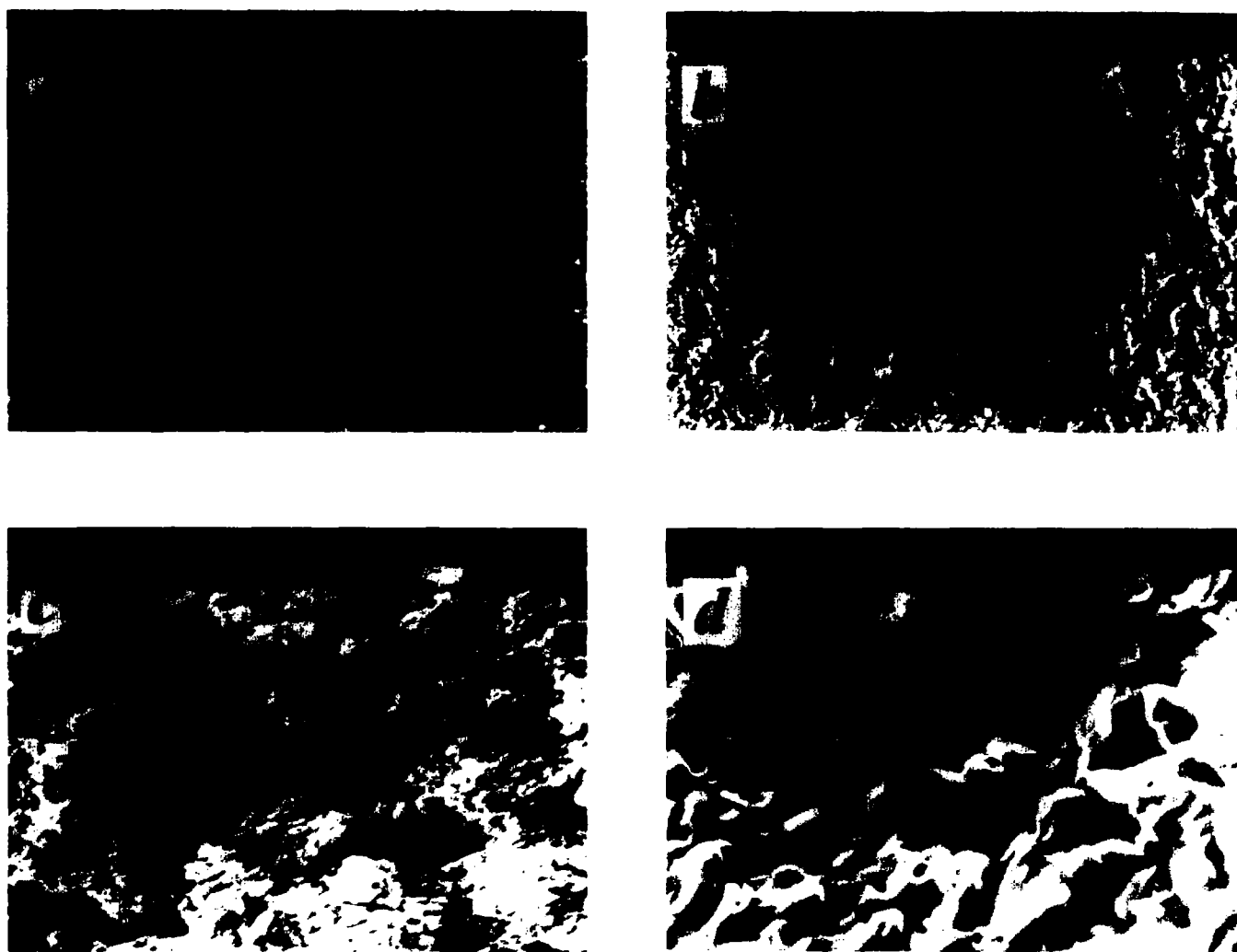^{b} Films ~70 μm were extracted in THF using a Soxhlet apparatus for 24 hours

Figure 9 Effect of caprolactone content in the functionalised perfluoroether adduct (FCMCG-x) on the morphology of corresponding silica hybrids (33.3 wt% silica in all cases): molar ratio of CA-perfluoroether to caprolactone: a, 1:0; b, 1:2; c, 1:5; d, 1:10

At a molar ratio of oligomer to CA equal to 1:1.5 (i.e. equivalent to a ratio of OH to COOH groups of 2:1.5), the time needed to complete the reaction at 150°C is 8 hours with intermittent stirring and 2 hours with continuous stirring. The reaction time is reduced to 15 minutes when the CA is ground into a fine powder. The absorbance peak for OH groups at $ca.$ 3400 cm^{-1} in the original oligomer is clearly visible in the FTi.r. spectrum (*Figure 2*). After reaction with CA the above peak disappears. Infrared measurements (*Figure 2*) and the titration results (*Table 1*) show that no further reactions occur for times longer than those specified earlier. Furthermore acid number measurements have confirmed that the reaction is complete and that the degree of polycondensation is very small.

These findings are supported by the ^{1}H-n.m.r. analysis, as shown in *Figure 3* and *Tables 2* and *3*. The peak at 7.3–75 ppm in FCM-1 or 7.8–8.2 ppm in FCM-4 (*Table 3*) is due to the hydrogen chemical shift of the COOH groups. The peaks at 3.95–4.05 ppm in FCM-1 or at 4.00–4.10 ppm in FCM-4 are due to the hydrogen formed by the opening of the CA ring. The peaks at 4.05–4.55 ppm in FCM-1 or 4.10–4.55 ppm in FCM-4 are attributed to the hydrogen of the CH$_2$ groups connected to ester groups. In the two samples the integral intensity of the peaks at 4.10–4.55 ppm is almost equal to that at 4.00–4.10 ppm, indicating that the CA has reacted fully with the fluoroligomer (Fomblin ZDOL-TX) within 15 minutes at 150°C.
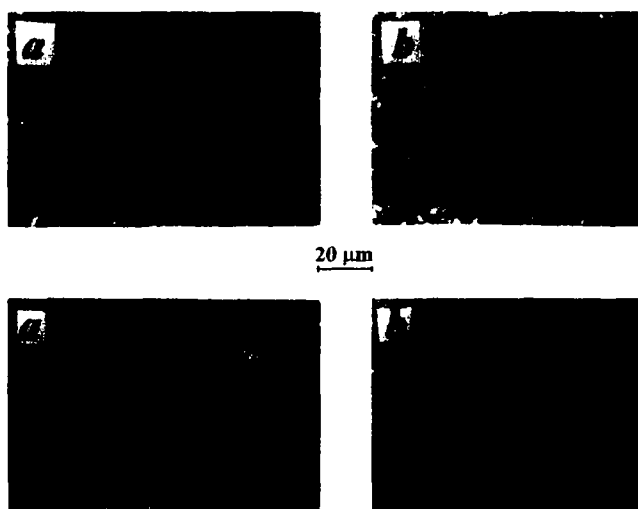

Figure 10 Optical micrographs of films for the following systems: *top*: silane functionalised CL extended CA-perfluoroether adducts; *bottom*: polyperfluoroether hybrids with 33.3 wt% silica content; *molar ratio of CA-perfluoroether to caprolactone*: a, 1:5; b, 1:10

The ratio of the integral intensity of COOH groups to the CH$_2$ groups linked to ester groups is close to 0.5 in FCM-1, showing that the CA adduct does not contain polycondensation products. In other words the CA adds to
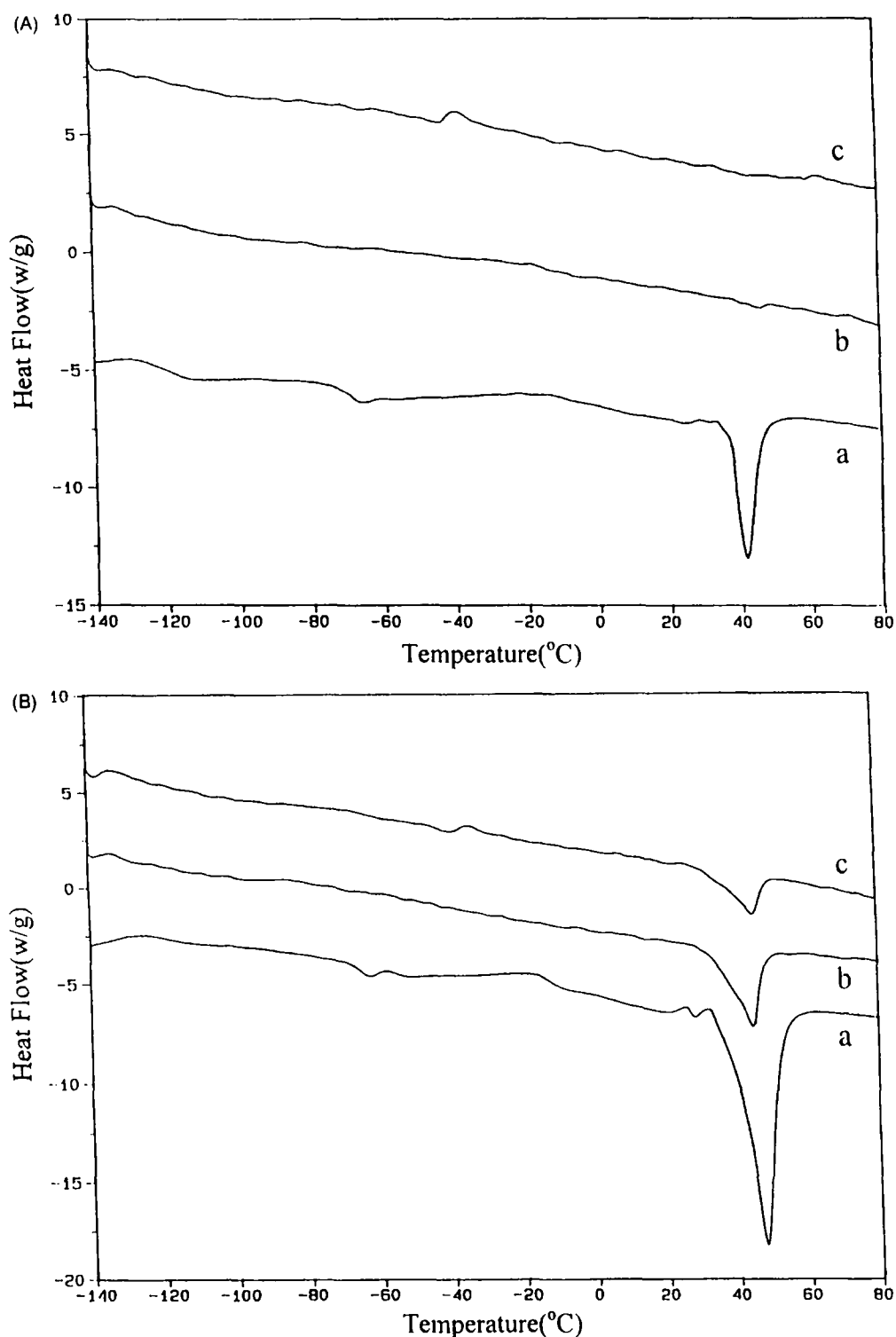
Figure 11 DSC thermograms of hybrids based on caprolactone extended CA-perfluoroether adducts (FCMCG-x): A, molar ratio of CA-perfluoroether to caprolactone 1:5; B, molar ratio of CA-perfluoroether to caprolactone 1:10; captions on graphs: perfluoropolyether to silica ratio: a, 1:0; b, 2:1; c, 3:2

the end of the fluoroligomer chains as single ester-acid units. When the reaction time was extended to 6 hours (FCM-4), on the other hand, the ratio of integral intensity of COOH to that of the CH_2 groups linked to the ester groups is somewhat less than 0.5, which indicates that part of the telechelically modified perfluoroether has become involved in polycondensation reactions. From the integral intensity of the two peaks it is estimated, in fact, that about 13% (molar) COOH groups have participated in polycondensation reactions.

Chain extension of CA-perfluoroether adducts with CL and alkoxysilane functionalisation

Visual observations on the perfluoroether adducts produced from the reaction with CA and subsequently reacted with different amounts of CL, corresponding to molar ratios of 1:2 (FCMC-1), 1:5 (FCMC-2) and 1:10 (FCMC-3), have revealed that at the higher molar ratios (i.e. 1:5 and 1:10) the solution was very viscous and turbid, but it became transparent on heating to 60°C. DSC analysis confirmed that this corresponds to the

melting of a polycaprolactone phase, which arises from homopolymerisation reactions (*Figure 4*). The DSC thermograms show melting peaks, respectively at 35°C for a molar ratio of 1:5 and at about 50°C for a molar ratio of 1:10. Some free polycaprolactone species were found to be present in the reaction products by *FT*i.r. analysis of the soluble fractions obtained from extraction tests in THF.

The ^{1}H-n.m.r. results have shown that, at a molar ratio of FCM-1 to CL of 1:2, the CL has reacted completely with the CA-perfluoroether adduct (*Figure 5*). However, the ratio of the integral intensity of the hydrogen in COOH to that in CH$_2$ linked with ester groups is 1:1.5, instead of the expected stoichiometric ratio of 1:2 for the reaction involving only one CL unit. From this it is deduced, therefore, that part of the CL forms a small amount of homopolymer or extended end chains even at low molar ratios. The functionalisation of the CA-perfluoroether adduct and the related CL extended products of the reaction with GOTMS (at a molar ratio of 1:1) takes place through reactions between the carboxylic acid groups in the perfluoroether and the epoxide groups of GOTMS. Infrared measurements have shown that the peak at 3200–3100 cm^{-1} for COOH disappears and a new peak is found at 3500–3400 cm^{-1}, corresponding to the hydroxyl group formed from the opening of the glycidoxy ring (i.e. CH$_2$CHOHCH$_2$) (*Figure 6*). From the ^{1}H-n.m.r. analysis it is estimated that the conversion of COOH is 85% (*Figure 7*). It was noted earlier that small amounts of unreacted GOTMS are not expected to affect the production of hybrids as these will become part of the siloxane network ([10,12]).

Effect of alkoxysilane functionalisation on the morphology of perfluoroether–silica hybrids

The solution mixtures cast as films on glass slides were all transparent initially, but the appearance and associated morphological state of the ceramer after evaporation of the solvent varied according to composition.

In *Table 3* are summarised the results of the effects of the molar ratio of CA-perfluoroether adducts to GOTMS on the physical state of the resulting ceramer films for a system containing 40% silica. This clearly shows that a high level of functionalisation (i.e. at least 20% and preferably 50% of all available carboxylic groups) is required to achieve an adequate level of compatibility for the formation of a morphology with nanoscale dimensions.

The data in *Table 4* indicate that, in general, transparent ceramers can be obtained with trimethoxysilane functionalised oligomers when the amount of CL in the extended chains is fairly low, and that a small amount of CL enhances the compatibility of the ceramer at low silica contents. This is expected to have resulted from enhanced solubility of the functionalised oligomer in the solvent used for the alkoxysilane solution (i.e. DMF). Typical morphologies of transparent films are shown in *Figure 8*. These show that the domains of the two phases are generally very small, possibly less than 100 nm. It was also found that the morphology becomes gradually finer with increasing silica content.

The micrographs in *Figure 9* show, furthermore, that increasing the amount of CL used in the chain extension reactions causes an increase in the dimensions of the domains due to the separation of a polymeric CL phase (see also *Figure 10*).

The DSC thermograms in *Figure 11* and thermal data in *Table 5* show that for systems with a molar ratio of CA-perfluoroether to CL equal to 1:5 the crystallinity of the original oligomer is lost in the formation of the ceramer.

At a molar ratio of 1:10 some of the crystallinity in the original functionalised oligomer is retained, however, in the final ceramer but the level of crystallinity is considerably lower than the expected value if the silica phase acted purely as a diluent. It is worth noting, furthermore, that the reduction in the level of crystallinity in the ceramers is accompanied by a small drop in melting point.

Taking this observation in conjunction with those made by Tian et al. for ceramers based purely on polycaprolactone[9], it is inferred that the caprolactone oligomeric species in the polyperfluoroether hybrids react with the products of the hydrolysis of TEOS.

The optical micrographs *a* and *b* in *Figure 10* show that the spherulites in the perfluoroether with high CL contents are very small and resemble those obtained from a high molecular weight polycaprolactone (Mn = 25000–65000)[20]. The micrographs *c* and *d* in the same figure reveal the existence of a microheterogeneous morphology, resulting from phase separation, which is responsible for the opaque appearance of the film and can be attributed to the presence of a discrete polycaprolactone phase.

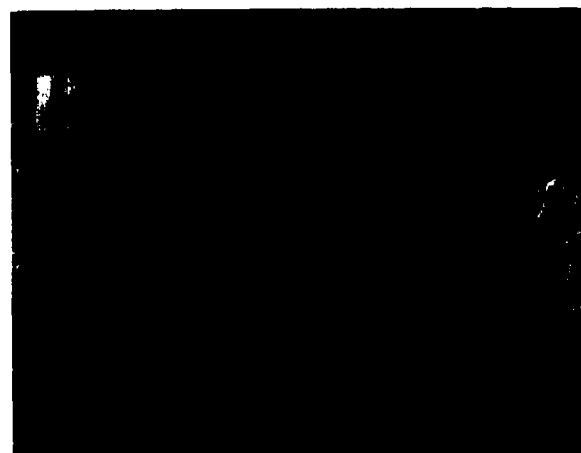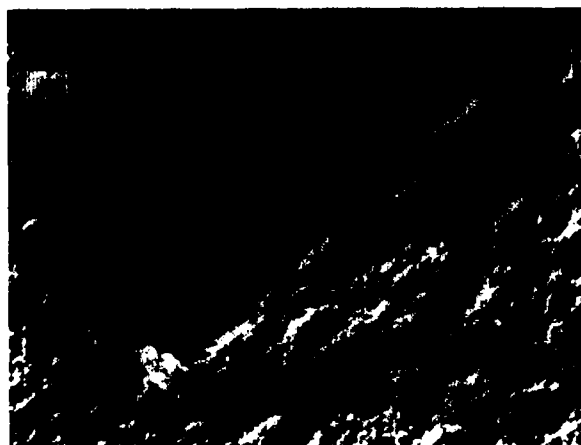The large holes visible in the SEM micrograph in *Figure*

Figure 12 Effect of weight ratio of silane functionalised CA-perfluoroether to silica (FCMG-1:silica) on the morphology of hybrids (FCMC:GOTMS = 1:1, at 45 wt% conversion); weight ratio of FCMC-1:silica: a, 3:2; b, 1:2
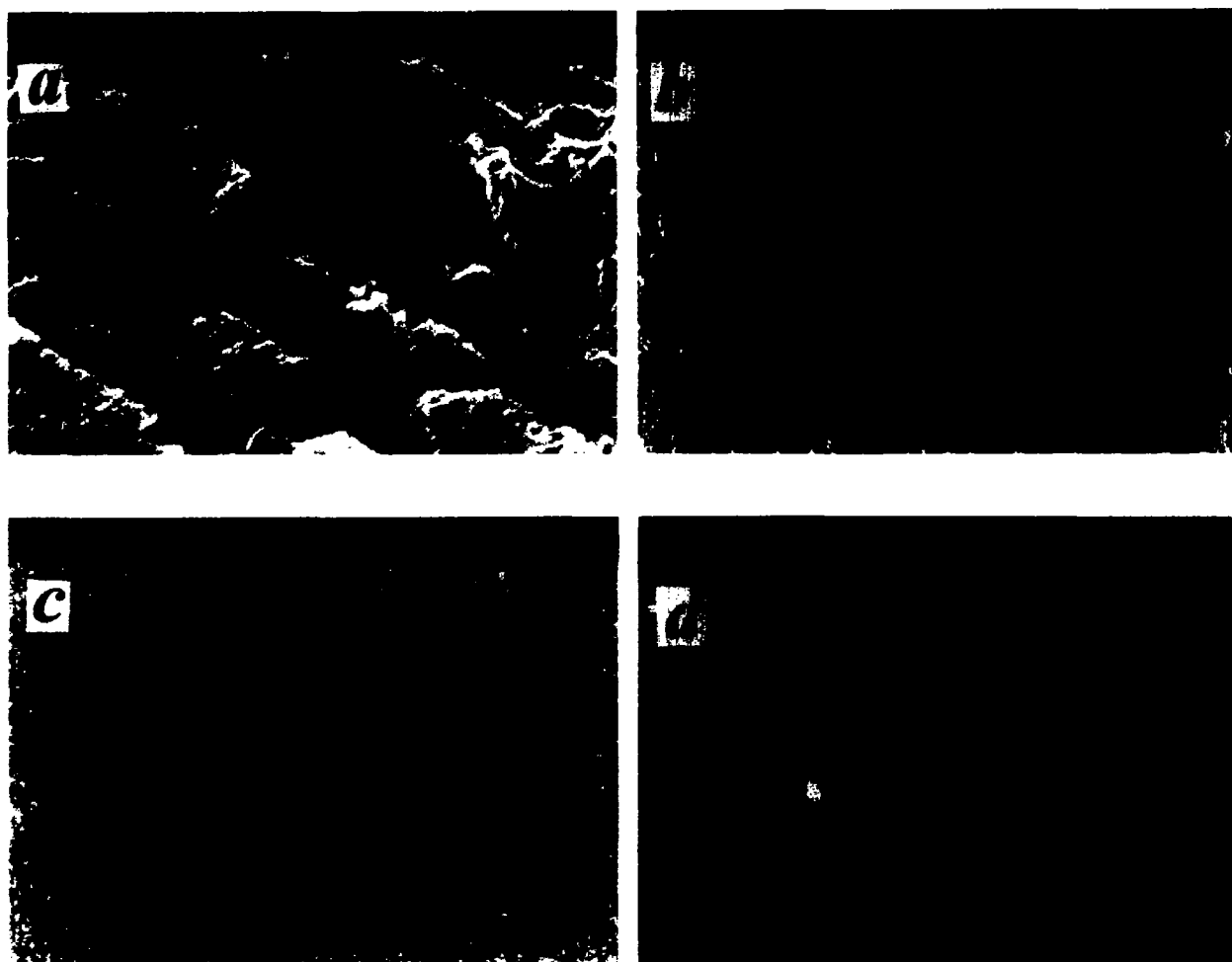
Figure 13 Influence of weight ratio of functionalised caprolactone extended CA-perfluoroether adduct to silica on the morphology of hybrids (FCMCG-x/silica); weight ratio of FCMCG-x to silica: a, 3:1; b, 2:1; c, 1:1; d, 1:3

9c, for the ceramer with a CA-perfluoroether to caprolactone molar ratio of 1:5, and the smooth appearance of the undulated fracture plane of the sample in *Figure 9d*, for the ceramer with a CA-perfluoroether to caprolactone molar ratio of 1:10, can be attributed, therefore, to the presence of large domains of a polycaprolactone phase. These are also indicative of a difference in the geometry of the poly-caprolactone domains in the two cases. At low contents of caprolactone the separated phase is in the form of discrete particles, whereas at high caprolactone contents the two main phases are co-continuous (see also optical micrographs in *Figure 10*).

It is worth noting also that the spherulites in the micrograph for the high caprolactone content ceramers are hardly visible in comparison to those displayed by the precursor oligomer, which is indicative of a restriction on the growth of the crystals by the surrounding silica phase.

The micrographs in *Figures 12* and *13* show the morphology of ceramers based on both types of modified perfluoroethers for different silica contents. In accordance with previous results the morphology of the resulting ceramer becomes gradually finer with increasing silica content. The data in *Table 6* indicate that when the SiO$_2$ content becomes less than 60 wt% (approx. 66 vol%) a certain amount of oligomer does not enter the siloxane network. One must bear in mind that, in this case, the molar ratio of GOTMS to CL extended perfluoroether was 1:1 (i.e. the stoichiometric molar ratio), and since the percentage conversion was about 85%, statistically it can be expected

that only about 85% of the total fluoroligomer would enter the network via the condensation reactions with the terminal methoxysilane groups. A small amount of extractable oligomer can be expected, therefore, to be present in all ceramers produced. The reason for the failure to detect an amount of extractable matter at high silica contents may be related to the very low level of dissolution achieved with the experimental conditions used when the silica phase predominates.

CONCLUSIONS

The main conclusions that can be drawn from this work are as follows:

(a) End-group reactions of hydroxyl terminated fluoro-alkane oligomers (perfluoroethers) with 1.5 moles of CA, and further telechelic extensions with 2.0 moles of CL, can be readily carried out in bulk to full conversion.

(b) End of chain functionalisation of the telechelic extended perfluoroether oligomers can be readily carried out in bulk, and to about 85%, without the use of catalysts by reacting the terminal carboxylic acid groups with GOTMS.

(c) Functionalisation of the chain extended perfluoroether oligomers with GOTMS at a molar ratio of 1:0.4 is sufficient to produce compatible ceramers with silica contents of greater than about 40%. At higher levels of functionalisation (e.g. at 1:1 molar ratio), a more

pronounced compatibility can be achieved, making it possible to produce ceramers with much lower silica contents, e.g. less than 25%, and with lower amounts of extractable residues.

(d) Telechelic extensions with low amounts of CL, prior to functionalisation with GOTMS, enhance the compatibility of resulting ceramers. Increasing the CL content in the precursor, on the other hand, gives rise to the formation of a microheterogeneous morphology.

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REFERENCES

1. Ajroldi, G., *Eur. Polym. J.*, 1988, **12**, 1211.
2. Tonelli, C., 12th International Symposium on Fluorine Chemistry, August 7–12, 1988, Santa Cruz, California, USA.
3. Mascia, L., Zitouni, F. and Tonelli, C., *J. Appl. Polym. Sci.*, 1994, **51**, 905.
4. Mascia, L., Zitouni, F. and Tonelli, C., *Polym. Eng. Sci.*, 1995, **35**, 1069.
5. Mascia, L., Zitouni, F. and Tonelli, C., ANTEC 93, New Orleans, May 9–13, 1993.
6. Mascia, L., *Trends in Polymer Science*, 1995, **3**, 61.
7. Huang, H. H., Wilkes, G. L. and Carlson, J. G., *Polymer*, 1989, **30**, 2001.
8. Huang, H. H., Orler, B. and Wilkes, G. L., *Macromolecules*, 1987, **20**, 1322.
9. Tian, D., Dubois, Ph. and Jerome, R., *Polymer*, 1996, **37**, 3683.
10. Wang, B., Wilkes, G. L., Hedrick, J. C., Liptak, S. C. and McGrath, J. E., *Macromolecules*, 1991, **24**, 3449.
11. Mascia, L. and Kioul, A., *Polymer*, 1995, **36**, 3649.
12. Kioul, A. and Mascia, L., *J. Non-Crystall. Solids*, 1994, **175**, 169.
13. Chen, J. P., Ahmad, Z., Wang, S., Mark, J. E. and Arnold, F.E., in *Hybrid–Organic -Inorganic Composites*, ed. J. E. Mark, C. Y.-C. Lee and P. A. Bianconi. AC Symposium Series 585. American Chemical Society, Washington, DC, 1995, ch. 13.
14. Mark, J. E., Premanchandra, J., Kumidinie, C., Zhao, W., Dang, T. D., Chen, J. P. and Arnold, F. E., in *MRS Symposium Proceedings Vol. 435. Better Ceramics Through Better Chemistry VII: Organic Inorganic Hybrids*, ed. B. K. Coltrain, S. Sanchez, D. W. Schaefer and G. L. Wilkes. Materials Research Society, Pittsburgh, PA, 1997, p. 13.
15. Yano, S., *Polymer*, 1994, **35**, 5565.
16. Fitzgerald, J. J., Landry, C. J. T. and Pochan, J. M., *Macromolecules*, 1992, **25**, 3715.
17. Huang, Z. H. and Qin, K. Y., *Polymer*, 1997, **38**, 521.
18. Betrabet, C. S. and Wilkes, G. L., *Pol. Reprints*, 1993, **34**, 438.
19. Wilkes, G. L., Huang, H. H. and Glaser, R. H., in *Silicon-based Polymer Science, A Comprehensive Approach*, ed. J.M. Ziegler and F.W.G. Fearon. Advanced Chemistry Series 224. American Chemical Society, Washington, DC, 1990.
20. Chen, H. L., Li, L. J., Ou-Yang, W. C., Hwang, J. C. and Wong, W. Y., *Macromolecules*, 1997, **30**, 1718.