



Perfluoropolyether–tetrafluoroethylene (PFPE–TFE) block copolymers: An innovative family of fluorinated materials

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ABSTRACT

A new technological platform, based on the chemistry of the peroxidic perfluoropolyethers, has been recently developed for the synthesis of innovative fluorinated materials. Perfluoropolyether–tetrafluoroethylene (PFPE–TFE) copolymers are one of the most representative examples of the potential and the flexibility of this technology. By tuning the reaction parameters, the structure of these copolymers can be easily modulated to obtain products with the desired chemical–physical and rheological properties. Applications are endless, from thin film lubrication to gel based greases, to additives for plastics, rubber and other compounds. This technology will lead to entirely new classes of PFPE materials that will fill many of the gaps existing today in markets not currently served by PFPEs.

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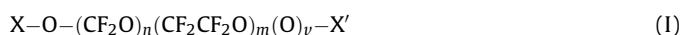
1. Introduction

An increasing demand for innovative fluorinated products has characterized the last two decades and it is expected to become even greater in the coming years. Solvay Solexis has always been engaged in answering to the most challenging needs, coming from high technology markets, by developing new fluoropolymers [1], new fluoroelastomers [2] and new fluorinated fluids [3].

Very recently, a new technological platform has been introduced for the synthesis of a pioneering class of fluorinated materials [4]: this technology, based on the radical reaction of peroxidic perfluoropolyethers (PFPE) with unsaturated fluorocompounds, can be applied for the preparation of a huge variety of fluorinated copolymers not achievable with conventional techniques. A representative example is the reaction of the peroxidic PFPE with tetrafluoroethylene (TFE), which provides copolymers containing perfluoropolyether blocks alternated with polytetrafluoroethylene blocks. These new materials, here indicated as PFPE–TFE copolymers, show peculiar properties that make them appealing for several applications in very different fields. In this paper, the synthesis, the characterization and the applications of the PFPE–TFE copolymers are presented and discussed.

2. Synthesis

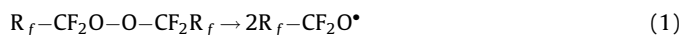
PFPEs can be obtained industrially by the low temperature oxy-polymerization of perfluorinated olefins [5–7]. In the case of tetrafluoroethylene, the product of this reaction is a linear peroxidic PFPE with the following structure:



where X and X' are mainly CF₃– and FC(O)CF₂– end groups, and –(O)_v– represents the peroxidic oxygen randomly distributed along the chain. The *n/m* ratio ranges from 0.5 to 2.0 and the average molecular weight ranges from 1000 to 200,000 [5].

The peroxidic units of (1) must be removed by thermal or photochemical treatment to obtain, after a final fluorination step, stable PFPEs commercially known as FOMBLIN[®] PFPE Z and FOMBLIN[®] PFPE M [8]. An alternative method for the peroxide removal is the catalytic reduction with molecular hydrogen [9]. This reaction gives PFPEs with lower molecular weight and with acylfluoride groups as chain ends that, after chemical modifications, yield different types of PFPE derivatives (SOLVERA[®] PFPE and FLUOROLINK[®] PFPE).

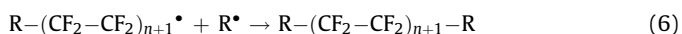
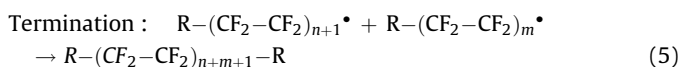
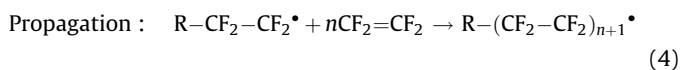
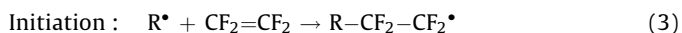
In the recent years the possibility of using (1) as a radical source for the synthesis of new classes of PFPE block copolymers has been thoroughly investigated and demonstrated [4,10]. In fact, when the peroxidic units of (1) undergo thermal or photochemical cleavage, perfluoroalkoxy and perfluoroalkyl radicals are generated according to the following reactions:



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The alkoxy radical of Eq. (1) can decompose and form a new alkyl radical and a molecule of carbonyl fluoride (Eq. (2)). In an inert atmosphere, the perfluoroalkyl and perfluoroalkoxy radicals recombine to give a stable and non-peroxidic PFPE (the FOMBLIN[®] PFPE Z and FOMBLIN[®] PFPE M mentioned above) whose repeating units are mainly $-CF_2O-$, $-CF_2CF_2O-$. However, when an olefin like TFE is present in the reaction medium, the radicals of Eqs. (1) and (2) can act as initiators for its polymerization, thus leading to the formation of TFE blocks inside the perfluoropolyether chain: the mechanism can be described by using the classic kinetic scheme of the radical polymerizations:



R^\bullet can be indifferently a perfluoroalkyl or perfluoroalkoxy radical coming from Eqs. (1) and (2). Due to the high reactivity of TFE, R^\bullet rapidly reacts with this monomer (Eq. (3)) and forms a new perfluoroalkyl radical that grows by addition of other molecules of TFE (Eq. (4)). The kinetic chain terminates by coupling with another radical of the same type (Eq. (5)) or with a R^\bullet primary radical (Eq. (6)).

PFPE-TFE block copolymers are synthesized by feeding TFE in a solution of (I) heated at a temperature sufficiently high to decompose the peroxidic units. At the end, the reaction product is fluorinated to convert the acyl fluoride end groups into the more stable and unreactive trifluoromethyl groups. For details, see Section 6.

The final structure of the PFPE-TFE block copolymers so obtained can be depicted by the following formula:



where A is a perfluoropolyether block containing $-CF_2O-$ and $-CF_2CF_2O-$ units, B is a $-(CF_2CF_2)-$ polytetrafluoroethylene block, t is the number of blocks B per chain.

Thanks to the flexibility of this chemistry, PFPE-TFE copolymers with different physical and rheological properties can be synthesized by tuning the reaction parameters. For example, copolymers with longer B blocks are obtained by increasing the amount of olefin fed into the reactor during the synthesis. It is also possible to regulate the number of B blocks per chain by changing the content of peroxidic units $-(O)_v-$ in (I). This can be done either during the photo-oxypolymerization or by carrying out a partial thermal treatment on (I) in an inert atmosphere (i.e., thermal treatment that destroys only a definite percentage of the initial peroxidic units). In the first case, the peroxidic content can be increased or lowered depending on the

Table 1¹⁹F NMR assignment of the repeating units of PFPE-TFE copolymers.

Chemical shift (ppm)	Assignment
-51.7	$-CF_2CF_2O-CF_2O-CF_2CF_2O-$
-53.2	$-CF_2CF_2O-CF_2O-CF_2O-$
-55.0	$-OCF_2O-CF_2O-CF_2O-$
-83.3	$-OCF_2CF_2(CF_2)_nCF_2CF_2O-CF_2CF_2O-$ with $n \geq 1$
-83.5	$-OCF_2CF_2CF_2CF_2O-CF_2CF_2O-$
-83.6	$-OCF_2CF_2CF_2O-CF_2CF_2O-$
-84.9	$-OCF_2CF_2(CF_2)_nCF_2CF_2O-CF_2O-$ with $n \geq 1$
-85.2	$-OCF_2CF_2CF_2CF_2O-CF_2O-$
-85.4	$-OCF_2CF_2CF_2O-CF_2O-$
-88.7	$-CF_2CF_2O-CF_2CF_2O-$
-90.4	$-OCF_2O-CF_2CF_2O-$
121.8	$-OCF_2CF_2(CF_2)_nCF_2CF_2O-$ with $n \geq 1$
-125.5	$-OCF_2CF_2(CF_2)_nCF_2CF_2O-$ with $n \geq 1$
-125.8	$-OCF_2CF_2CF_2CF_2O-$

reaction parameters selected for the photo-oxypolymerization whereas, in the second case, the peroxidic content can be only decreased.

3. Characterization

3.1. Structure

Three prototypes of PFPE-TFE copolymers, one liquid and two solids, were synthesized. Since all of them are soluble in fluorinated solvents, the ¹⁹F NMR technique was used for their structural characterization after dissolution in hexafluorobenzene. In Table 1 the chemical shifts and the assignments of the repeating units are listed whereas, in Table 2, the structural data are reported for the three samples synthesized: numerical average molecular weight of the copolymer (Mn), numerical average molecular weight of the two blocks (A and B) and average number of B blocks per chain.

The main structural differences among the samples concern the average length of the two blocks (A varies from 2300 amu to 11,000 amu and B varies from 430 amu to 1130 amu or, expressed as carbon atoms, from 8.6 to 22.6) and the number of blocks per chain (from 1 to 13). The content of A block in the copolymers is always higher than 78% by weight and this explains their excellent solubility in fluorinated solvents.

3.2. Physical properties

The state of the PFPE-TFE copolymers can be liquid, wax or solid depending on their composition. An internal study carried out on copolymers with different structures indicates that the length of the B block is the parameter that mostly influences the physical state of the copolymer [11]. In particular, for copolymers with short B blocks, indicatively below 10 carbon atoms, the formation of crystallites is avoided and the copolymer is totally amorphous and liquid at room temperature. By increasing the B block length, the perfluorocarbon sequences can crystallize, as evidenced by the presence of a melting transition, and the PFPE-TFE copolymers become wax-like (B block length approximately between 10 and

Table 2

Structural characterization of the PFPE-TFE copolymer.

Sample	Physical state	Mn of the copolymer (u.m.a)	Polytetrafluoroethylene block (B)			PFPE block (A)
			Average length (n^0 of carbon atoms)	Number of B block per chain	Content in the copolymer (% w/w)	Average length (u.m.a)
1	Liquid	27,000	8.6	7	10.9	3000
2	Wax	41,000	14.2	13	21.8	2300
3	Solid	34,000	22.6	2	6.3	11,000

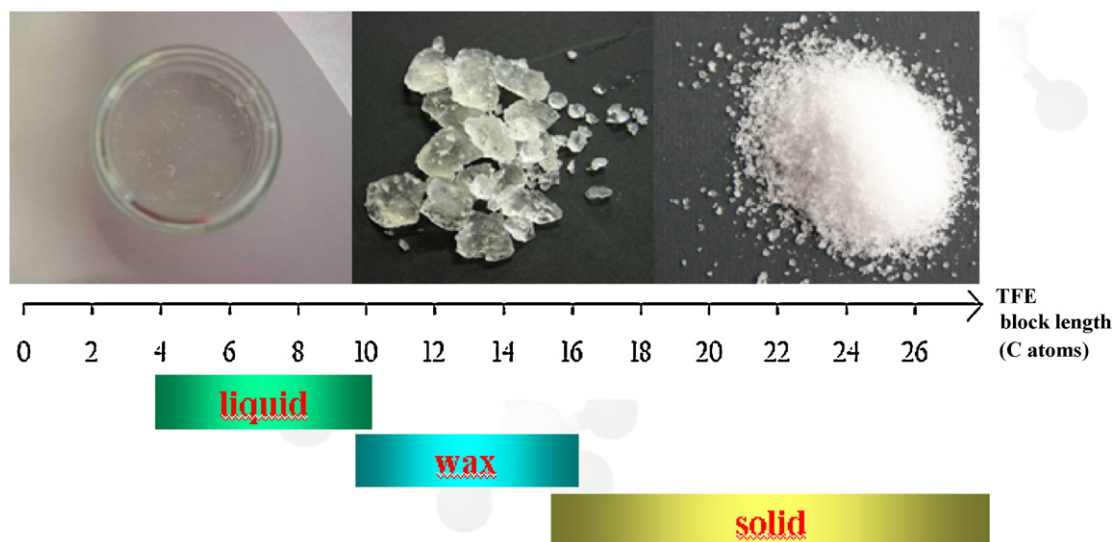


Fig. 1. Variation of the physical state of the PFPE-TFE copolymers as a function of the B block length.

Table 3

Glass transition and melting point of the PFPE-TFE copolymers (DSC analysis).

Sample	T_g (°C)	ΔC_p (J/g °C)	M_p (°C)	ΔH melting (J/g °C)
1	-114	0.234	-	-
2	-114	0.208	106	-2.1
3	-117	0.215	210	-6.1

15 carbon atoms) or solid (B block length approximately longer than 15 carbon atoms). In Table 3 the glass transition (T_g), its corresponding specific heat capacity (ΔC_p) and the melting temperature are reported whereas Fig. 1 exemplifies the variation of the physical state vs. the block B length.

A glass transition, ascribable to the very mobile perfluoropolyether A blocks, is always present at temperatures between -114 °C and -117 °C, values that are in line with those reported in the literature for perfluoropolyethers [5]. Moreover, this narrow range of temperatures indicates that this transition is not influenced by the content and the length of the B blocks, being the amorphous domains substantially unperturbed by the crystallized perfluorocarbon domains. In similar bi-phasic systems where the soft amorphous blocks are organized in nanoscopic domains, a significant effect of the confinement on the glass transition, increasing with the decreasing size of the domain, has already been evidenced [12].

Melting point data of a series of copolymers [11] have been plotted against the length block B and compared with those reported in literature [13] for linear perfluorocarbons of general formula $CF_3-(CF_2)_n-CF_3$ and with n comprised between 12 and 24 (see in Fig. 2).

As shown in Fig. 2, the melting point of the PFPE-TFE copolymers increases with the block B length following a trend very similar to that of the linear perfluorocarbons, but shifted upward by about 20–25 °C, being greater the distance for shorter lengths. This behavior could be explained by considering that perfluorocarbons have CF_3- as chain ends whereas the TFE blocks are linked, at their ends, to PFPE blocks, and thus some effect related to the size and the surface interactions of the crystallized domains can be expected. Another reason could be due to the polydispersity of the B blocks within the PFPE-TFE copolymers whereas the data of perfluorocarbons are relative to neat compounds.

With the aim of better understanding the physical structures of these copolymers, X-ray diffraction analyses were carried out. The

spectra, reported in Fig. 3, evidence a semi-crystalline structure where the crystalline peak at $2\theta = 18.2^\circ$ is superimposed on the amorphous halo.

Through the fitting procedure suggested in the literature [14], the 2 components (the crystalline and the amorphous one) can be separated and the crystallinity of the copolymer (X_c) can be calculated from the ratio of crystalline area to total area. Moreover, using the Scherrer method [15], the size of the crystallites domains can also be estimated from the peak FWHM (full width at the half maximum intensity). Both X_c and the crystallite size increase with the B blocks length, as reported in Table 4.

The position of the crystalline peak, corresponding to the (1 0 0) reflection of a PTFE crystal, and its sharpening with the increasing length of the B segment, fit with a model where the hard blocks crystallize in a PTFE-like structure of growing perfection with the increased dimension of the segregated hard phase.

These data confirm that the hard B blocks form small morphological domains that serve as reinforcement sites: the architecture of these copolymers can thus be represented as a two-phase physical network composed of soft (PFPE) and hard (TFE) blocks (Fig. 4).

The melting point and the physical properties of this material are thus dominated by the crystallite size, also in accordance with previous studies [16,17], which mainly depends on the average length of B blocks in the copolymer.

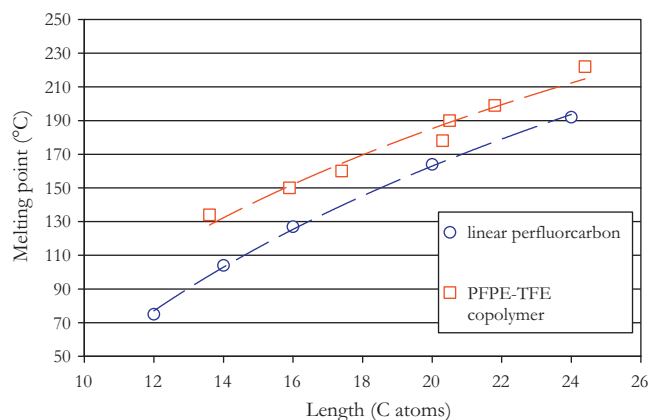


Fig. 2. Melting point of the PFPE-TFE copolymers as a function of the B block length in comparison with the melting point of linear perfluorocarbons of formula $CF_3-(CF_2)_n-CF_3$.

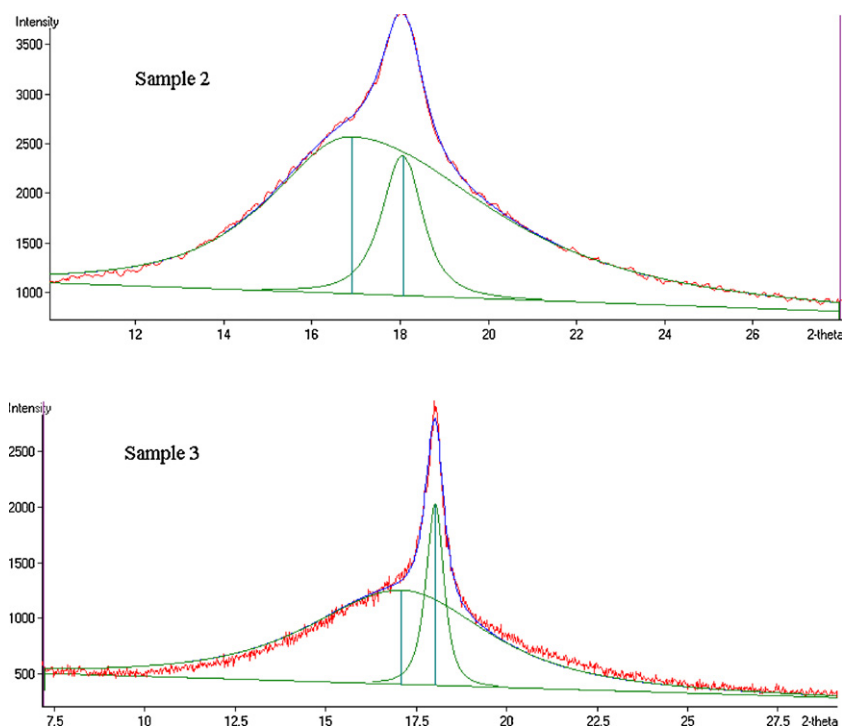


Fig. 3. X-ray diffraction spectra of the PFPE-TFE copolymers.

Table 4
Crystallite fraction and average dimension of the crystallites determined by X-ray diffraction spectra.

Sample	Crystallite fraction Xc	Average dimension of the crystallites (Å)
2	0.14	84
3	0.16	154

The thermogravimetric analyses were carried out under inert atmosphere (nitrogen) and the results are reported in Table 5.

The degradation, considering the 10% weight loss as reference, occurs at temperature higher than 450 °C thus indicating a very high thermal stability for these structures. Differences among the samples at low weight loss values (1 and 2%) can be ascribed to the evaporation of low molecular weight fractions or residual traces of the solvent used for the synthesis. For Sample 2, the thermogravimetric analysis was repeated, at the same heating rate, in air (see Table 4) without evidencing significant differences in comparison with the analysis done under nitrogen flow. The intrinsic high thermal stability of these copolymers, both in an inert and in an oxidative environment, is due to their totally fluorinated structure. The effect of oxygen can be observed only at high temperatures (indicatively above 400 °C) when the C–C bonds

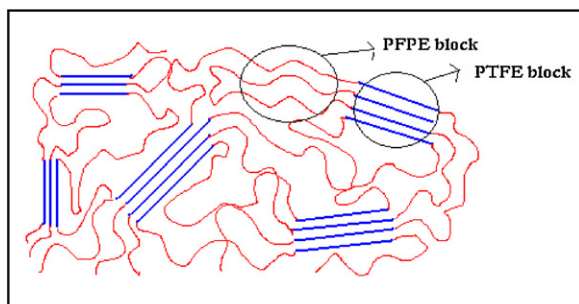


Fig. 4. Simplified representation of the architecture of the semi-crystalline PFPE-TFE copolymers.

start breaking and form perfluoroalkyl radicals. In the presence of oxygen, perfluoroalkyl radicals are converted into the less stable perfluoro-peroxy and perfluoro-oxy radicals that rapidly decompose, through a radical unzipping mechanism, forming carbonyl difluoride as one of the main gaseous degradation product.

3.3. Rheological properties

The kinematic viscosity of the liquid sample 1 was measured at three different temperatures and the values are reported in Table 6 together with the viscosity index. In the same table, the data of an experimental PFPE oil with a linear structure (obtained by photo-oxypolymerization of TFE) and of FOMBLIN[®] PFPE YR1800, a commercial PFPE oil with a non linear structure (obtained by photo-oxypolymerization of hexafluoropropylene), are reported for comparison. Due to the presence of the rigid B block, the viscosity of the liquid PFPE-TFE copolymer is much higher than that of the experimental PFPE, even if the numeric average molecular weight of the two samples is comparable. Quite surprisingly the viscosity index, a parameter that indicates the viscostaticity of the oils, does not significantly differ between the linear PFPE and the copolymer whereas, as predictable, it is much higher than that of FOMBLIN[®] PFPE YR1800 due to the effect, in this sample, of CF₃-side groups along the chain.

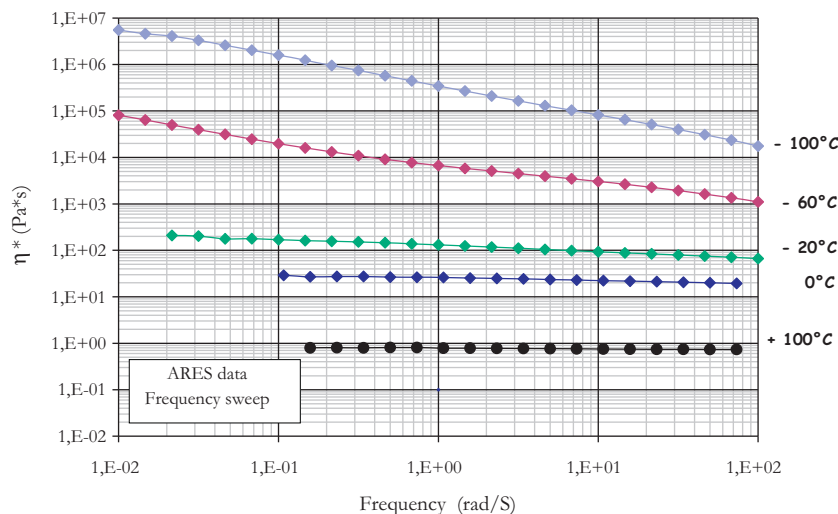
Rheological measurements of the complex viscosity (η^*) were carried out, during forced harmonic oscillation of shear stress, on

Table 5
Thermogravimetric analysis (TGA).

Sample	Carrier	Weight loss vs. temperature			
		1% vs. T (°C)	2% vs. T (°C)	10% vs. T (°C)	50% vs. T (°C)
		T (°C)			
1	Nitrogen	261	300	450	559
2	Nitrogen	308	362	529	600
2	Air	313	376	465	579
3	Nitrogen	252	316	482	564

Table 6Kinematic viscosity and viscosity index of sample 1 in comparison with an experimental PFPE (linear structure) and with FOMBLIN[®] PFPE YR 1800 (branched structure).

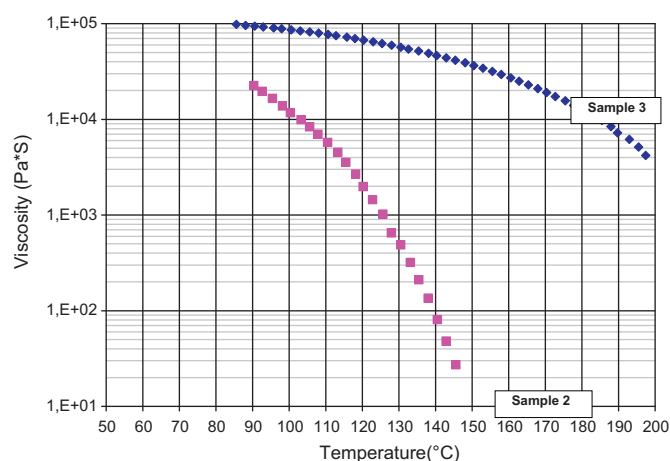
Sample	Mn	Kinematic viscosity (cSt)			Viscosity Index (ASTM D2270)
		20 °C	40 °C	100 °C	
1	27,000	5203	2363	488	381
Linear PFPE	25,000	1300	700	200	375
FOMBLIN [®] PFPE YR 1800	7250	1850	510	47	135

**Fig. 5.** Complex viscosity of sample 1 measured in oscillatory conditions (1 rad s⁻¹) at different temperatures.

sample 1 in a wide range of temperatures (between –100 °C and +100 °C). As reported in Fig. 5, the behavior of this liquid is Newtonian at temperature higher than 0 °C, since the value of η^* is constant in the examined range of frequency and for a fixed value of temperature. A non-Newtonian behaviour appear at 0 °C and becomes more evident at lower temperatures, when the stiffness effect, associated with the rigid perfluorocarbon B block, becomes stronger.

The values of complex viscosity measured at 1 rad s⁻¹ as a function of temperature are reported, for sample 2 and for sample 3, in Fig. 6.

In both cases the viscosity decreases with the increase of temperature thus indicating a higher mobility of the chains. The viscosity of sample 2 is lower than that of sample 3 and starts to decrease at a temperature lower than that of sample 3. This behavior can be explained considering the melting of the blocks B

**Fig. 6.** Complex viscosity of sample 1 measured in oscillatory conditions at different temperatures.

that takes place around 100 °C in the case of the sample 2 and around 210 °C in the case of the sample 3.

4. Established applications

The PFPE–TFE copolymers are a new class of materials that combines the properties of perfluoropolyethers with those of perfluoropolymers. Thanks to this combination, the PFPE–TFE copolymers show excellent lubricant properties, a very good thermal and chemical stability, solubility in fluorinated solvents and perfluoropolyether oils, UV resistance, non-toxicity and non-flammability. Moreover, the possibility of regulating their physical state and their melting point is an undoubted advantage that guarantees a fine tuning of their properties.

PFPE–TFE copolymers were tested with success as:

- Lubricating oils: liquid PFPE–TFE copolymers (sample 1) show excellent lubricant properties, good viscostaticity and low values of wear and friction [4,18]. Being their molecular weight are higher than that of the commercial perfluoropolyether oils, their evaporation loss is lower and, for this reason, they can be used in high temperature or under vacuum applications.
- Lubricating gel solid PFPE–TFE copolymers (sample 2 and sample 3) are soluble in perfluoropolyether oils like FOMBLIN[®] PFPE Y and FOMBLIN[®] PFPE Z and M. When they are dissolved in these oils at a concentration generally higher than 10% by weight, a lubricant gel formulation is obtained [4]. The gel differs from both the perfluorinated oils, that are fluid, and the perfluorinated greases, that are dispersion of PTFE powders in oils. These new gel lubricants have some very interesting features: as they are monophasic systems they do not separate under storage or usage, they are transparent and characterized by very good lubricating properties, in particular in terms of low wear and low friction. As a consequence they can find application in those sectors, for example the lubrication of microgears and sliding hinges, where

the absence of solid particles and a high viscosity are required. The gel lubricants can also be diluted in solvents, including supercritical carbon dioxide, and deposited by means of conventional techniques like spray coating, dip coating and spin coating, followed by the evaporation of the solvent.

- When the solid PFPE-TFE copolymers are dissolved in oils, preferably fluorinated oils, at low concentration (indicatively below 5%) they function as a thickener, determining an increase of the viscosity and a decrease of wear without worsening the viscosity index.
- PFPE-TFE copolymers can be added to conventional fluorinated and non-fluorinated greases, also in low loadings (lower than 10% by weight) as additives to modify the final characteristics of the grease. Improvements are obtained, for example, in terms of better boundary lubrication, lower wear, reduced oil separation, and improved viscosity index.
- PFPE-TFE copolymers (liquid and solid) or their compositions mentioned above (solutions, gels, dispersions) can find application as lubricants in different industrial sectors such as oil and gas, aerospace, nuclear, refrigeration, electronic and electrical, just to name a few. Lubrications of sintered metal bearings, compressors, metal chains and centrifuges are typical target applications.
- Processing aid: the lubricating properties of these innovative copolymers can be exploited in the field of the polymer processing aid. In several tests carried out with both fluorinated and hydrogenated polymers [19,20], PFPE-TFE copolymers have shown a strong processing aid effect at very low concentration (below 0.5% by weight). Due to the low compatibility with most polymeric matrices, the PFPE-TFE copolymers easily migrate toward the surface and lubricate the surface in contact with the metal extruder or with the molding apparatus, thus improving the processability and the molding release. Unlike PFPEs that, being liquid, are difficult to be homogeneously dispersed, the solid PFPE-TFE copolymers can be easily fed into the processing apparatus, alone or as masterbatch. The high thermal stability of the PFPE-TFE copolymers make them particularly useful for those polymers, like perfluorinated and aromatic polymers, that require high processing temperatures that are not tolerated by the traditional processing aids (hydrogenated additives). Moreover, the possibility of regulating the melting point of these copolymers allows the optimization of the processing aid effect on the basis of the characteristics of the polymeric materials that have to be extruded.
- Polymer additives: when the PFPE-TFE copolymers or their formulations are added to polymeric materials, both hydrogenated and fluorinated, show the ability to modify the surface properties, also at low loads. Improvements have been observed, without negatively affecting the bulk properties of the material, in terms of lower coefficient of friction, better chemical resistance, higher hydro and oleophobicity and self cleaning properties.

5. Future trends

PFPE-TFE copolymers are new to the world products and their potential, in terms of applications, has not been fully explored. For example, PFPE-TFE copolymer, or similar PFPE terpolymers containing functional groups, could be used as lubricants in a variety of high-performance applications, for example to lubricate hard disc drive media, as well as to lubricate precision mechanical instruments to minimize mechanical wear. They could also function as anti-wetting and corrosion-protective agents on metal-containing substrates, particularly in magnetic recording

devices such as magnetic recording disks and magnetic recording heads.

Low molecular weight copolymers or their formulations could be used as heat transfer and testing fluids or for the preparation of micro-emulsion for the polymerization of fluorinated monomers. Due to their chemical inertness, possible applications as safe fluids can also be imagined, for example in those activities involving oxygen or hazardous gas handling.

PFPE-TFE copolymers could be used for the surface treatment of, for example, textiles and fabrics to improve properties like hydro and oleo-phobicity and to reduce wear and friction or, in the field of polymers, as additives for the modification of the mechanical properties, in particular at low temperatures since their glass transition is below $-100\text{ }^{\circ}\text{C}$. The PFPE-TFE copolymers could be used as dielectric and protective coating, for example for the protection of electric circuit boards. Membranes, prepared by dip and spin coating or by impregnation, can be imagined for application in fields like gas separation or as dielectric coatings.

The PFPE-TFE copolymers could also be used, analogously to PTFE, as additive for paint and inks.

As the chemistry developed for the synthesis of the PFPE-TFE block copolymers is easily applicable to other olefins, both fluorinated and hydrogenated, and also to fluoroaromatic compounds [21], a number of new structures and possible applications may be foreseen upon full exploitation of the technology.

6. Experimental

6.1. Methods of analysis

^{19}F NMR spectra were recorded on Varian Mercury 200 MHz spectrometer using CFCl_3 as internal standard. The PFPE-TFE samples were analyzed in a solution of hexafluorobenzene (2%, w/w).

Differential scanning calorimetry (DSC) analyses were carried out by using a calorimeter Perkin Elmer DSC 2C (calibrated with Indium and cyclohexane). The samples were cooled at $-170\text{ }^{\circ}\text{C}$, and after 3 min at $-170\text{ }^{\circ}\text{C}$, they were heated up to $350\text{ }^{\circ}\text{C}$ at the heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$.

The thermogravimetric (TGA) analyses were carried out with a Perkin Elmer PYRIS 1 TGA. The samples were heated from $30\text{ }^{\circ}\text{C}$ to $750\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$.

The kinematic viscosity at a given temperature has been determined by using capillary viscosimeters of the Cannon-Fenske type in accordance with the ASTM D445 method.

The rheological properties were measured with the dynamic mechanical spectrometer Rheometric ARES (geometry: Parallel Plates 25 mm and Couvette geometry) with a dynamic frequency sweep test in a dry nitrogen environment.

The wide angle X-ray diffraction (WAXD) investigations were performed at room temperature on a Philips X-Pert Pro MRD diffractometer, using the radiation of $\text{CuK}\alpha$ with a nickel filter. X-ray diffraction patterns were recorded in the range of 2θ from 5° to 30° , with a step scanning equal to 0.02° and at counting time of 10 s. The crystallinity of the samples was calculated by separating the crystalline peak from the amorphous halo with the procedure proposed by Murthy and Minor [14].

6.2. Synthesis of the PFPE-TFE copolymers

The PFPE-TFE copolymers were prepared according to the following general procedure.

In a 1 l glass flask, equipped with probe for the temperature, mechanical stirring, bubbling inlet for the adduction of nitrogen and of TFE, GALDEN[®] PFPE HT230, and a peroxidic PFPE are introduced. The reaction mixture is heated under stirring and

Table 7

Reactants and solvent used for the synthesis of the PFPE–TFE copolymers.

Sample	Peroxide (g)	GALDEN [®] PFPE HT230 (g)	TFE (NI h ⁻¹)
1	125	1125	0.8
2	250	1000	1.3
3	250	1000	1.4

Table 8

Peroxidic PFPE used for the synthesis of the PFPE–TFE copolymers—data are referred to formula (I).

Sample	Mn	n	m	ν
1 and 2	39,000	171	168	65
3	31,000	197	141	10

under nitrogen flow (2 NI h⁻¹) up to 190 °C, temperature at which the nitrogen feed is stopped and the feed of TFE starts. The mixture is maintained under stirring at 190 °C for 1.5 h, then brought to 200 °C and maintained at this temperature for 1.5 h and, lastly, increased to 210 °C for 1 h. The TFE feed is then interrupted and that of nitrogen opened (2 NI h⁻¹) and the temperature is raised up to 230 °C and maintained constant for 3 h. At the end of the thermal treatment the mixture is left to cool down to 180 °C when a flow of fluorine is fed (4 NI h⁻¹ for a total of 15 h) into the reactor always under stirring. At the end of the fluorination, the solvent is distilled off and the product recovered.

The structure and the amount of peroxidic PFPE and the TFE flow used for the synthesis of the three samples are reported in Tables 7 and 8.

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