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Synthesis, characterisation and aqueous behaviour of a one-ended perfluorocarbon-modified poly(ethylene glycol)

F. Boschet[a], C. Branger[a,*], A Margaillan[a], E. Condamine[b]

[a]*Equipe d'Accueil Matériaux à Finalités Spécifiques, Laboratoire de Chimie Appliquée, Université de Toulon et du Var, BP132, 83957 La Garde Cedex, France*

[b]*UMR CNRS 6014, Equipe de Chimie Organique et Biologique Structurale, Institut de Recherche en Chimie Organique Fine, Université de Rouen, BP 08, 76131 Mont Saint Aignan, France*

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Abstract

Establishing structure–properties relationships for an associative polymer requires a precise knowledge of its structure. In previous works, we studied water-soluble telechelic perfluorocarbon (C_8F_{17}) derivatives of poly(ethylene glycol)s. They exhibit stronger hydrophobic intermolecular associations than the corresponding hydrocarbon derivatives (C_8H_{17}). We now report the synthesis and study of one-ended perfluorocarbon derivative of poly(ethylene glycol). The composition and structure of this polymer were elucidated before analysing its behaviour in aqueous solution by viscosimetry and ^{19}F NMR. The synthesis procedure allows us to reach total grafting. This polymer presents a micellar behaviour above 2×10^{-4} g/ml and an associative behaviour above 10^{-3} g/ml.

Keywords: Hydrophobically associating PEG; Rheological properties; Fluorine NMR

1. Introduction

From a theoretical and practical point of view, the study of associative polymers has recently drawn a considerable interest due to their original and specific rheological properties [1–3]. These properties distinguish them from others polymers concerning the viscosity enhancement and the reversibility of the associative phenomenon. These particular rheological properties are explained by the incompatibility between various groups, for example hydrophilic and hydrophobic groups, within the same macromolecule. Depending on the importance of the repulsion and attraction forces (steric, electrostatic, etc.), these compounds may have a more or less marked antagonistic character [4–12].

There is a considerable and growing interest in the interpretation and the understanding of the structure–properties relationships of associative polymers [13–17]. The establishment of these relationships requires the precise knowledge of the polymer structure. Classical radical and micellar polymerisation mainly produce associative polymers for which it is difficult to determine the exact structure due to its polymolecularity or composition variation (preferential consumption of one monomer compared to another monomer during the polymerisation). Therefore, the given structure corresponds to an average structure, which cannot be used for structure–properties relationship interpretation because some properties are related only to a fraction of the sample. Recent improvements of controlled radical polymerisation could allow to access the requested structure (very low polydispersity) [18–20].

In order to obtain a model compound, we decided to carry out the synthesis of new water-soluble associative polymers consisting of an hydrophobically modified poly(ethylene glycol)s (PEG). The perfluorocarbon C_8F_{17} group was chosen as hydrophobic group for its higher hydrophobicity compared to hydrocarbons.

We previously reported the synthesis and the aqueous behaviour of telechelic perfluorocarbon derivative of poly(ethylene glycol)s (PEG) [21]. These fluorinated compounds exhibit a strong associative behaviour.

We now report the synthesis and the study of one-ended perfluorocarbon derivative of poly(ethylene glycol). To access the one-ended structure, we have grafted a

* Corresponding author. Tel.: +33-4-9414-2433; fax: +33-4-9414-2598.
E-mail address: branger@univ-tln.fr (C. Branger).

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poly- (ethylene glycol) monomethylether (PEGMe) of 5000 g/mol.

2. Experimental section

2.1. Reagents

3-Perfluorooctylpropanoyl chloride was prepared and purified as described by Jouani et al. [22] from the 3-perfluorooctylpropanoic acid (ATO).

Poly(ethylene glycol) monomethylether 5000 g/mol (Aldrich/Fluka) was degassed under a secondary vacuum (10^{-6} mbar) for several hours to remove residual water and was characterised by size exclusion chromatography (SEC) to check its molar mass, polymolecularity and purity.

Chloroform and petroleum ether 35–60 (SDS pure for synthesis) were used as received.

Argon 4.5 (Linde B50) was used as inert gas for the synthesis.

2.2. Instrumentation

2.2.1. NMR measurements

NMR experiments were performed on a BRUKER AVANCE DMX 600 MHz spectrometer equipped with a 5 mm *z*-shielded gradient TXO triple resonance $^{19}F/^{13}C/^{1}H$ probe interfaced to a Silicon Graphics O2 workstation. All spectra were recorded at a temperature of 25 °C with samples of various concentration of modified PEGMe in D_2O or with a sample of 0.5 mol/l of perfluorooctylpropanoic acid in CD_3OH. CF_3SO_3Na (−78.25 ppm) was used as internal standard for ^{19}F signals in D_2O. For 3-perfluorooctylpropanoic acid study, ^{1}H and ^{13}C were referenced, respectively, to a ^{1}H residual signal (3.31 ppm) and ^{13}C signal (49.15 ppm) of CD_3OH. $CFCl_3$ was used as external standard for ^{19}F signals. All data were processed on an INDIGO2 SGI computer using XWINNMR and AURELIA software (BRUKER package).

The aqueous behaviour was studied using modified PEGMe. Several 1D ^{19}F (564.69 MHz) NMR experiments were performed with 3891 scans (5.47×10^{-5} g/ml sample), 10,240 scans (2.20×10^{-4} g/ml sample), 3276 scans (2.74×10^{-4} g/ml sample), 5120 scans (3.83×10^{-4} g/ml), 3072 scans (4.90×10^{-4} g/ml), 3276 scans (1.10×10^{-3} g/ml), 510 scans (5.37×10^{-3} g/ml) of 64K points on 33,333 Hz of spectral width. Having estimated the longitudinal relaxation time of the system, the relaxation delay was fixed to 20 s for all spectra. Data were processed with multiplication prior to Fourier transformation by an exponential function and without zero filling. After data integration, the concentrations were calculated by comparison to CF_3SO_3Na, which was dissolved in exact quantity.

2D NMR experiments namely, $^{1}H-^{13}C$ (600.13–150.90 MHz) heteronuclear single quantum correlation (HSQC) [23] via double INEPT transfer with decoupling during acquisition, heteronuclear multiple bond connectivity (HMBC) [24] via heteronuclear zero and double quantum coherence with no decoupling during acquisition and $^{13}C-^{19}F$ (150.90–564.69 MHz) heteronuclear correlation spectroscopy (hetero-COSY) [25] were used for unambiguous assignment of 3-perfluorooctylpropanoic acid. HSQC was made in the sensitive phase mode and used the time proportional phase incrementation for quadrature detection [26]. HMBC and hetro-COSY spectra were recorded in the absolute value mode. HSQC and HMBC were 256 ($t_1 = 3$ μs) increments each averaging 32 transients of 2048 points, with 1201 and 25,202 Hz of spectral width in ω_2 and ω_1, respectively. Hetero-COSY was 512 ($t_1 = 3$ μs) increments each averaging 80 transients of 8192 points, with 25,202 and 31,619 Hz of spectral width in ω_2 and ω_1, respectively. Data were zero filled in ω_1 dimension to 512 (HSQC and HMBC) or 1 K (hetero-COSY) points, thus yielding a digital resolution of 0.6 and 49.2 Hz/points (HSQC and HMBC) or 3.1 and 30.9 Hz/points (hetero-COSY) in ω_2 and ω_1, respectively. A 90°-shifted sine-squared (HSQC) and 22.5° shifted sine-squared (HMBC and hetero-COSY) filter were applied to both ω_2 and ω_1 before Fourier transformation. Evolution delay for $^{1}J_{CH}$ coupling in HSQC and long range coupling evolution delay in HMBC amounted to 1.8 and 70 ms, respectively. Relaxation delay was 2 s for all 2D experiments.

2.2.2. SEC measurements

The chromatograph used was a WATERS 501 coupled with a WATERS 401 refractive index detector. We used four WATERS Styragel columns HR0.5 (molar weight from 0 to 1000 g/mol), HR1 (molar weight from 100 to 5000 g/mol), HR3 (molar weight from 500 to 30,000 g/mol) and HR4 (molar weight from 5000 to 500,000) conditioned in THF. The eluant used was THF (HPLC Grade from SDS) at 1.0 ml/min. All chromatograms were recorded at 25 °C using narrow distribution PEG calibration standards (between 1000 and 10,000 g/mol). All data were processed on a PC computer using Baseline 810 software (WATERS).

2.2.3. Viscosity measurements

Measurements were carried out on Ubbelhode #1c capillary (ROTH) immersed in a thermostated bath at 25 °C. Flow time was measured and converted into viscosity from the conversion charts provided by the manufacturer. These cinematic viscosities allow the reduced viscosity of the samples to be calculated.

2.3. Synthesis

19.6 g (3.9×10^{-3} mol) of PEG Monomethylether 5000 g/mol were melted at 80 °C under strong flow of argon (PEGMe melting point close to 65 °C). 4.6 g (9.0×10^{-3} mol) of acyl chloride were added by portions

to the material. Stirring, heating and gas flow were maintained for 3 h at 85 °C then 1 h at 100 °C. At the end of the reaction, when no more hydrochloric acid was observed, the mixture was cooled down to ambient temperature in an argon atmosphere. The polymer was then dissolved in a small amount of chloroform, precipitated in petroleum ether 35–60 then filtered. The operation is repeated twice and the final product was obtained after drying (20.3 g; yield = 95%).

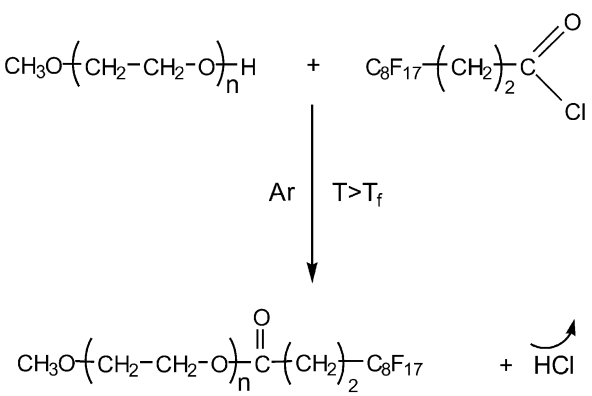
3. Results and discussion

3.1. Synthesis

Copolymerisation reactions were not chosen for various reasons. The principal reason is that it is difficult to control the structure and the composition of the copolymer obtained. Moreover, this way does not allow a comparison with a non-associative precursor. Actually, the final structure of these copolymers would be mainly grafted structure and not telechelic, which is inappropriate.

The synthesis consists of a chemical modification of a commercial Poly(ethylene glycol) monomethylether (PEGMe) by esterification with a carboxylic acid containing the hydrophobic perfluorocarbon group C_8F_{17} (Scheme 1). To obtain a stable ester bridge, it is be necessary to introduce an hydrocarbon chain between the carboxyl group and the fluorinated group in order to reduce the electro-attractive character of the fluorinated group and thus to limit the hydrolysis sensitivity of the ester bridge. With contrast to the work of Collet et al. [27], the hydrocarbon chain is shortened to limit its effect on the hydrophobic character of C_8F_{17}.

To improve the reactivity of the fluorocarboned carboxylic acid, Collet et al. [27] used the association DCC/DMAP (*N*,*N*-dicyclohexylcarbodiimide/dimethylaminopyridine) reagents. Francois [28–30] enhanced the reactivity of the PEG by end-groups ionisation, while LIU [31] used mesylates, without reaching the complete grafting of the polymers.



Scheme 1. Modification of PEGMe 5000.

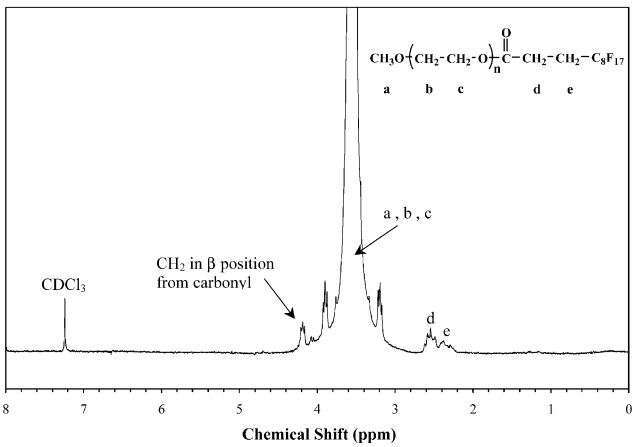


Fig. 1. ^{1}H NMR spectra of PEGMeF (10 mg/ml, $CDCl_3$, 25 °C, 200 MHz).

Due to low concentration of hydroxyl end-groups on PEG, the reaction was carried out in bulk without solvent in order to enhance the reaction kinetics. Carboxylic acid was converted to acyl chloride for improving its reactivity. The acyl chloride is rather easy to obtain and more reactive than the corresponding carboxylic acid. In the final esterification reaction, total conversion was obtained by eliminating the hydrochloric acid gas formed (achieved through a constant flow of argon within the reactor). The formed hydrochloric acid was trapped with an alkaline solution, which could be titrated at the end of the experiment.

Characteristics of PEGMe are presented in Table 1. The functionalisation ratios were determined from the ^{1}H NMR signal integration (2.2–2.7 ppm) of the two methylene groups of the hydrophobic group (Fig. 1).

3.2. NMR chemical shifts assignments of perfluorooctylpropanoic acid

To the best of our knowledge, only a report on C_6F_{13} [32,33] is found in the literature and it was interesting to determine the C_8F_{17} residue assignment.

Complete ^{1}H, ^{13}C and ^{19}F were obtained from ^{1}H–^{13}C HSQC, HMBC and ^{13}C–^{19}F hetero-COSY (Table 2). Sequence of fluoride carbons was easily realised by means of hetero-COSY experiment. Indeed, on this spectrum, intense ^1J cross peaks and weak ^2J cross peaks allow unambiguous ^{13}C and ^{19}F assignments of the C_8F_{17} part (Fig. 2). Then HSQC and HMBC revealed the connectivity of the rest of the molecule. We can note that the CF_3 signal is isolated from others at −83.2 ppm. So we will focus on it to study the chemical environment of ^{19}F nuclei. ^{1}H signal of the carboxylic acid (OH) was not observed because of the fast exchange of this proton with the solvent (CD_3OH).

3.3. Solution properties

Fig. 3 shows variation of the reduced viscosity according to the polymer concentration for PEGMeF. The study

Table 1
Characteristics of fluorocarbon modified PEGMe derivatives

Nom	$\bar{M}_n$ GPC H_2O (g/mol)	I_p	Grafting ratio (RMN ^1H)	R_F	Bridge
PEGMe	5250	1.11	–	–	–
PEGMeF	5700	1.10	96%	C_8F_{17}	Ester
PEGMe, Zhang et al. [34]	6000	1.09	95%	C_8F_{17}	Urethan

Table 2
NMR chemical shifts of $C_8F_{17}-CH_2-CH_2-COOH$ in methanol-d_3

CF_3-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CH_2-CH_2-COOH

1 2 3 4 5 6 7 8 9 10 11

Peak	δ ^{13}C (ppm)	δ ^{19}F (ppm)	δ ^1H (ppm)
CF_3 1	118.57	−83.2	–
CF_2 2	109.89	−128.0	–
CF_2 3	111.70	−124.4	–
CF_2 4	112.24	−123.6	–
CF_2 5	112.29	−123.5	–
CF_2 6	112.65	−123.4	–
CF_2 7	112.48	−125.2	–
CF_2 8	119.66	−116.6	–
CH_2 9	27.59	–	2.46
CH_2 10	26.08	–	2.59
COOH 11	174.72	–	Not observed

reveals a marked associative behaviour: the reduced viscosity is systematically higher than that of the non-modified PEGMe and the evolution with the concentration is not linear. From these curves, one can measure the intrinsic viscosity ($[\eta]$), the Huggins constant (K_H) and the overlap concentration ($C^* = 1/[\eta]$) (Table 3). It is worth noting that intrinsic viscosity and so overlap concentration is close to those of the non-modified PEGMe. This shows

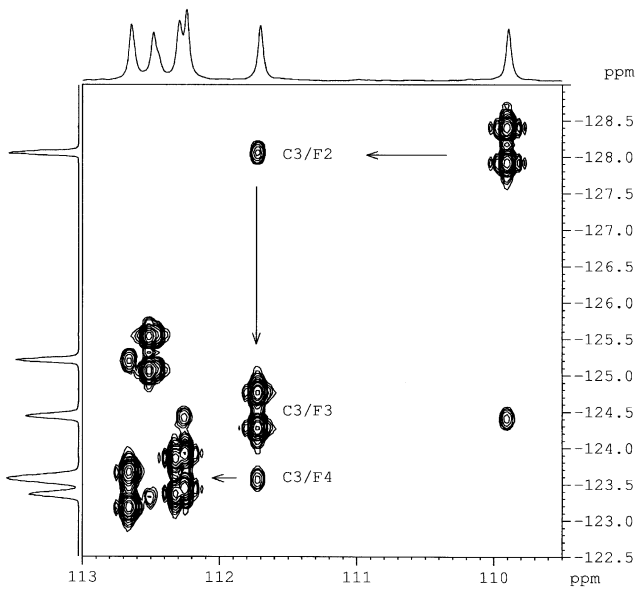


Fig. 2. Part of the $^{13}C-^{19}F$ hetero-COSY correlation maps of PEGMeF with the 1D ^{13}C {^1H, ^{19}F} and ^{19}F spectra along the top and the side. As an example, sequence assignment for the F2–C3–F4 residue is drawn.

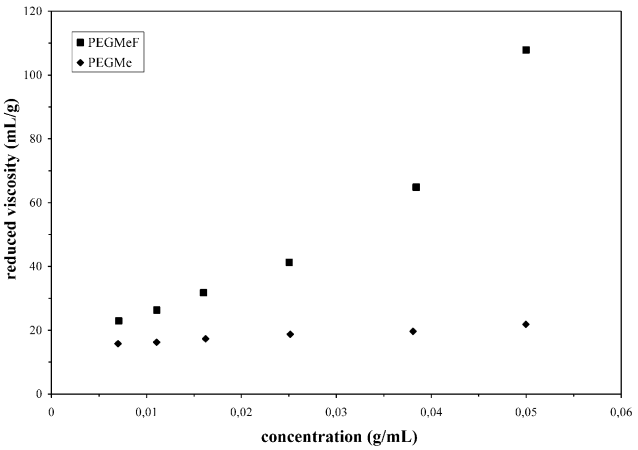


Fig. 3. Concentration study of PEGMeF at 25 °C.

that the compound does not exhibit intramolecular associations. It is also interesting to note that the hydrophobic associations appear far below the overlap concentration C^* which is about 0.06 g/ml.

Fig. 4 shows the ^{19}F NMR signal concentration dependence of the CF_3 end moiety in PEGMeF. Below 2.7×10^{-4} g/ml, only a single CF_3 absorption is observed (−80.2 ppm) while a second upfield resonance (−82.4 ppm) appears above. Similar changes are observed for the CF_2 resonances [21]. The upfield resonance appears to be due to associated polymer, while the downfield resonance may represent a dissociated form [21,34]. The integration of these two peaks allows the determination of the associated and dissociated species concentrations (Table 4). Above 2×10^{-4} g/ml, the concentration of the dissociated form seems to be independent of the total polymer amount, while associated form quantity increase with the polymer concentration. This behaviour was observed on perfluorocarbon surfactants [35]: above the critical micellar concentration (CMC), the monomeric surfactant quantity is independent of that of the total surfactant concentration and this concentration stays equal to the CMC which is estimated about 2×10^{-4} g/ml for PEGMeF.

Table 3
Rheological constants for both modified and unmodified PEGMe

Nom	$[\eta]$ (ml/g)	K_H	C^* (g/ml)
PEGMeF	15.6	4.0	0.064
PEGMe	14.9	0.61	0.067

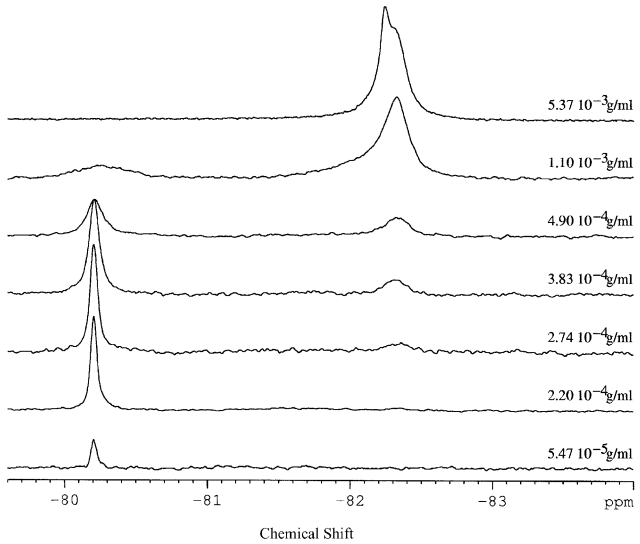


Fig. 4. ^{19}F NMR concentration study of PEGMeF (D_2O, 25 °C, 564.69 MHz).

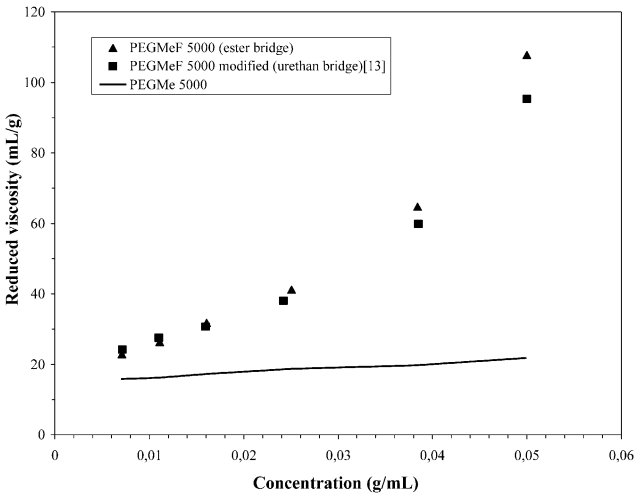


Fig. 5. Comparison between PEGMeF (ester bridge) and an equivalent modified PEGMe with urethan bridge.

The same behaviour was already observed by Zhang et al. [34]. These authors made a study on PEGMe 5000 and 10,000 g/mol with perfluorocarbon end-groups connected to PEGMe by an urethan bridge (isophorone diisocyanate). They showed by ^{19}F NMR that C_6F_{13} derivatives generate dimers formation whereas C_8F_{17} leads to a micellar behaviour.

A comparison is carried out between our modified PEGMe 5000 (PEGMeF) and the one from Zhang et al., (Fig. 5). It appears from these results that the nature of the bridge (urethan or ester) has no influence on the aqueous behaviour of these polymers (in the concentration range studied). The CMC of modified PEGMe 5000 with urethan bridge (9×10^{-6} g/ml) is approximately 20 times lower than that of PEGMeF: this could be explained by the more hydrophobic character of the cyclohexyl group in the urethan bridge.

However, a purely micellar behaviour cannot explain the strong increase in viscosity noted for modified PEGMe compared to their precursors above 0.007 g/ml (Fig. 5). An increase in viscosity can be interpreted only by the existence of an associative behaviour to the higher concentrations. In a purely micellar system, there is no formation of intermolecular hydrophobic associations (apart from micelles) and the system behaves like a non-associative polymer. To explain this associative behaviour, Zhang et al. [34] proposed a 'binding', namely an association between PEG chain and fluorocarbon groups, also observed on hydrocarbon surfactants, which appears to be partially hydrophobic in nature.

Multiple associated forms seem to be detectable by fluorine NMR. In Fig. 4, it is possible to notice that for the spectrum recorded at 5.37×10^{-3} g/ml, a second upfield peak is present. The signal at -82.3 ppm, which is the only one observed for lower concentrations, can be attributed to the micellar associated form. So the peak at -82.2 ppm should be relative to the binding phenomenon. This is consistent with the sharpest peak observed for associated molecules compared to micelles, which give broad peaks due to their lower degree of mobility.

4. Conclusion

The synthesis of a new perfluorocarbon functionalised PEGMe allows us to obtain complete grafting of the hydrophobic end-group C_8F_{17} via an ester bridge. Aqueous SEC and ^1H NMR were used to determine molar mass, polymolecularity and grafting ratio.

Table 4
Concentration dependence of associated and dissociated species for PEGMeF

Polymer concentration (g/ml)	Concentration of dissociated forms (g/ml)	Concentration of associated forms (g/ml)
5.5×10^{-5}	5.5×10^{-5}	–
2.2×10^{-4}	2.0×10^{-4}	1.6×10^{-5}
2.7×10^{-4}	2.3×10^{-4}	4.1×10^{-5}
3.8×10^{-4}	3.0×10^{-4}	8.2×10^{-5}
4.9×10^{-4}	2.9×10^{-4}	2.0×10^{-4}
1.1×10^{-3}	1.9×10^{-4}	9.1×10^{-4}
5.4×10^{-3}	–	5.4×10^{-3}

Coupling ^{19}F NMR and viscosimetry techniques made it possible to highlight the existence of micelles beyond a CMC of 2×10^{-4} g/ml. Above the aggregation concentration, ranging between 10^{-3} and 5×10^{-3} g/ml, coexist two forms with intermolecular interactions: micelles and binding interactions.

The viscosimetric study allows investigation on the influence of the bridge nature (ester or urethan). The associative behaviour of these two polymers appears to be very similar.

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