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Comparison of the associating behaviour between neutral and anionic alkylperfluorinated pullulan derivatives

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Abstract

New hydrophobically modified pullulans were synthesized in two ways: (i) neutral derivatives (HMPFs) obtained by direct esterification of pullulan with a perfluoroalkyl carboxylic acid ($C_8F_{17}CH_2CH_2COOH$), and (ii) ionic derivatives (HMCMPs) obtained by amidation of carboxymethylpullulan with two perfluoroalkylamines ($C_7F_{15}CH_2NH_2$ and $C_8F_{17}CH_2CH_2NH_2$). The molar hydrophobe contents ranged from 1.1 to 4.8% with respect to the anhydroglucose units. Associative properties in aqueous solutions were studied by rheological and size-exclusion chromatography/light-scattering measurements. In dilute solution, the polymers form intermolecular aggregates with a more compact conformation than that of precursors. In semi-dilute solution, the ionic derivatives are more viscosifying than neutral because of their better solubility. This effect is significant as the alkylperfluorinated chain length increases. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Associative perfluorinated pullulans; Hydrophobic modification; Rheology

1. Introduction

Hydrophobically associating polymers are materials constituted mainly of water-soluble backbone bearing a small amount of hydrophobic side groups or end groups for instance long alkyl chains. They are an important class of thickeners because of their unique rheological properties.

In aqueous solution, above a critical polymer concentration, these materials exhibit viscosities of several orders of magnitude higher than their precursors. This behaviour results from the existence of hydrophobic intermolecular associations which lead to a structured network. As a consequence of their physical character, these interactions are reversible. The polymer associations are readily broken under shear giving a typical pseudoplastic behaviour. However, upon removal of the shear, the intermolecular associations form again and the viscosities of the polymer solutions completely recover their initial low shear values.

The synthesis of associating polymers can be carried out by copolymerization of a hydrophilic monomer, such as acrylamide, with a comonomer containing a hydrophobic group [1–4]. Another approach consists of grafting long hydrophobic chains onto water-soluble polymers such as poly(oxyethylene) [5], polyvinylalcohol [6], polyacrylate [7,8] or polysaccharides [9–15].

Most of the synthesis and solution properties concern synthetic polymers. Owing to new environmental considerations, an increasing interest is being focused on natural polysaccharides which present the advantage of being non-toxic, biodegradable and biocompatible. Thus, many studies have recently been devoted to cellulose (HEC, CMC) [9–13], galactomannans [14] and alginates [15] grafted with C_8 to C_{22} alkyl chains.

Hydrophobically modified pullulans have been much less studied. The macromolecular structure of this exopolysaccharide consists of linear chain of maltotriose units connected by two α,1-4 and one α,1-6 linkages which confers a flexible character to the backbone (Scheme 1). Sunamoto et al. [16,17] described the synthesis of non-ionic hydrophobized pullulans containing small contents of palmitoyl groups or cholesteryl moieties. They have shown that the cholesteryl-substituted pullulan forms stable and monodisperse nanoparticles in water by self-aggregation and complexes with various small hydrophobic molecules.

There are relatively few fluorocarbon-containing associating polymers which have been studied in detail. Fluorocarbons are known to possess low values of surface energy and particularly substantial hydrophobic and oleophobic characters [18]. This explains why fluorocarbon surfactants

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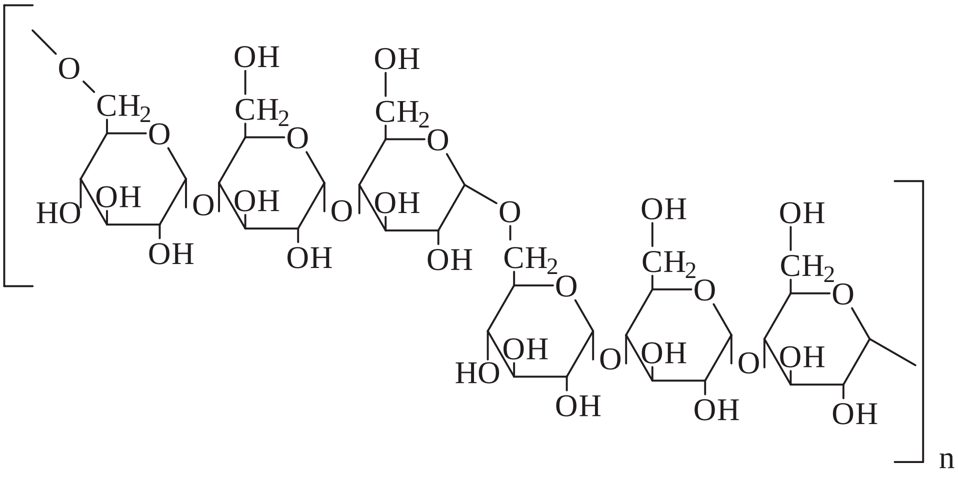


Scheme 1.

self-aggregate with a stronger tendency than hydrocarbon ones with a comparable chain length [19]. In the same way, water-soluble polymers bearing perfluorinated groups exhibit much higher viscosifying properties than their hydrogenated analogs. These are mainly synthetic materials based on neutral polyacrylamide [20–23] derivatives (HMPAM) or charged polyacrylate [24,25] derivatives (HMPA). Contrary to neutral HMPAMs which contain less than 2 mol% of perfluoroalkyl groups, the HMPAs can be grafted with significant amount of the same groups up to 10 mol%. This difference is ascribed to the presence of anionic charges on the backbone which increases water-solubility. As concerns water-soluble perfluorinated polysaccharides, the literature only reports some examples of modifications of HEC [26–28].

In our group, different works dealing with hydrophobically modified pullulan derivatives have already been reported. The rheological studies in dilute and semi-dilute solutions on adenine and thymine substituted pullulans and on aromatic amine substituted carboxymethylpullulans [29] revealed mainly intramolecular hydrophobic associations. On the contrary, for ionic pullulan modified with a linear alkyl C_{16} chain [30,31], we observed the formation of intermolecular hydrophobic associations in the semi-dilute regime. Moreover, we have shown that if the substitution is more than 6 mol%, the C_{16}-modified pullulan derivatives behave as a “physical gel”.

As mentioned before, replacing alkyl- by perfluoroalkyl group affords improved rheological properties. Therefore perfluoroalkylated (PF) pullulan derivatives should be expected to be good candidates as viscosifying and gelifying materials.

In the present article we report the synthesis of new PF pullulan derivatives, i.e. non-ionic by esterification with a perfluoroalkyl carboxylic acid and ionic by amidation of carboxymethyl pullulan with two perfluoroalkylamines. Both compounds were characterized in dilute and semi-dilute regime, in water and in 0.1 M NaCl, respectively. The effect of various parameters such as hydrophobe content and chain length, polymer concentration on rheological properties were examined.

2. Experimental

2.1. Materials

PF pullulan of average molecular weight $\bar{M}_w = 300\,000$ g/mol (determined from size-exclusion chromatography/multi-angle laser light-scattering, SEC/MALLS measurements) was purchased from Hayashibara Biochemical Laboratory (Okayama, Japan). 1H, 1H, pentadecafluorooctylamine ($C_7F_{15}CH_2NH_2$) was purchased from Fluorochem and 2H, 2H, 3H, 3H, heptadecafluoroundecanoic acid ($C_8F_{17}CH_2CH_2COOH$) was kindly supplied by Société Française Elf Atochem. Both were used without further purification. 1H, 1H, 2H, 2H, heptadecafluorodecylamine ($C_8F_{17}CH_2CH_2NH_2$) was synthesized using a previously published procedure [32]. Dimethylsulfoxide (DMSO) (Acros) was purified by distillation over potassium hydroxide pellets under reduced pressure and dried over 4 Å molecular sieves. Dimethylaminopyridine (DMAP) (Merck), dicyclohexylcarbodiimide (DCCI) (Fluka), sodium chloroacetate (Fluka), dimethylacetamide (DMA), chloroform ($CHCl_3$), ethanol and isopropanol (Acros) were used as received.

2.2. Synthesis

2.2.1. Hydrophobically modified neutral pullulans

PF pullulan (2 g, 12.3 mmol) dried in vacuo for 24 h at 70°C and DMSO (30 ml) were introduced into a two-necked flask and stirred for 18 h at 60°C. Separately, 2H, 2H, 3H, 3H, heptadecafluoroundecanoic acid (0.575 g, 1.17 mmol) was dissolved in DMSO (10 ml) together with DCCI

(0.24 g, 1.17 mmol), the mixture was vigorously stirred for 1 h at room temperature, and then added to the PF pullulan solution with 0.02 g of DMAP used as catalyst. The reaction was carried out under vigorous stirring for 24 h at 40°C. The resulting polymer was isolated by pouring the reaction mixture in an excess of acetone followed by filtration. It was purified twice by precipitating aqueous solutions into an excess of ethyl alcohol and dried in vacuo at 40°C for 24 h. FTIR (polymer film): $\nu_{\mathrm{COOR}} = 1740\ \mathrm{cm}^{-1}$.

2.2.2. Carboxymethylpullulan

The sodium salt of carboxymethylpullulan (CMP, Na^+) was synthesized in water/isopropanol medium by reacting the hydroxyl groups of PF pullulan with sodium chloroacetate in the presence of sodium hydroxide according to a procedure already described [18]. A CMP, Na^+ with (degree of substitution) DS = 0.85 and $\bar{M}_{\mathrm{w}} = 340\ 000$ g/mol (from SEC/MALLS experiments) was transformed into its acid form (CMP, H^+) by percolating aqueous polymer solution through a cationic resin (H^+ form; Amberlite IRN-77). Water was removed by freeze-drying and the polymer was then dried in vaccuo for 3 h at 30°C.

2.2.3. Hydrophobically modified charged carboxymethylpullulans

CMP, H^+ (2.66 g, 12.6 mmol) was dissolved in DMSO (60 ml). DCCI (0.211 g, 1.02 mmol) solubilized in 5 ml DMSO was added with 0.02 g of DMAP to the polymer solution and the reaction mixture was stirred for 1 h at 35°C. 1H, 1H, pentadecafluorooctylamine (0.396 g, 0.99 mmol) or 1H, 1H, 2H, 2H, heptadecafluorodecylamine (0.44 g, 0.95 mmol) dissolved in 5 ml DMSO/DMA/$\mathrm{CHCl_3}$ solvent mixture (v/v/v; 2/1/2) was slowly added to the reaction mixture. The reaction was allowed to continue for 30 h at 35°C. The PF polymer was then precipitated in an excess of ethanol, filtered off, dissolved in water and transformed into its salt form with NaOH 1 N. Then it was dialysed against deionized water until neutral pH and finally freeze-dried. FTIR (polymer film): $\nu_{\mathrm{CONH}} = 1650\ \mathrm{cm}^{-1}$; $\nu_{\mathrm{COONa}} = 1600\ \mathrm{cm}^{-1}$.

2.2.4. Characterization of carboxymethylpullulan and hydrophobically modified neutral and charged derivatives

IR spectra were recorded on a Perkin–Elmer FTIR-2000 spectrophotometer.

The DS of CMP defined as the number of carboxymethyl groups per anhydroglucose unit, was determined by Eyler's titration [33] using a conductimetric radiometer type CDM-2.

The percentage (mol%) of PF side chains was calculated from fluorine elemental analysis.

2.3. Solution properties

2.3.1. Preparation of the polymer solutions

Concentrated stock solutions of neutral modified pullulans were prepared by direct solubilization in Milli-Q water at least 24 h before use. Resulting solutions were cloudy showing that solubilization is partial. This phenomenom was attributed to the presence of macromolecular chains with high hydrophobe content. This fraction which represents from 5 to 10% of a polymer's weight (depending on perfluorocarbon content) was removed by filtration through a 8 μm Millex SC-type membrane for the less concentrated solutions ($C < 15$ g/l) and by centrifugation for the higher ones. The concentration of cleared stock solutions were determined from dried extracts. Solutions at desired polymer concentrations were obtained by dilution of the appropriate volume of stock solutions and allowed to stand for about 24 h at 4°C.

Concentrated stock solutions of ionic polymers were prepared 24 h before use and their concentrations were determined after filtration (8 μm membrane) from dried extracts. Final polymer solutions of the desired concentrations were prepared by addition of 0.4 M NaCl and deionized water to the appropriate volume of stock solution and left equilibrated 24 h at 4°C.

2.3.2. Coupling size-exclusion chromatography/multi-angle laser light-scattering measurements

Absolute determination of molecular weight distribution of polymers was performed by coupling SEC with a MALLS photometer (MALLS-Wyatt Dawn-F photometer) and a differential refractive index (DRI) detector (Shimadzu RID-6A). The SEC system consisted of a SWXL guard column and two TSK-gel G4000SWXL and G3000SWXL columns (Toso Haas) in 0.1 M $\mathrm{LiNO_3}$. Data collection from MALLS photometer and DRI detector were carried out using ASTRA software and the results were analysed using EASI software (Wyatt Technology).

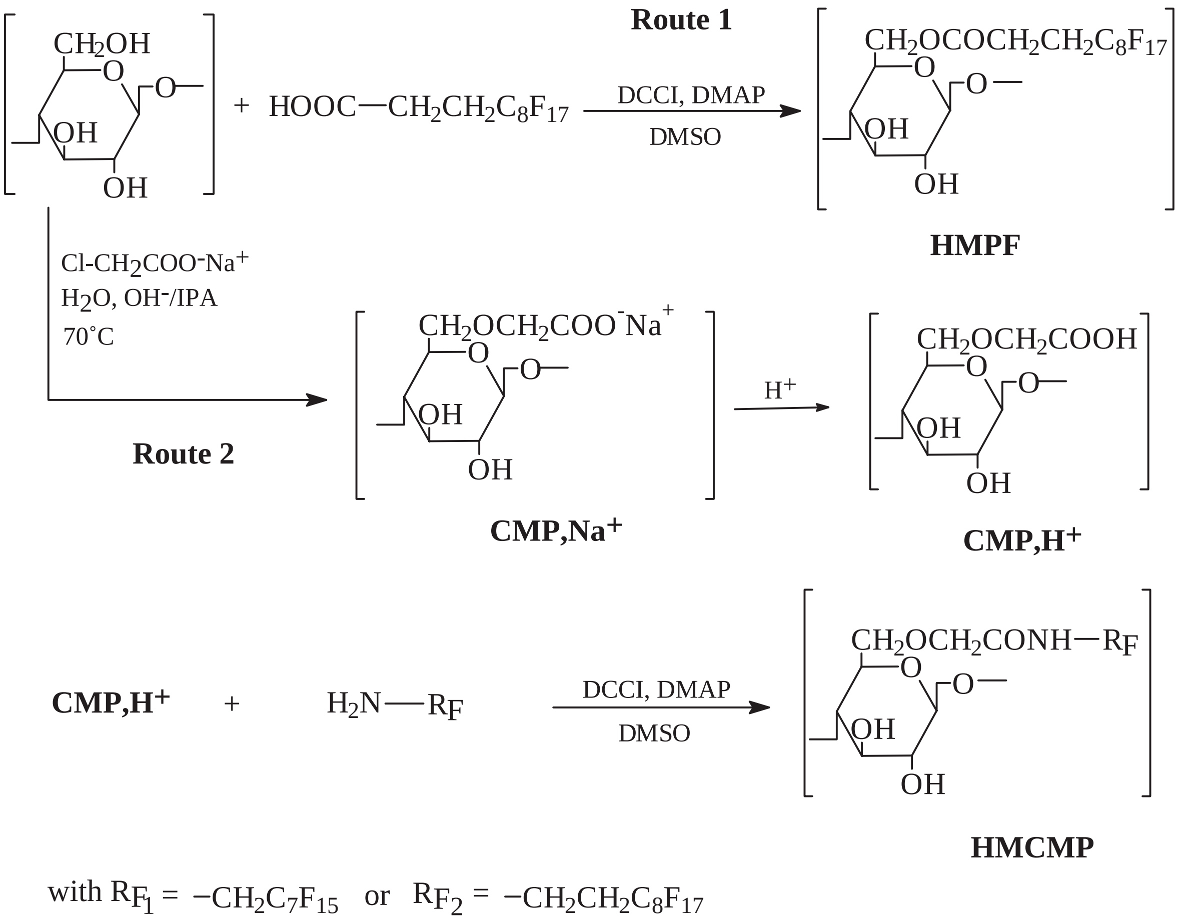
A polymer sample ($C_{\mathrm{p}} = 2$ mg/ml in 0.1 $\mathrm{LiNO_3}$) filtered through a 0.45 μm Millex-HV type membrane was eluted by 0.1 M $\mathrm{LiNO_3}$ at a flow rate of 0.6 ml/min (0.1 ml was injected) at room temperature.

2.3.3. Rheological measurements

Viscosity measurements of modified and unmodified polymers were performed at low shear rate ($\dot{\gamma} = 6\ \mathrm{s}^{-1}$) using a Couette-type viscosimeter (Contraves Low-Shear 30) thermostated at 25°C.

Flow curves and oscillatory shear responses were determined using a Carri Med CSL 100 (Rheo) controlled stress rheometer fitted with a Peltier temperature control device. All the measurements were performed with a solvent trap to prevent any evaporation of solvent.

The linearity of viscoelastic properties was checked for all the investigated solutions before the measurements of storage (G') and loss (G'') moduli. Two types of measuring geometries were used, the 4 cm/2° cone/plate for viscous solutions of the hydrophobically modified CMP and double concentric cylinder for fluid solutions of pullulan derivatives and precursors.



Scheme 2.

3. Results and discussion

3.1. Synthesis of perfluoroalkylated neutral and charged pullulans

Hydrophobically modified PF pullulan derivatives were obtained via two different synthetic pathways as shown in Scheme 2.

The samples prepared by esterification (route 1) were designated as: PF-xC_{11} refers to a pullulan which is substituted by x-$COCH_2CH_2C_8F_{17}$ chains per 100 anhydroglucose units (AGU).

The samples obtained by amidation (route 2) were designated as: CMP-xC_8 or xC_{10} refers to a carboxymethylpullulan which is substituted by x-$CH_2C_7F_{15}$ or x-$CH_2CH_2C_8F_{17}$ chains per 100 AGU.

The characteristics of synthesized samples are reported in Table 1. The grafting efficiency was low, less than 30% for neutral pullulans as against 60% for ionic pullulans. This difference could be attributed to the poor solubility of the perfluorinated acid in DMSO. As a consequence the carboxylic functions of the modifier are not totally activated by DCCI. Moreover a non-statistic grafting probably occurs with neutral pullulans. Attempts were made with the theoretical grafting ratio at 20% without success as the obtained derivative ($\tau = 5$ mol%) was insoluble in water.

In contrast, in the case of CMP, the carboxylic groups were very reactive and easily activated thus explaining higher extent of grafting.

3.2. Size-exclusion chromatography/multi-angle laser light-scattering measurements

The molecular characteristics of neutral and charged PF pullulans were investigated by SEC/MALLS and compared with their corresponding precursors. The semi-logarithmic plot of molecular weight and refractive index (RI) profiles versus elution volume of PF and PF-3.4C_{11} are reported in Fig. 1. It can be noticed that the distribution of molecular weight is not linear with the elution volume showing that the samples were not thoroughly separated in 0.1 M $LiNO_3$. In contrast, we observed that about 40% of the injected mass was not detected by refractometry. This means that interactions between the polymer and the column phase gel probably exist. As a consequence, the intrinsic molecular characteristics cannot be precisely determined. Nevertheless, elution profiles of precursor and modified derivative are similar and a qualitative comparison between

Table 1
Synthesis of HMPF and HMCMP derivatives

Sample	Precursor	Perfluorinated reagent	Modified added[a] (mol%)	Incorporated[b] (mol%)	Grafting efficiency[c] (%)
PF-1.1C$_{11}$	PF[d]	$C_8F_{17}(CH_2)_2COOH$	5	1.1	22
PF-3.4C$_{11}$	PF[d]	$C_8F_{17}(CH_2)_2COOH$	10	3.4	34
PF-5C$_{11}$	PF[d]	$C_8F_{17}(CH_2)_2COOH$	20	5[f]	20
CMPF-4.8C$_8$	CMPF[e]	$C_7F_{15}CH_2NH_2$	8	4.8	60
CMPF-4.5C$_{10}$	CMPF[e]	$C_8F_{17}(CH_2)_2NH_2$	8	4.5	56

[a] With respect to AGU.
[b] Determined by fluorine elemental analysis.
[c] Defined as the Incorporated/Added molar ratio.
[d] With $\bar{M}_w = 300\,000$ g/mol (from light-scattering experiments).
[e] With $\bar{M}_w = 340\,000$ g/mol (from light scattering experiments) and DS = 0.85 (from conductimetry).
[f] Insoluble in water.

themselves is possible. The apparent molecular weights of PF-3.4C$_{11}$ are found much higher than that of the parent pullulan. This clearly indicates that strong intermolecular associations leading to aggregates could exist even in dilute solution.

Similar results were obtained in the case of charged PF pullulan derivatives also indicating the existence of supramolecular structures in dilute solution. The same behaviour has been observed for pullulan containing few cholesteryl groups [17] or carboxymethylpullulans bearing hexadecyl groups [18] and a similar explanation was used to describe the results.

3.3. Viscosity measurements in dilute and semi-dilute solution

Fig. 2 displays the variation of the reduced viscosity ($\eta_{red} = \eta_{sp}/C_p$) in water as a function of polymer concentration (C_p) for the PF precursor and hydrophobically modified pullulans. At low C_p, HMPF's viscosities does not differ very much from that of PF. In contrast, at higher C_p the viscosity gradually increases with the hydrophobe content. Comparable results were obtained for HEC derivatives modified with 0.2–0.7 mol% of perfluorooctylepoxide [26]. Although the viscosity enhancements are relatively

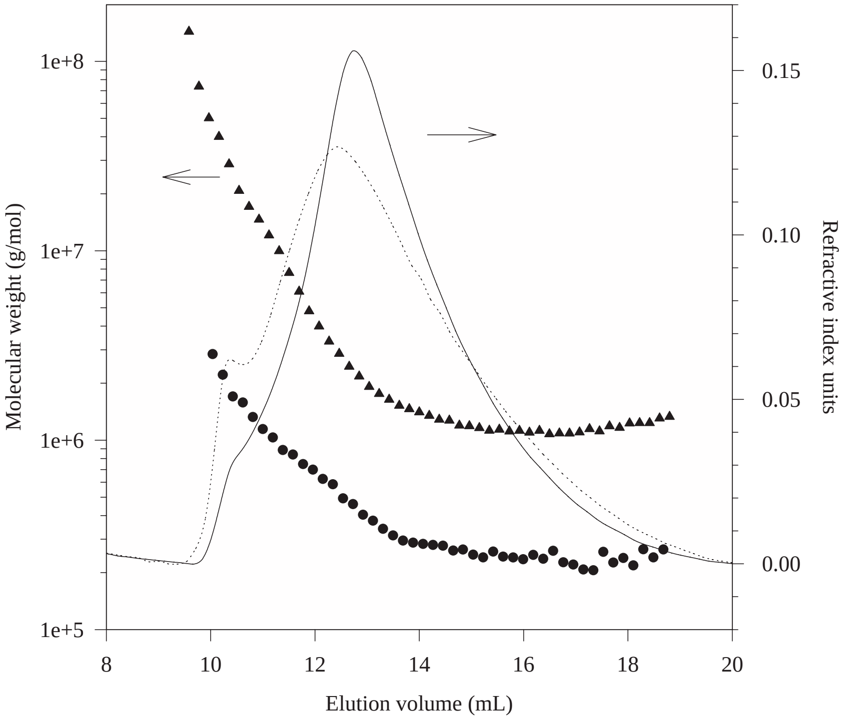


Fig. 1. Molecular weight distribution and RI chromatogram versus elution volume of PF and PF-3,4C$_{11}$. PF (● and —); PF-3.4C$_{11}$ (▲ and …), (mobile phase LiNO$_3$ 0.1 M; C_p = 2 g/l; flow rate = 0.6 ml/min).

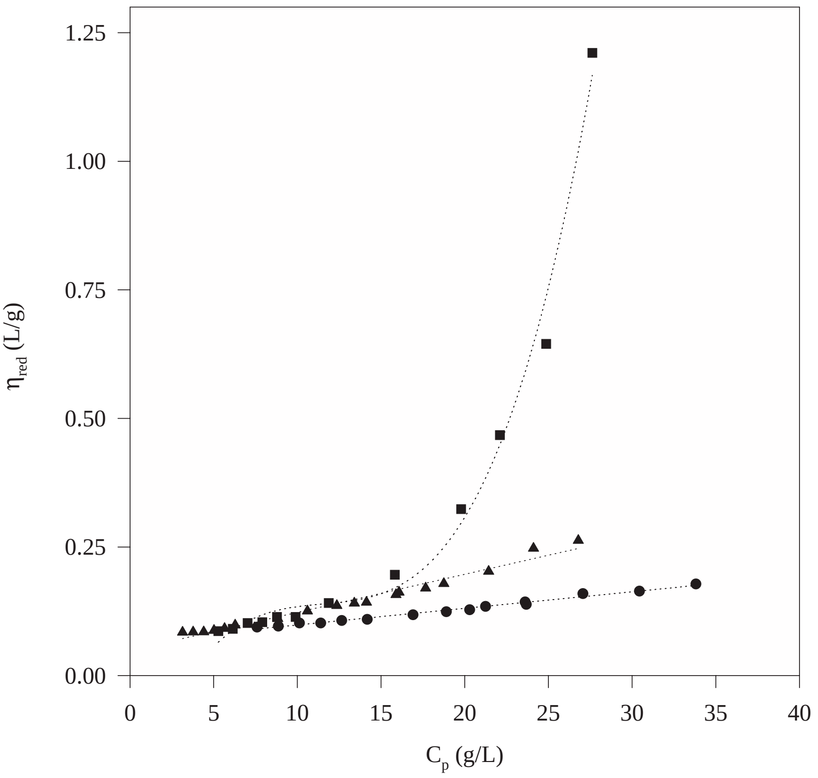


Fig. 2. Reduced viscosity η_{red} versus polymer concentration for PF and HMPFs in water PF (●); PF-1.1C_{11} (▲); PF-3.4C_{11} (■).

modest compared with that of the perfluorocarbon-modified polyacrylamides [22], it seems clear that the increases are because of similar factors. Interchain associations induced by PF moieties form polymolecular structures and this increases as the modifier content increases, resulting in a larger hydrodynamic volume and thus an enhancement of the viscosity of the polymer solution.

In the case of PF-3.4%C_{11}, it was possible to determine a critical concentration C_p^{cr} (Table 2) above which the viscosity sharply increased with the C_p concentration. Moreover, for both modified pullulans the intrinsic viscosity $[\eta]$ evaluated by using Huggin's equation [32], was found to be lower than that of the precursor (Table 2) in favour of a reduction of hydrodynamic polymer volume in dilute solution. At the same time, as found from SEC/MALLS (Fig. 1), modified pullulans have large $\bar{M}_w$ and aggregates are detected at very low C_p. Therefore, hydrophobic interchain associations exist even in dilute solution and generate the formation of compact self-aggregates with a lower apparent hydrodynamic volume compared to the parent pullulan. In contrary, it was found that the intrinsic viscosity of 0.4 mol% perfluorooctyl modified-HEC was higher than that of the unmodified HEC [26]. As the intermolecular associations subsist at the lowest concentrations for both modified polysaccharides, this difference in viscosity may be attributed to the rather flexible backbone of pullulan. In dilute solution, perfluorinated pullulans chains can associate and form more easily compact aggregates compared to the semi-rigid backbone of HEC.

Table 2
Intrinsic viscosity and critical concentration for neutral PF and HMPF derivatives in water and CMP and HMCMP derivatives in 0.1 M NaCl

Sample	$[\eta]$[a] (ml/g)	C_p^{cr}[b] (g/l)
PF	75	—
PF-1.1C_{11}	65	—
PF-3.4C_{11}	53	14.5[c]
CMP	260	—
CMP-4.8C_8	230	9[d]
CMP-4.5C_{10}	103	5.8[d]

[a] Determined by Huggin's equation [34].
[b] Determined by Utracki and Simha representation [35].
[c] In water.
[d] In 0.1 M NaCl.

CMP and modified CMP samples were studied in their fully ionized form (sodium carboxylate form) at pH≈7. Owing to their polyelectrolyte nature, the viscosities were measured in the presence of 0.1 M NaCl.

Fig. 3 shows the variation of the reduced viscosity as a function of C_p in 0.1 M NaCl for unmodified CMP and perfluorinated derivatives with the same hydrophobe content (≈4.5%) but differing in the length of side PF chains (C_8 and C_{10}). In the presence of 0.1 M NaCl, the charges are screened and no polyelectrolyte behaviour at low C_p is observed. Whereas the reduced viscosity of CMP varies linearly with C_p, the modified derivatives clearly exhibit a

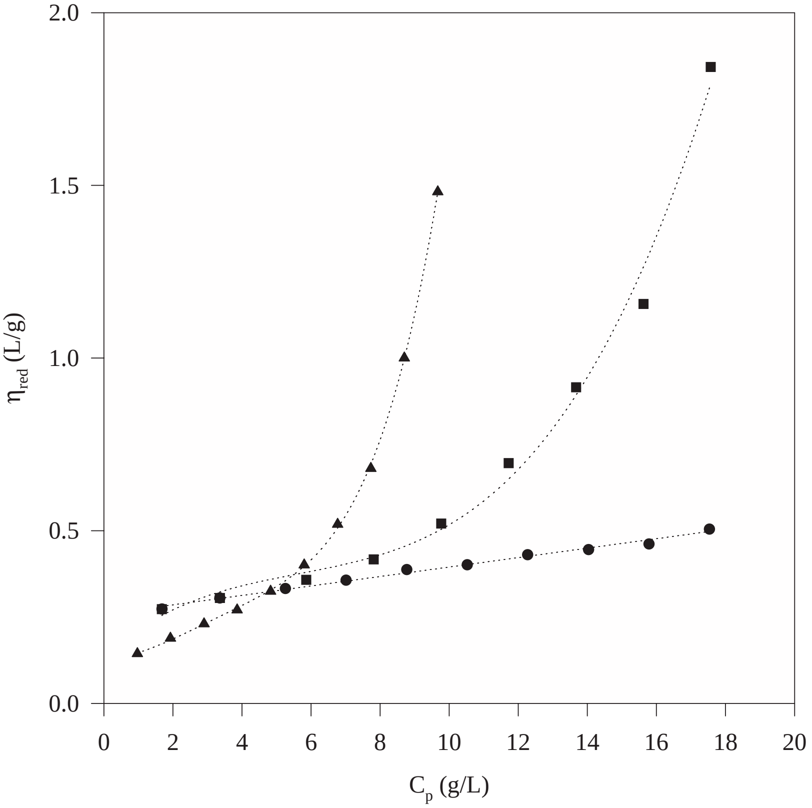


Fig. 3. Reduced viscosity η_{red} versus polymer concentration for CMP and HCMPs in 0.1 M NaCl. CMP (●); CMP-4.8C_8 (■); CMP-4.5C_{10} (▲).

different behaviour. At low polymer concentration, the viscosities are slightly lower than that of CMP and the intrinsic viscosities $[\eta]$ particularly for CMP-4.5C_{10}, are lower as compared to that of the precursor CMP. Above a critical concentration C_p^{cr}, the viscosity drastically increases above that of CMP (Table 2).

Considering the high molecular weight of HMCMP as found from SEC/MALLS measurements in dilute solution, the low measured viscosity could reflect the presence of intramolecular hydrophobic associations and compact interchain aggregates in dilute solution. Above C_p^{cr} intermolecular associations between aggregates should exist hence the viscosity increases.

The comparison between the intrinsic viscosities of CMP-4.5C_{10} and CMP-4.8C_8 clearly shows that the length of the hydrophobic unit is responsible for the more compact conformation as a consequence of stronger intramolecular associations in dilute solution. In contrast, the critical concentration C_p^{cr} of CMP-4.5C_{10} is lower than that of CMP-4.8C_8 (Table 2) and above C_p^{cr}, CMP-4.5C_{10} is the most efficient viscosifier. This difference can be attributed to the significant hydrophobicity of C_{10} group and its stronger tendency to associate itself compared to C_8 one. This behaviour was also reported for PF polyacrylates [24,25].

As all the viscosity measurements were performed in the salinity condition (0.1 M NaCl) where all the electrostatic interactions are screened, the conformations of neutral and charged derivatives can be compared. It is clear that in the same concentration range (0–20 g/l), charged HMCMP derivatives develop higher viscosities as compared to neutral HMPF derivatives. Such an enhanced viscosifying power is related to the fact that the presence of carboxylate groups affords a better hydrophilic/hydrophobic balance.

3.4. Rheological measurements in concentrated solution

Rheological measurements were performed on concentrated solutions of both modified polymers showing the most interesting viscosifying properties i.e. PF-3.4C_{11} and CMP-4.5C_{10} and bearing the same hydrophobic group. Both systems were compared with their parent polymers.

3.5. Flow curves

The shear rate ($\dot{\gamma}$) dependence of apparent viscosity (η_{app}) of PF and modified derivative, PF-3.4C_{11}, in water at $C_p = 33$ g/l, is given in Fig. 4. In these experiments the shear rate was increased up to a maximum ($\dot{\gamma} = 1100\ s^{-1}$) and then immediately decreased to a lower shear rate. The PF exhibits a Newtonian plateau over the whole shear rate range whereas the modified polymer is slightly pseudoplastic; after a Newtonian plateau (0–50 s^{-1}) the viscosity decreases with increasing shear rate. Whatever be the shear rate, the apparent viscosity of HMPF is always larger than that of the precursor. Moreover, PF and HMPF

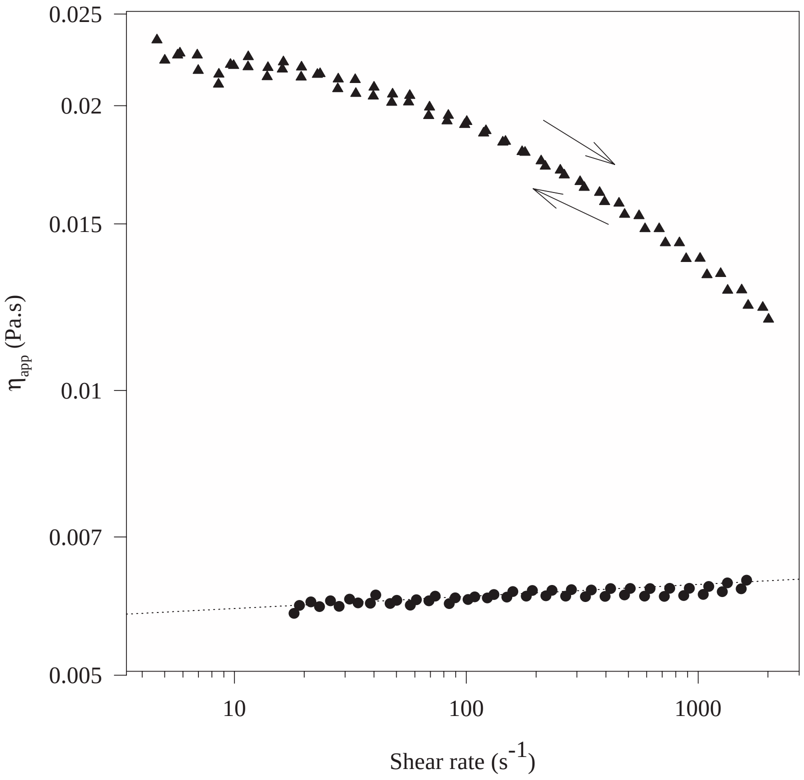


Fig. 4. Flow curves of PF (●) and PF-3.4C_{11} (▲) at $C_p = 33$ g/l in water.

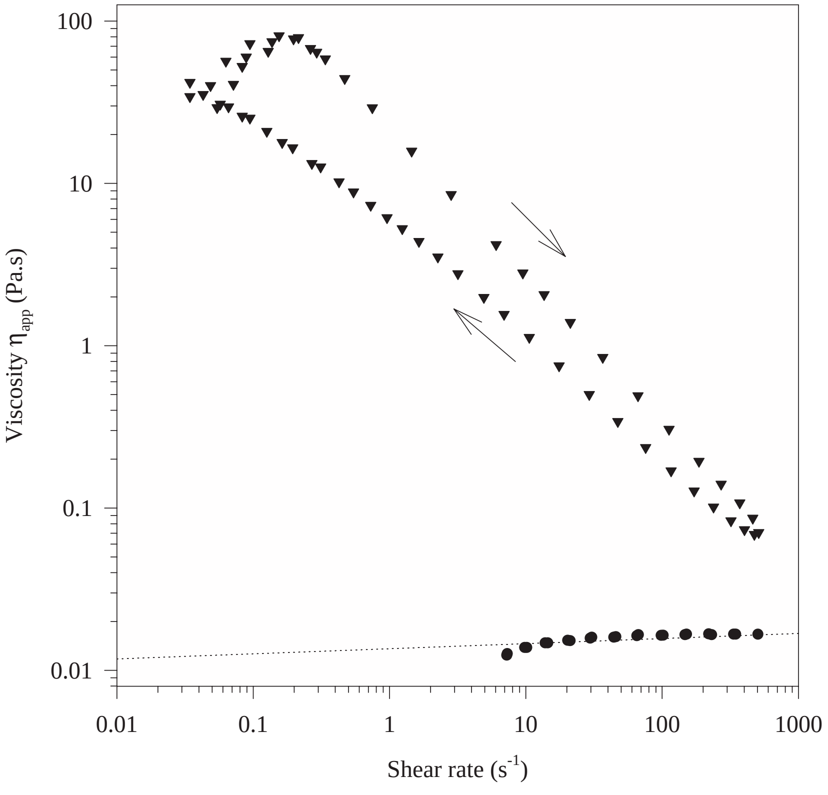


Fig. 5. Flow curves of CMP (●) and CMP-4.5C_{10} (▼) at $C_p = 20$ g/l in 0.1 M NaCl.

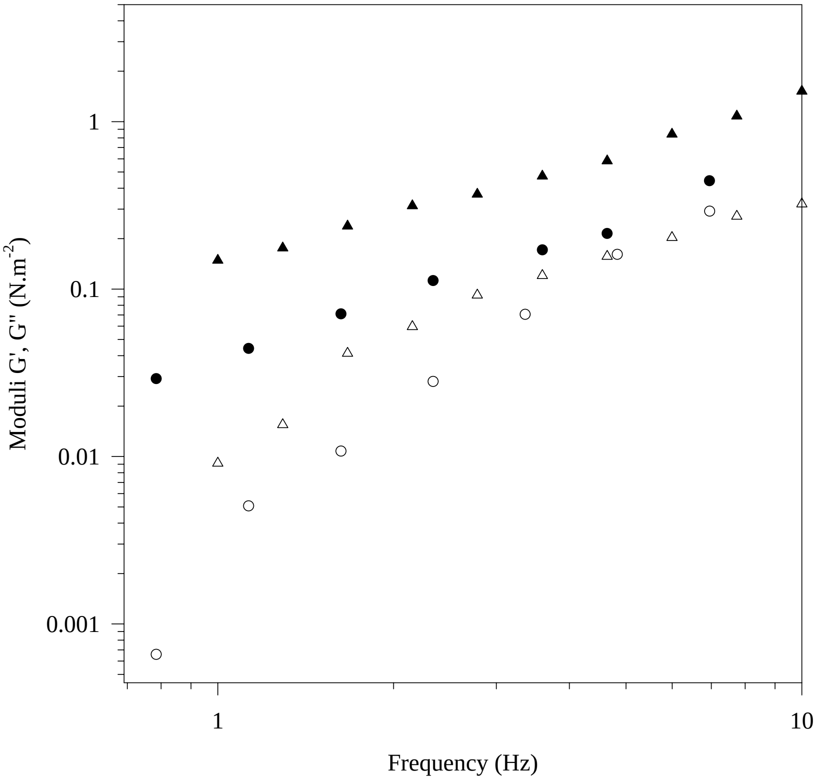


Fig. 6. Storage (G'; open symbols) and loss (G''; filled symbols) moduli versus frequency of PF (●) and PF-3.4C$_{11}$(▲) at $C_p = 33$ g/l in water.

solutions show no-time dependence; they instantaneously recover their original viscosity after shear removal.

It should be noted that the rheological behaviour of HMP does not correspond to the classical pattern usually observed for semi-dilute solutions of hydrophobically modified polymers [15,28,31]. As described in literature, the main characteristics are a pronounced shear thinning behaviour under shear and a thixotropic effect when the shear rate is decreasing. Indeed, the behaviour of PF-3.4C$_{11}$ in solution is consistent with the existence of intermolecular interactions which leads to larger aggregate. A slight shear-thinning effect is caused by the orientation of these particles under shear. As the interactions are not totally disrupted under shear, a slight viscosifying effect persists even at a higher shear rate.

Plots of the apparent viscosity as a function of the shear rate are given in Fig. 5 for CMP and CMP-4.5C$_{10}$ ($C_p = 18$ g/l) in 0.1 M NaCl. CMP behaves like PF and shows a Newtonian plateau over all the shear rate range. Contrary to this was previously observed for HMP, the shear-dependence behaviour of hydrophobically modified CMP is typical of associative polymer systems [3,15,31]. Polymer shows a markedly shear thinning behaviour upon increasing the shear rate. At lower shear rate, the viscosity of CMP-4.5C$_{10}$ is much larger than that of CMP. At high shear rates a slight difference in viscosity between CMP and HCMP persists. Moreover this sample requires time to return to its initial state when decreasing the shear rate. This explains the hysteresis loop typical of a thixotropic solution.

The effectiveness of viscosifying effect at lower shear rate clearly indicates that hydrophobical interactions occur between polymer chains generating a three-dimensional structure. The considerable loss in viscosity for HMCMP corresponds to the progressive rupture of the weakly bound hydrophobic groups as the shear rate is increasing. Some of these associations persist at higher shear rates and are responsible for the slight viscosifying effect compared to the precursor. Moreover the thixotropic behaviour points out that the destructuration and/or restructuration of the system is not an instantaneous process.

In comparison with neutral derivatives, the charged polymers show a much more important enhancement of viscosity at lower shear rate. For example, the ratio $\eta_{\text{app modified}}/\eta_{\text{app unmodified}}$ at $\dot{\gamma} = 10\ \text{s}^{-1}$ is 206 for CMP-4.5C$_{10}$/CMP system at $C_p = 18$ g/l and only 3.7 for PF-3.4C$_{11}$/PF system at $C_p = 33$ g/l. These results can be explained by the presence of a great number of intermolecular hydrophobic associations which are involved in the establishment of a structured physical network. In the case of the neutral derivative, its poor solubility in water does not permit the formation of a large supramolecular structure. Its low viscosifying properties may be attributed to the presence of aggregated particles in solution.

3.6. Mechanical spectra

Frequency sweep measurements give useful information

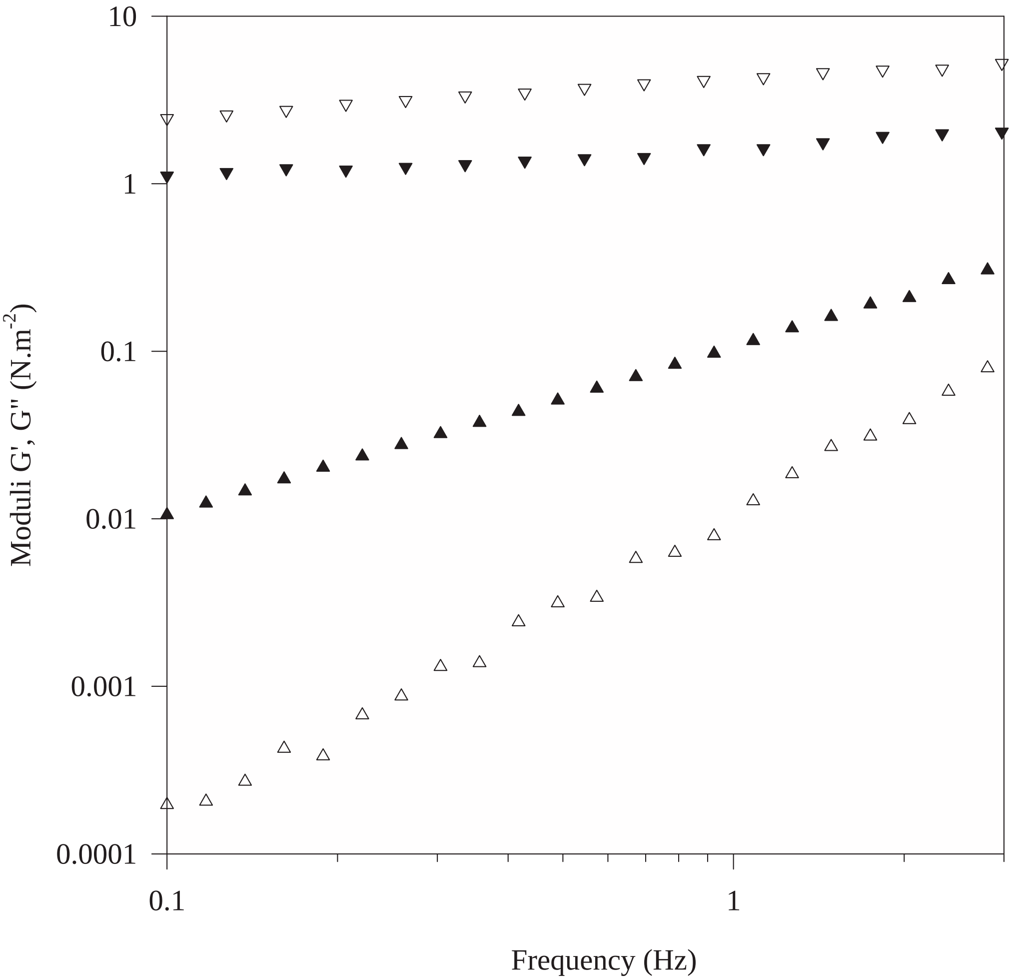


Fig. 7. Storage (G'; open symbols) and loss (G''; filled symbols) moduli versus frequency of CMP (▲) and CMP-4.5C$_{10}$ (▼) at $C_p = 20$ g/l in 0.1 M NaCl.

about viscoelastic properties. The storage G' and loss G'' moduli were measured as a function of frequency at 25°C under low applied stress (σ), in the linear viscoelasticity domain, i.e. the domain were the dynamic moduli that are strain-independent.

In Fig. 6, the moduli for PF and PF-3.4C$_{11}$ ($C_p = 33$ g/l) are plotted as a function of the frequency ($\sigma = 1$ N/m^2). The profiles of these curves are those typical of viscous polymer solutions with $G' > G''$. The storage and loss moduli of the modified polymer are only slightly larger compared to PF. Such behaviour is typical of entangled polymer systems and was also observed for HEC modified by PF groups [28].

Fig. 7 shows the viscoelastic response of CMP and CMP-4.5C$_{10}$ ($C_p = 20$ g/l) in 0.1 M NaCl under applied stress $\sigma = 1$ N/m^2. The modified derivative exhibits mechanical properties markedly different from that of the precursor; the moduli are clearly larger and independent of a frequency at least in the frequency range covered. Moreover the behaviour of the modified polymer is mainly elastic $G' > G''$ whereas CMP is mainly viscous $G'' > G'$. These properties are typical of a weak physical gel [15,31]. These results confirm the presence of many intermolecular hydrophobic interactions in concentrated aqueous solutions of perfluorinated CMP. These associations act as strong cross-links leading to an elastic structural network.

4. Conclusion

New hydrophobically modified neutral HMPFs and ionic HMCMPs polysaccharides with PF side groups were obtained by modification of pullulan and carboxymethylpullulan, respectively. In each case, viscosity and light-scattering measurements showed that, even in dilute solution, intermolecular associations between PF groups persist and lead to aggregates with a more compact conformation than that of precursor. The comparison of rheological properties of HMPF in water and HMCMPs derivatives in 0.1 M NaCl in semi-dilute regime pointed out that the ionic samples are more viscosifying than neutral ones. This difference was ascribed to the presence of carboxylate groups which enhances the hydrophilic character of the backbone and also the expansion of the polymer conformation that favours the ability of the PF groups to associate and thus, the establishment of a structured network. Further studies are in progress to investigate the effect of varying the side chain length on the thickening properties of charged pullulans derivatives.

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