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Fluorocarbon-Modified Water-Soluble Cellulose Derivatives

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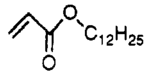
ABSTRACT: 1,1-Dihydroperfluorobutyl, 1,1-dihydroperfluorooctyl, and octyl derivatives of (hydroxyethyl)-cellulose (HEC) were prepared by reaction of the Na salt of HEC in aqueous isopropyl alcohol with 1,1-dihydroperfluorobutyl or octyl *p*-toluenesulfonate (4 or 5), with 1,1-dihydroperfluorobutyl or octyl glycidyl ether or (8 or 9), and with octyl glycidyl ether (12). The degrees of substitution of HEC were determined using ^{19}F NMR and varied between 0.023 and 1.20 mol % of anhydroglucose units (AGU). The HEC derivatives modified with 4, 5, and 8 were sparingly soluble or insoluble, and their aqueous solutions were generally low in viscosity. In contrast solutions of HEC modified with 9 did have significantly enhanced viscosities with respect to unmodified HEC or compared to HEC modified with the octyl glycidyl ether, having the same chain length as 9. The Brookfield viscosity plotted against perfluorocarbon content of aqueous solutions of HEC modified with 9 was shown to go through a maximum at about 0.42 mol % (0.92 wt %) with respect to AGU's. The solutions of this and similar polymers were shown to be highly pseudoplastic. Furthermore, increases in viscosity were observed upon addition to NaCl. These observations are consistent with the very strong intermolecular hydrophobic association of the perfluorocarbon groups.

1. Introduction

The synthesis and properties of hydrophobically associating polymers have been topics of considerable activity in recent years[1-13] in part because of their characteristic and unique rheological properties. The enhanced viscosities of the polymer solutions are ascribed to the clustering of the hydrophobic pendant groups, in a similar to fashion micellization of a surfactant. Polymers of this type can be prepared by grafting hydrophobic groups onto a water-soluble polymer or by copolymerizing a water-soluble monomer with a small amount of hydrophobe-containing comonomer. Recently we reported on the synthesis, characterization, and properties of several copolymers of acrylamide and perfluorocarbon-containing comonomers (2 and 3).[14,15] After dilution, the polymers were shown to be strongly viscosifying compared with lauryl acrylate (1)-polyacrylamide copolymers (AL-3). For copolymers of 2 and 3, the Brookfield viscosities are from 1 to 3 orders of magnitude more viscous compared with the solutions of a typical lauryl acrylate copolymer (AL-3) and of the polyacrylamide homopolymer prepared under identical copolymerization conditions. In all cases, viscosity maxima were observed in the Brookfield viscosity versus comonomer content at constant polymer concentration. Unexpectedly, for the copolymers of 2 and 3, the comonomer contents corresponding to the viscosity maxima are from 1 to 2 orders of magnitude lower compared to the acrylamide copolymer of 1. The increased tendency of the perfluorocarbons to associate in aqueous solutions compared to hydrocarbons is not unexpected[16,17] and is also reflected in the lower critical micelle concentrations of perfluorocarbon surfactants compared with their hydrocarbon analogs.[18]



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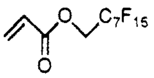

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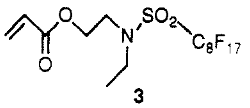

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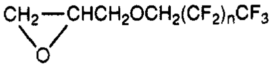
However, these hydrophobically modified copolymers are not well-defined with regard to both molecular weight and comonomer (hydrophobe) content. Therefore, in order to investigate the effect of hydrophobic content on the viscosity of the polymer solution, the modification of a water-soluble polymer of known molecular weight with hydrophobic groups which can be monitored is a plausible approach.

Polysaccharides belong to important class of viscosifying polymers not only because of their low cost but also because of their hydrophilicity, lack of toxicity, and biodegradability. The hydrocarbon derivatives of (hydroxyethyl)-cellulose (HEC) and similar polymers have been intensively studied in recent years.[3,4] In the following, we report the synthesis, characterization, and properties of several perfluorocarbon derivatives of HEC (prepared by reaction of HEC with modifiers 4, 5, 8, 9, and 12) and the quantitative analysis of the hydrophobic content in the resulting polymers.

$TsOCH_2(CF_2)_nCF_3$

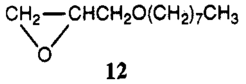
4, n = 2

5, n = 6


CH_2—$CHCH_2OCH_2(CF_2)_nCF_3$ (epoxide, O)

8, n = 2

9, n = 6


CH_2—$CHCH_2O(CH_2)_7CH_3$

12

2. Experimental Section

2.1. **Reagents and Solvents.** (Hydroxyethyl)cellulose (HEC; dry powder) with a hydroxyethyl molar substitution level (Ms) of 2.0 and a MW of 90 000-105 000 was obtained from Polysciences. The 1,1-dihydroperfluoro alcohols ($CF_3(CF_2)_nCH_2OH$, n = 2 or 6), 2-(2-chloroethoxy)ethanol, epichlorohydrin, tosyl chloride, and sodium hydride were commercial materials supplied by Aldrich Chemical Co. The perfluoro alcohols were dried under vacuum for at least 2 days before use. Epichlorohydrin (EPC), 2-(2-chloroethoxy)ethanol, and octyl glycidyl ether (OGE) were distilled over CaH_2 before use.

Solvents, such as isopropyl alcohol (IPA), dioxane (DOX), triethylamine (TEA), anhydrous diethyl ether (DEE), and acetone were obtained from Mallinckrodt and were used as received.

2.2.1. **1,1-Dihydroperfluoroalkyl *p*-Toluenesulfonates (4 and 5).** These were prepared by reaction of the 1,1-dihydroperfluoro alcohol with tosyl chloride in aqueous media.[19] After recrystallization from petroleum ether, the structure of the product was confirmed by IR and NMR. Proton NMR ($CDCl_3$) spectra show the characteristic peaks of *p*-toluenesulfonate at δ 2.45 (s, 3H, $-CH_3$), 4.43 (t, 2H, $-CH_2R_f$), 7.35 and 7.78 (d, 2H, aromatic protons). The 1,1-dihydroperfluorobutyl *p*-toluene-

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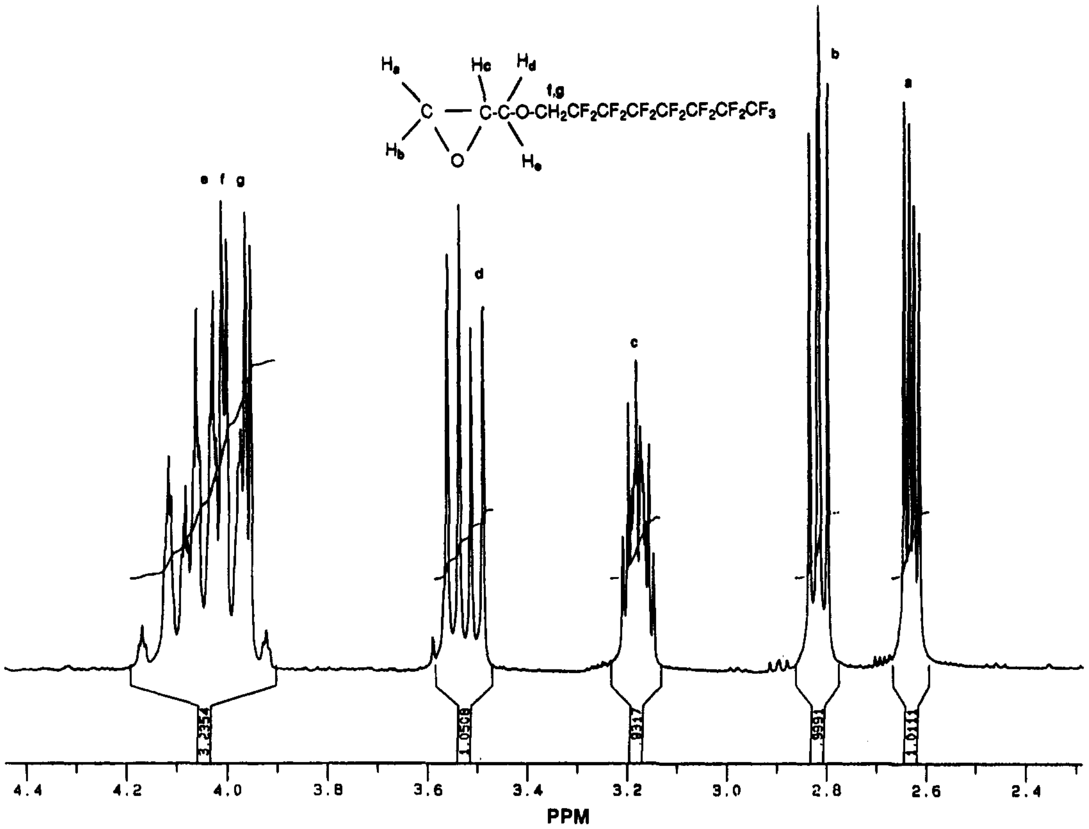


Figure 1. ^{1}H NMR spectrum of modifier PFOGE (9).

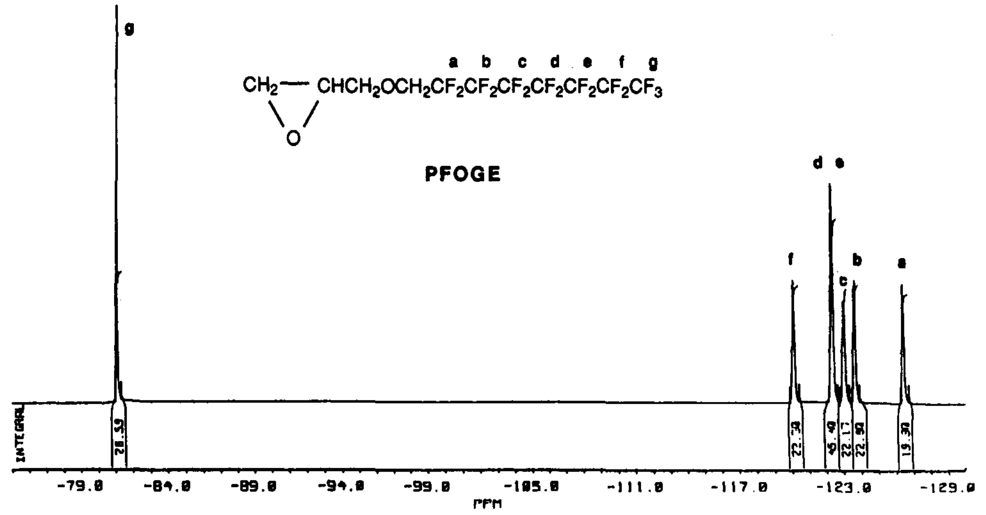


Figure 2. ^{19}F NMR spectrum of modifier PFOGE (9).

sulfonate (PFBOTs; 4) was obtained in 83% yield (mp 27–28 °C) and 1,1-dihydroperfluorooctyl *p*-toluenesulfonate (PFOOTs; 5) in 65% yield (mp 57–59 °C).

2.2.2. 1,1-Dihydroperfluorooctyl Glycidyl Ether (PFOGE) (9).[20] In a typical experiment, 3.5 g of a sodium hydride dispersion in mineral oil (0.0875 mol) was treated with three portions each of 40 mL of anhydrous diethyl ether to remove mineral oil. To the slurry of NaH and 150 mL of fresh anhydrous diethyl ether was added with stirring at room temperature over a period of 20 min 25 g (0.0625 mol) of 1,1-dihydroperfluorooctanol, $CF_3(CF_2)_6CH_2OH$, dissolved in 80 mL of diethyl ether. Epichlorohydrin (7.0 g, 0.076 mol) was then added into the mixture that was stirred overnight. After removal of 160 mL of diethyl ether by passing through nitrogen gas, an additional quantity of 50 g of epichlorohydrin was added. Upon removal of the last traces of ether while raising the temperature, the reaction mixture was refluxed for 4 h with stirring. An equal volume of water was then added to the cooled reaction mixture. The organic layer was separated by means of a separatory funnel. The aqueous layer was extracted three times with 50 mL of diethyl ether. The combined ether solution was dried over $MgSO_4$. Reduced-pressure distillation provided a center fraction (bp 73–75 °C) at 1.5 mmHg with 53% yield. Elemental analysis (Galbraith, Knoxville, TN) confirmed the structure. Calcd for $C_{11}F_{19}H_7O_2$: C, 28.96; F, 62.47; H, 1.55. Found: C, 28.74; F, 62.35; H, 1.56. Proton NMR ($CDCl_3$) shows peaks at δ 2.63 (q, 1H), 2.82 (t, 1H), 3.18 (m, 1H), 3.53 (q, 1H, $-OCH_d-$), 3.97 (q, 1H, $-OCH_e-$), and 3.92–4.16 (m, 2H, $-OCH_2R_f$). Proton and fluorine NMR spectra are shown in Figures 1 and 2. The ^{1}H NMR peaks at 2.63, 2.82, and 3.18 ppm are characteristic epoxide peaks. The two quartets at 3.53 and 3.97 ppm represent the two nonequivalent protons, H_d and H_e. The multiple peaks at 4.04 ppm are due to the protons next to the fluorocarbon chain. In the ^{13}C NMR spectrum, the carbon α to the fluorocarbon chain is split by the adjacent fluorines into the expected triplet centered at 68.6 ppm. The carbons bearing fluorine instead of hydrogen atoms show very small multiple peaks between 105 and 124 ppm, which is due to the strong deshielding caused by the fluorine atoms. Modifier 9 also shows a clean ^{19}F NMR spectrum. The sharp downfield peak (−82 ppm) is due to the $-CF_3$ end group, and it is this peak that was chosen in the determination of the modifier content in modified polymer.

The 1,1-dihydroperfluorobutyl glycidyl ether (PFBGE; **8**) was prepared using a similar procedure. The boiling point was found to be 75–78 °C (40 mmHg), and the yield was 60%. Proton and fluorine NMR show the same characteristic peaks as those of **9**.

2.3. Modification of (hydroxyethyl)cellulose (HEC).[4,21,22] (Hydroxyethyl)cellulose (8.0 g) was added into 100 mL of isopropyl alcohol and then sparged with nitrogen for 1 h. Sodium hydroxide (2.0 g) dissolved in 4 mL of H_2O was then added dropwise over a period of 10 min. The mixture was stirred for another 1 h with a slow flow of nitrogen gas. The mixture was heated to 50 °C, and a certain amount of modifer (**4**, **5**, **8**, **9**, **12**, etc.) dissolved in 10 mL of isopropyl alcohol was added dropwise over 1 h. The reaction mixture was kept at 60 °C for another 3 h. The cooled reaction mixture was neutralized with acetic acid and then filtered. The solid product was washed with four portions each of 100 mL of solvent (1:4 water/acetone) and then pure acetone repeatedly. The product was dried in vacuum at 50 °C for 24 h.

To the dry powder product was added a suitable amount of deionized water, and the mixture was then transferred into Spectra/por 1 (MWCO = 6–8000) dialysis tubing and dialyzed against deionized water for 7 days. The polymer was then precipitated out from the resulting solution in a large amount of acetone and dried in vacuum at 50 °C for 24 h. These dry polymers were then used for the determination of the modifier content. To be sure that unbound modifier can be removed quantitatively in this way from HEC derivatives, we mixed HEC with an appropriate amount of fluorine-containing modifier, which was then allowed to go through the purification procedure described above. Fluorine NMR could not detect any signal from the resulting polymer, indicating all the unbound modifier can be removed quantitatively from HEC derivatives by dialysis and precipitation.

2.4. Determination of the Modifier Content. Using the purified polymers, aqueous solutions were prepared with sodium triflate (CF_3SO_3Na) as the internal standard and subjected to ^{19}F NMR analysis. Since $CFCl_3$ is insoluble in aqueous polymer solutions, we used $CFCl_3$ (dissolved in $CDCl_3$) as the external reference. From the ratio of the peak areas ($NaSO_3CF_3$ at −80.8 ppm and $-(CF_2)_nCF_3$ at −82.8 ppm), the weight percent of fluorine in the polymer and the molar ratio of the modifier over the anhydroglucose unit (AGU) were calculated.

2.5. Polymer Dissolution and Viscosity Measurements. Solutions of HEC derivatives were prepared by dissolving the dry powder polymer in an appropriate amount of deionized water. The suspensions were stirred gently for at least 3 days in order to obtain homogeneous solutions prior to viscometry measurements. The visocity of unmodified HEC treated in the same manner without addition of modifier was also measured for comparison. Brookfield viscometry measurements were carried out, by using a Wells–Brookfield viscometer equipped with different sizes of spindles, at various shear rates. The Brookfield viscosity (cP) and shear rate were obtained by direct readout and rotational speed (rpm), using the range table supplied by the manufacturer. The apparent intrinsic viscosities of modified and unmodified HEC were also measured by using an Ubbelohde viscometer.

2.6. NMR Measurements. The ^1H NMR spectra were recorded at 35 °C on a 250-MHz Bruker spectrometer using $CDCl_3$ as the solvent. The ^{19}F NMR spectra of modified polymers were obtained on a Bruker WM 270 spectrometer at 254 MHz using deionized water as the solvent, and chemical shifts were given relative to external $CFCl_3$. The acquisition parameters were as follows: spectral width, 12 820 Hz; relaxation delay, 20 s; acquisition time, 1.27 s; pulse width, 16 Hz. The T_1 value of the CF_3SO_3Na internal standard was measured and found to be 4 s, appreciably longer than that of the CF_3 group of the polymer (<1 s).

3. Results and Discussion

The synthesis of the 1,1-dihydroperfluoroalkyl derivatives of HEC is shown in eqs 1–3. The 1,1-dihydroperfluorobutyl(hydroxyethyl)cellulose (**6**) is prepared by reaction of a HEC–NaOH slurry with 1,1-dihydroperfluorobutyl tosylate (PFBOTs) (**4**) at 50 °C in various solvents including dioxane (DOX), isopropyl alcohol (IPA), and triethylamine (TEA). The incorporation of perfluorocarbon modifier ([modifier]/[AGU]) into the substrate polymer was evaluated from fluorine elemental analysis in some cases. However, with the exception of very few samples the products were generally insoluble especially when the mole percent of **4** with respect to anhydroglucose units (AGU) was large (>25%). Below 25 mol %, partially soluble products were generally obtained. In the case of polymer **7** modified by **5** (0.5 mol %) mostly insoluble product was obtained. In all cases low viscosity solutions were observed. Similar results were obtained in the case of HEC derivatives **10** modified by **8** under basic conditions. Only partially soluble products were obtained and the viscosities of the filtered solutions were generally low.

However, completely water-soluble polymers were obtained in the case of **9** as the modifier. Thus upon reaction

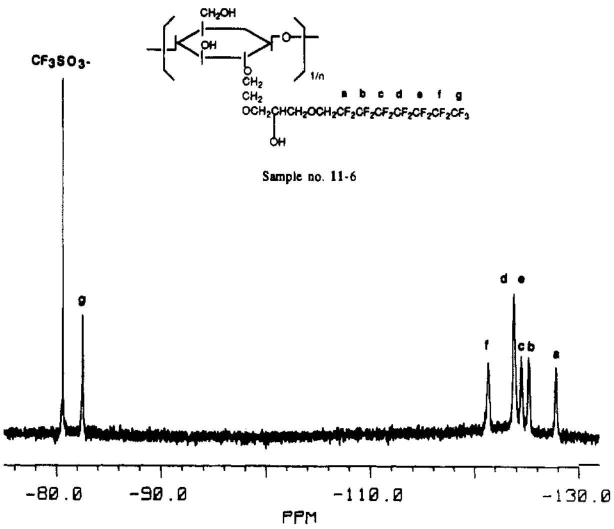
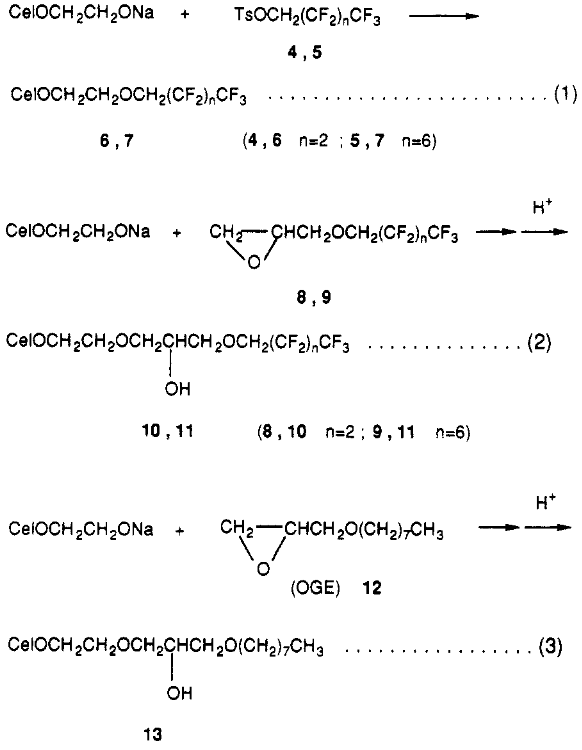


Figure 3. ^{19}F NMR spectrum of HEC (sample no. 11-6) modified with **9**.



$$\text{CelOCH}_2\text{CH}_2\text{ONa} + \underset{\mathbf{4,5}}{\text{TsOCH}_2(\text{CF}_2)_n\text{CF}_3} \longrightarrow$$

$$\underset{\mathbf{6,7}}{\text{CelOCH}_2\text{CH}_2\text{OCH}_2(\text{CF}_2)_n\text{CF}_3} \quad (\mathbf{4,6}\ n=2\ ;\ \mathbf{5,7}\ n=6) \qquad (1)$$

$$\text{CelOCH}_2\text{CH}_2\text{ONa} + \underset{\mathbf{8,9}}{\overset{\text{O}}{\text{CH}_2\text{—CHCH}_2\text{OCH}_2(\text{CF}_2)_n\text{CF}_3}} \xrightarrow{\text{H}^+}$$

$$\underset{\mathbf{10,11}}{\text{CelOCH}_2\text{CH}_2\text{OCH}_2\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{OCH}_2(\text{CF}_2)_n\text{CF}_3} \quad (\mathbf{8,10}\ n=2\ ;\ \mathbf{9,11}\ n=6) \qquad (2)$$

$$\text{CelOCH}_2\text{CH}_2\text{ONa} + \underset{(\text{OGE})\ \mathbf{12}}{\overset{\text{O}}{\text{CH}_2\text{—CHCH}_2\text{O(CH}_2)_7\text{CH}_3}} \xrightarrow{\text{H}^+}$$

$$\underset{\mathbf{13}}{\text{CelOCH}_2\text{CH}_2\text{OCH}_2\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{O(CH}_2)_7\text{CH}_3} \qquad (3)$$

Table I. Synthesis[a] and Brookfield Viscosities (cP)[b] of HEC Derivatives

sample no.	modifier added (mol %)[h]	Incorporated[f]		polym concn (wt %) for Brookfield viscosities				grafting[g] efficiency (%)
		mol %[h]	wt %[i]	0.5	1.0	1.5	2.0	
HEC	0	0	0	55	695	3600	9 600	
11-1[d]	0.12	0.023	0.051	50	570		10 800	19
11-2[d]	1.13	0.249	0.551	75	565		12 400	22
11-3[d]	2.0	0.363	0.806	145	1010	5520	20 560	18
11-4[d]	3.0	0.415	0.917	175	1200	6240	33 400	14
11-5[d]	4.0	0.789	1.781	160	920	6080	23 320	20
11-6[d]	5.0	1.198	2.520				10 400	23
11-7[d]	10.0	2.448[k]	5.252[k]				650[j]	24
10-1[c]	1.0						70[j]	
10-2[c]	3.0						80[j]	
13-1[e]	3.0						5 520	

[a] At 50 °C, isopropyl alcohol as solvent. [b] At 25 °C, shear rate is 0.40 s^{-1}. [c] Modified by PFBGE (8). [d] Modified by PFOGE (9). [e] Modified by OGE (12). [f] Calculated from ^{19}F NMR analysis. [g] Obtained from [incorporated modifier]/[added modifier]. [h] With respect to AGU. [i] Wt % of modifier in polymer. [j] Solutions only partially soluble. Viscosities are of filtered solutions. [k] Calculated from fluorine elemental analysis.

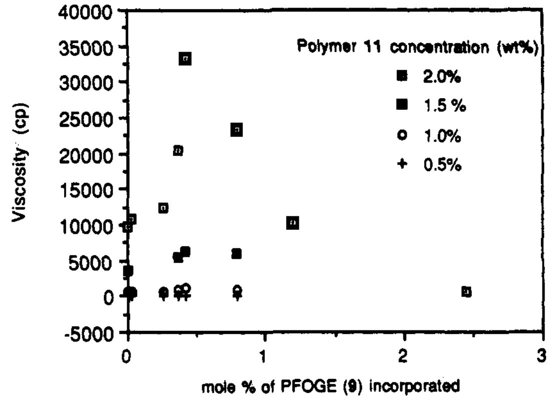


Figure 4. Effect of comonomer 9 content on polymer viscosity.

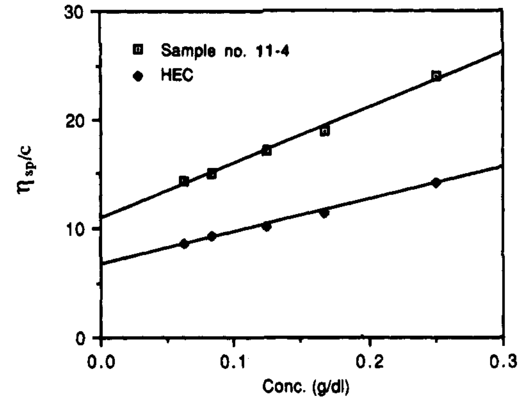


Figure 5. Specific viscosity of polymer 11-4 and the unmodified HEC as a function of polymer concentration.

of HEC with 9 under basic conditions as shown in eq 2, HEC derivatives 11 were formed. The fluorine NMR spectra of the corresponding modified polymers (11-6) are shown in Figure 3. Although the peaks and the chemical shifts of the bound modifer are quite similar to those of 9, the set of three peaks at 122–124 ppm is shifted slightly upfield and the peak width is also slightly broadened. The molar fraction of 9 with respect to AGU was kept between 0.12 and 10.0 mol %. Evidently, the modification reaction is inefficient, since the actual incorporated molar content of perfluorocarbon groups with respect to AGU was found to be between 0.023 and 2.45 mol % (Table I). Thus, the grafting efficiency was found to be between 14 and 24%. The results of the Brookfield viscometric measurements at 0.40 s^{-1} at 25 °C (Table I) show that there is a substantial enhancement at a modifier level of between 0.3 and 0.7 mol %. Thus, at 0.45 mol % of modifier, the viscosity of a 2.0 wt % polymer solution is increased more than 200% compared to that of the unmodified HEC. Significantly, as the modifier is increased to 0.8 and 1.2 mol %, the viscosity decreases. Thus, at 1.2 mol % of 9, the Brookfield viscosity of the product is decreased to about the value of the unmodified HEC. Furthermore, at 2.5 mol % of PFOGE, the polymer becomes partially insoluble and the viscosity plunges to a very low value (<100 cP). A plot of the Brookfield viscosities of 2.0 wt % solutions of samples 11-1 to 11-7 against incorporated 9 shows a clear maximum at about 0.45 mol % (Figure 4). Similar maxima have been observed in HEC derivatives modified with hydrocarbon epoxides.[4] Although the increases in viscosity are relatively modest compared with that of the polyacrylamide copolymers previously studied, it seems clear that the increases are due to similar factors. Starting with very low mole fractions of perfluorocarbon groups, hydrophobic association is largely intermolecular to form networklike structures and this increases as the mole fraction of perfluorocarbon groups increases, resulting in an increase of the apparent hydrodynamic size and thus of the viscosity of the polymer in aqueous solution. However, at higher perfluorocarbon content, intramolecular hydrophobic association of the perfluorocarbons becomes more prevalent and this of course tends to compete with intermolecular association. Thus, at even higher perfluorocarbon content, intramolecular association prevails, causing "collapse" of the polymer coils and resulting in lower viscosity. Such effects have been observed by Landoll for analogous hydrocarbon derivatives of HEC, and a similar explanation was used to describe the results.[4]

It is interesting that HEC derivatives 11 show distinct ^{19}F NMR absorptions. This is in contrast to the copolymers of acrylamide and perfluorocarbon-containing acrylates 2 and 3 that do not show a ^{19}F NMR signal.[23] This may indicate that the extent of hydrophobic association of 11 is considerably smaller so that the ^{19}F signal is due to the unassociated perfluorocarbon groups. This would be in accordance with the much greater extent of association of the perfluorocarbon polyacrylamide derivatives. On the other hand, it is possible that the hydrophobic association of 11 is of a different nature than that of the perfluorocarbon derivatives of polyacrylamide.

Figure 5 shows that the apparent intrinsic viscosity of the modified polymer (11-4) is higher (10.9 dL/g) than that of the unmodified HEC (6.6 dL/g). This fact is consistent with the existence of hydrophobic association formed by the bound fluorocarbon chains in this system. Comparable results were obtained for the acrylamide copolymers of 3.[14,15] Apparently, intermolecular association of sample 11-4 still prevails at the lowest concentration (about 0.06 g/dL). Recent dynamic light scattering

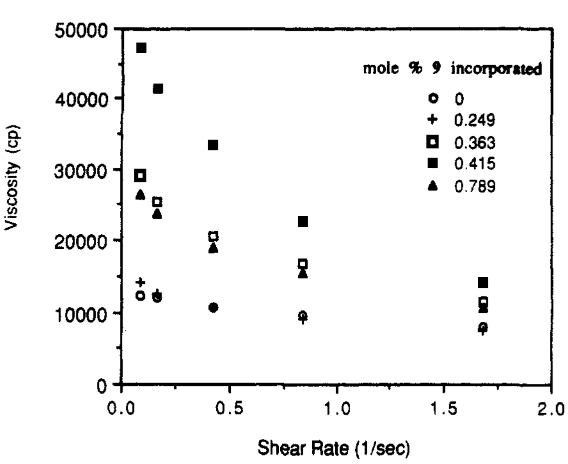


Figure 6. Brookfield viscosity of polymer 11 solutions (2 wt % concentration) as a function of the molar content of 9 and shear rate.

Table II. Shear Rate-Dependent Viscosities of HEC and HEC Derivatives, 11 (Modified by Varying the Amount of 9)

sample no.	comonomer content (mol %)	shear rate (s^{-1}) 0.084	0.168	0.420	0.840	1.680
HEC	0	12 200	12 150	10 800	9 500	7 990
11-2	1.13	14 200	12 500	10 660	9 120	7 550
11-3	2	29 100	25 500	20 560	16 820	11 400
11-4	3	47 200	41 350	33 400	22 800	14 200
11-5	4	26 400	23 800	19 080	15 440	10 600

data for the above polyacrylamide copolymers indicate that hydrophobic association persists at concentrations as low as 100 ppm.[24]

The corresponding hydrocarbon equivalent of 9, OGE (12), was also used as the modifier at 3.0 mol % modifier feed with respect to AGU's (eq 3). As was the case for the polyacrylamide copolymers, the viscosity of the corresponding HEC derivative, 13, was found to be significantly (about 6 times) lower than that of 11-4 formed at the same modifier level (Table I).

As in the case of the polyacrylamide copolymers, the (2.0 wt %) solutions of 11 were found to be highly pseudoplastic (Table II). The sharp decreases of viscosity with increasing shear (see Figure 6) are most likely due to the shear-induced disruption of the weakly associating hydrophobic groups.[5-11,15] Furthermore, when the shear was removed, the viscosities of the solutions recovered completely, indicating that the formation of the hydrophobic aggregates is reversible.

Additional evidence for intermolecular hydrophobic association is provided by the effect on the Brookfield viscosity by the addition of NaCl. For example, the viscosity of a 1.5 wt % aqueous solution of sample 11-3 increases from 5520 to 7280 cP by adding 2 wt % NaCl (further addition of NaCl has no significant effect on the viscosity). Although the viscosity increases (about 30–40%) for the NaCl effect on perfluorocarbon HEC derivatives are modest compared with those on perfluorocarbon polyacrylamide derivatives, these increases appear to correlate well with the known effects of NaCl on hydrophobic association.[16,17,25]

4. Conclusions

The above results, at least qualitatively, confirm similar behavior for hydrophobically modified HEC and polyacrylamides. For the first time, the hydrophobic contents of the hydrophobe-modified copolymers could be determined by ^{19}F NMR. As in the case of the polyacrylamide copolymers, the perfluorocarbon-containing HEC polymers are generally more strongly viscosifying compared to the hydrocarbon analogs. In the case of HEC derivative 11, there is clearly a viscosity maximum with regard to perfluorocarbon content. Similar observations were made by Landoll for alkyl derivatives of HEC.[4] As in the case of the polyacrylamide copolymers, the solutions of the perfluorocarbon-modified HEC were found to be highly pseudoplastic.

Studies aimed at elucidating the effects of hydrophobe and hydrophilic spacer length are in progress.

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