Synthesis and characterization of fluorocarbon-modified poly(*N*-isopropylacrylamide)

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Abstract: Poly(*N*-isopropylacrylamide) copolymers (PNIPAMs) containing pendent perfluoroalkyl (R_F) or dodecyl groups have been synthesized by copolymerization of NIPAM with small amounts of R_R-acrylates or -methacrylates containing a sulfonamido moiety between the acrylate and R_F groups or with dodecyl acrylate. Evidence for strong intermolecular hydrophobic association of the fluorocarbon groups is provided by large viscosity increases with copolymer concentration and upon addition of NaCl and surfactants. These interactions appear to be much stronger than that of the corresponding copolymers of poly(*N,N*-dimethylacrylamide) with similar comonomer contents.

Hydrophobic association between the R_F groups is found to be much stronger than that of the corresponding dodecyl groups. The viscosity of some of the copolymer solutions, particularly in the presence of perfluorocarbon surfactants, was unusually temperature sensitive, decreasing by a factor of at least 1000 upon increasing the temperature from 10 to 20 °C. This large decrease is most probably related to the collapse of the copolymer coils near the lower critical solution temperature. This is in sharp contrast to the corresponding polyacrylamide or poly(*N,N*-dimethylacrylamide) R_F-acrylate copolymers that show viscosity increases with increasing temperature in the 40–60 °C range. The NIPIAM copolymers were also found to be different from the acrylamide or *N,N*-dimethylacrylamide perfluorocarbon acrylate copolymers in that they were found to be Newtonian at a low R_F content but dilatant at a higher comonomer content.

Keywords: hydrophobic association; poly(*N*-isopropyl acrylamide); LCST; fluorocarbons; water-soluble polymers

INTRODUCTION

Hydrophobic interactions play an important role in surfactant micellation and related phenomena, including association of hydrophobically modified water-soluble polymers.[1–10] Solutions of such polymers containing pendent hydrophobic groups can form polymer clusters by intermolecular hydrophobic association, thereby increasing hydrodynamic volume and thus solution viscosity. Such polymers have attracted considerable attention because of their interesting rheological properties and their potential applications, including mobility control agents, thickeners for coatings and cosmetics.

We and others have recently synthesized water-soluble polymers containing fluorocarbon pendent groups or end-groups.[11–21] Compared to the corresponding hydrocarbon analogues, these copolymers show much stronger hydrophobic association and at a much lower hydrophobe content.

In aqueous solutions poly(*N*-isopropylacrylamide) (PNIPAM), unlike polyacrylamide, precipitates out at a lower critical solution temperature (LCST) and this gives rise to interesting properties. The LCST behaviour of PNIPAM and its hydrophobically modified copolymers has been studied, but the investigations on the copolymers were only concerned with the hydrocarbon derivatives.[22–26] In this paper, we report the synthesis of PNIPAMs containing pendent R_F groups by copolymerization of NIPAM with 2-(*N*-ethylperfluoro-octane/sulfonamido) ethyl acrylate (FX-13) or with the corresponding perfluorocarbon methacrylate (FX-14) (Scheme 1). We also describe the characterization of the copolymers by light scattering and their rheological and aqueous solubility properties. The effect of additives and the influence of fluorocarbon group content and structure on the LCST of the copolymers were investigated. Hydrophobic association of these copolymers was previously

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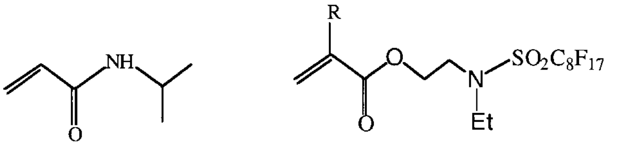

NIPAM FX-13, R=H; FX-14, R= methyl

Scheme 1. Structure of monomer and comonomers.

investigated by fluorescence spectroscopy using both pyrene and fluorocarbon-substituted pyrenes as probes[27] and by light scattering.[28,29]

EXPERIMENTAL

Reagents

N-Isopropylacrylamide (NIPAM) (Eastman Kodak) was recrystallized from hexane/benzene (65/35 vol%). The comonomers 2-(*N*-ethylperfluorosulfoamido) ethyl acrylate (FX-13) and 2-(*N*-ethylperfluoro-octane/sulfoamido) ethyl methacrylate (FX-14) were recrystallized from methanol. Perfluorocarbon monomers and surfactants contain small amounts of lower molecular weight branched perfluorocarbon groups (see also ref 13, 14, 28, 29). Lauryl acrylate (Polysciences) was distilled before use. Potassium perfluoro-octanate (FC-143) (3M Co) was used as received. Azobisisobutyronitrile (AIBN) (Aldrich) was recrystallized from methanol. Benzene, 1,4-dioxane and THF were refluxed over sodium and distilled, and acetone was used as received.

Polymer synthesis

NIPAM (2.26g, 20mmol), a certain amount of hydrophobic monomer and 16.4mg (0.1mmol) AIBN dissolved in 40ml dioxane were placed in a 50ml round-bottomed flask. After purging with purified nitrogen for 15min, the mixture was heated for 24h at $60 \pm 0.5\,°C$ in an oil-bath with magnetic stirring and was then cooled to room temperature and exposed to air. After precipitation in 500ml ethyl ether, filtering and drying, the precipitate was dissolved in 20ml acetone and reprecipitated in 500ml ethyl ether, followed by drying in a vacuum oven at 40°C for 24h. The polymerizations and work-up in benzene were carried out in a similar manner, except that the polymerizations were carried out at 50°C and that 40mg AIBN was used. However, in this case the PNIPAM precipitated during polymerization (suspension polymerization). All homopolymerizations were carried out in the same way as reported for the copolymerizations except for the absence of comonomer.

Polymer characterization

Because of the low comonomer content of several of the copolymers, the fluorocarbon content of the copolymers could not be determined by standard elemental analysis techniques. Therefore we used anion chromatography using a Dionex 2110i instrument.[28–31] Intrinsic viscosities were measured using an Ubbelohde capillary viscometer. The shear dependence of the viscosities was measured by a Brookfield LVT viscometer with the temperature being controlled by a Polyscience constant temperature circulator bath. Lower critical solution temperatures (LCST) were measured by a differential scanning calorimeter on the DSC-50 instrument (Shimadzu Co), the rate of heating being $1\,°C\,min^{-1}$ and using water or water containing certain additives as the reference. The LCST was defined as the temperature corresponding to the absorption maximum. The laser light-scattering and fluorescence studies were carried out as reported previously on 0.2–0.5wt% solutions.[27–29]

RESULTS

Synthesis

The copolymerizations of NIPAM and FX-13 or FX-14 were carried out in dioxane or benzene.[28,29] The copolymerizations are generally homogeneous in dioxane (D-series) but in benzene (B-series) the polymerization led to the formation of a NIPAM homopolymer or copolymer precipitate soon after initiation.

The synthesis and characterization of the copolymers by light scattering and viscometry is summarized in Tables 1–3. The NIPAM homopolymers and the copolymer containing dodecyl acrylate are shown for comparison. The NIPAM conversions are nearly quantitative and the comonomer conversions are between about 40 and 90% with comonomer molar contents (determined by anion chromatography) ranging between about 0.04 and 1.50mol% (Table 1).

Generally the MWs of the homopolymers determined by light scattering are similar in water and THF, and are larger for the B than for the D homopolymers. For the D copolymer series, the apparent MWs determined by light scattering in water are generally larger when compared to the corresponding values determined in THF, but this is not always the case (see Discussion). There is no evidence for significant association of D-13-1, D-14-1, B-13-1, B-14-1 all having very low comonomer contents. In some cases where the comonomer contents per chain are high (samples D-14-6, D-13-6, B-13-4) the apparent MWs in water are comparable or smaller than in THF (see Discussion).

Solution rheology

As shown in Table 2 the intrinsic viscosities and Huggins' constants of dilute solutions (<1wt%) of homopolymer and copolymers D-13-4 and B-13-4 in THF are roughly consistent with the light scattering data. Thus the B homo- and copolymer have larger intrinsic viscosities than the D homo- and copolymer. The intrinsic viscosities of the D homopolymer and copolymer in water are consistent with that in THF. The lower intrinsic viscosity of the B-13-4 copolymer

Table 1. Synthesis and characterization of NIPAM copolymers.[a]

Polymer	Comonomer in feed[b] (mol%)	Comonomer content[c] (mol%)	Comonomer conversion[d] (%)	$M_w \times 10^{4}$ [f] In THF (g mol^{-1})	$M_w \times 10^{4}$ [f] In water (g mol^{-1})	N_{FC}[g]
Homo-D	0	0	/	6.2	6.4	0
D-13-1	0.085	0.077	91.1	8.7	8.5	0.6
-2	0.16	0.13	78.8	7.5	11.0	0.9
-3	0.32	0.26	79.8	7.5	12.0	1.7
-4	0.64	0.39	61.0	6.5	16.0	2.2
-5	1.26	0.82	64.8	7.3	13.0	5.3
-6	2.50	1.52	60.0	Insoluble	8.3	11.0
D-14-1	0.078	0.06	76.3	7.3	7.3	0.4
-2	0.16	0.10	65.3	6.0	8.6	0.5
-3	0.32	0.21	65.6	6.0	12.0	1.1
-4	0.62	0.42	67.0	6.0	15.0	2.2
-5	1.24	0.88	70.8	6.0	12.0	4.7
-6	2.44	1.50	61.6	6.0	4.7	8.0
Homo-B	0	0	–	12.0	11.0	–
B-13-1	0.08	0.035	43.9	6.0	4.7	0.19
-2	0.16	0.099	61.6	8.0	8.1	0.7
-3	0.32	0.23	72.1	7.9	7.1	1.6
-4	0.64	0.39	61.6	23.0	21.0	7.9
-5	1.26	1.01	80.2		Insoluble	16.8
B-14-1	0.078	0.046	58.3	7.2	5.4	0.29
-2	0.16	0.12	74.4	8.7	9.1	0.92
-3	0.31	0.23	72.4	7.2	7.3	1.50
-4	0.64	0.49	76.6	11.0	15.0	4.70
-5	1.25	0.88	70.2	Insoluble		–
B-LA[e]	1.52	–	–	7.3	6.8	9.70

[a] D-series, copolymerization in dioxane; B-series, copolymerization in benzene; polymer concentrations between 0.005 and 0.50 wt%.
[b] For synthesis conditions see Experimental section.
[c] Determined by anionic chromatographic method.
[d] Calculated values.
[e] Comonomer is dodecyl acrylate.
[f] Determined by laser light scattering.
[g] Average number of comonomers per chain calculated from M_w and comonomer content.

in water compared with that in THF is also consistent with the light scattering data.

The Huggins' constant (K_H) values of both the B and D copolymers in water are much larger compared to that of the homopolymers and compared to the copolymer values in THF; this is consistent with extensive aqueous intermolecular hydrophobic association occurring at the higher concentrations. The K_H value of sample B-13-4 in 2.0% NaCl solution is 7.8, which is larger than in water ($K_H = 5.6$). This result is similar to that observed earlier for the PAM and PDMA copolymers of FX-13 and indicates stronger association in the salt solution.[11] Similar effects have been documented for the FX-13 copolymers of PDMA.[15]

The rheology of semi-concentrated (about 1–5 wt%) aqueous solutions of the NIPAM B-copolymers as measured by Brookfield viscometry at low shear rate is shown in Table 3 and in Fig 1. Table 3 and Fig 1 show that the viscosities of semidilute soliutions (2.5 or 5.0 wt%) increase sharply with comonomer concentration until molar contents of at least 0.39 mol% and 0.49 mol% for FX-13 and FX-14, respectively. A comparison of copolymers B-13-1 to B-13-3 and B-14-1 to B-14-3 is of interest because the MWs are almost the same and the comonomer contents vary. At extremely low (<0.04 mol%) comonomer content, the solution viscosities of the B homopolymer and the B-13-1 and B-14-1 copolymers are similar; this is consistent with the absence of significant association. As the FX-13 and FX-14 contents increase from about 0.04 to 0.23 mol% the viscosity of the copolymer solutions increases by factors of between 350 and and 500, respectively. This would tend to indicate that association of the FX-14 copolymer is stronger compared with that of the FX-13 copolymers (see

Table 2. Dilute solution viscometry of PNIPAM copolymers[a]

Sample	THF [η] dl g^{-1}	27°C K_H	Water [η] dl g^{-1}	20°C K_H
Homo-D	0.28	0.1	0.38	0.24
D-13-4	0.23	0.1	0.28	2.16
Homo-B	0.84	0.63	1.44	0.29
B-13-4	0.90	0.44	0.58	5.57
B-13-4[b]			0.51	7.79

[a] Measured between 1.0 and 0.05 g dl^{-1}.
[b] In 2.0% aqueous NaCl at 20°C.

Table 3. Viscosity of semi-concentrated solutions of NIPAM copolymers[a]

Sample	*Measured comonomer content (mol%)*	*2.5 wt% (cP)*		*5.0 wt% (cP)*	
		10°C	*20°C*	*10°C*	*20°C*
B-13-1	0.035	–	–	601	50
-2	0.099	90	85	1100	900
-3	0.23	1000	800	21600	12400
-4	0.39	56000	20200	$>2\times10^5$	$>2\times10^5$
-5	1.01	Turbid	Turbid	–	–
B-14-1	0.046	–	–	90	80
-2	0.12	105	95	5300	3700
-3	0.23	2100	1050	48000	27300
-4[b]	0.49	108400	28000	$>2\times10^5$	$>2\times10^5$
-5	0.88	Turbid	Turbid	–	–
B-Lauryl	1.52[c]	95	85	1500	1250
Homo-B	0	–	–	50	45

[a] Shear rate is 0.40 s^{-1}.
[b] Shear rate is 0.28 s^{-1}.
[c] Comonomer in feed.

below). For 2.5 wt% solutions of copolymer B-13-4 having a comonomer content of 0.39% there are further increases of factors of about 25 and 50 at 20 °C and 10 °C, respectively. The corresponding increases of 2.5 wt% solutions of the B-14-4 copolymer compared to that of B-14-3 are roughly of the same magnitude as are the increases with comonomer content of the 5.0 wt% solutions.

Similar changes are seen in Fig 1. The concentration at which significant viscosity increases are seen changes to lower values with increased comonomer content and molecular weight. Thus for samples B-13-3 and B-13-4 with comonomer contents of 0.26 mol% and 0.39 mol% respectively, the onset of the association-induced viscosity increase changes from about 2.5 wt% to about 1.5 wt%, respectively (curves 2 and 4). This is also the case for samples B-14-3 and for B-13-4 (curves 3 and 5). The data again indicate that the viscosification effects are stronger for the FX-14 comonomer than for FX-13. For instance, Fig 1 shows that the viscosities of B-14-4 exceed that of B-13-4, even though the MW of B-14-4 is about half that of B-13-4.

As shown in Fig 1 and Table 3, the copolymers containing pendent dodecyl groups are far less strongly associating compared to the FX-PNIPAM copolymers. This was observed also for the PAM copolymers of FX-13, but the effects here are even more dramatic. Thus the concentrations for the onset of association of the B-13 and B-14 copolymers is much lower than for

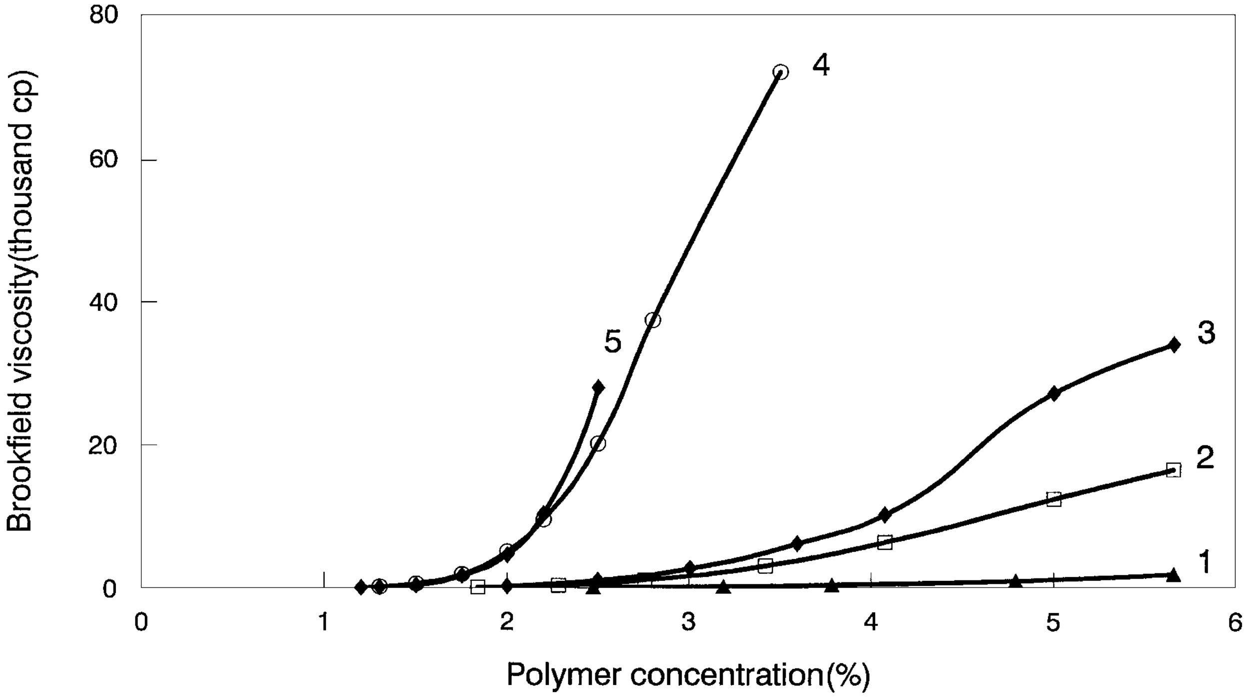

Figure 1. Viscosity dependence on polymer concentration of R_F-modified PNIPAM copolymers (Table 1): curve 1, BLA; curve 2, B-13-3; curve 3, B-14-3; curve 4, B-13-4; curve 5, B-14-4.

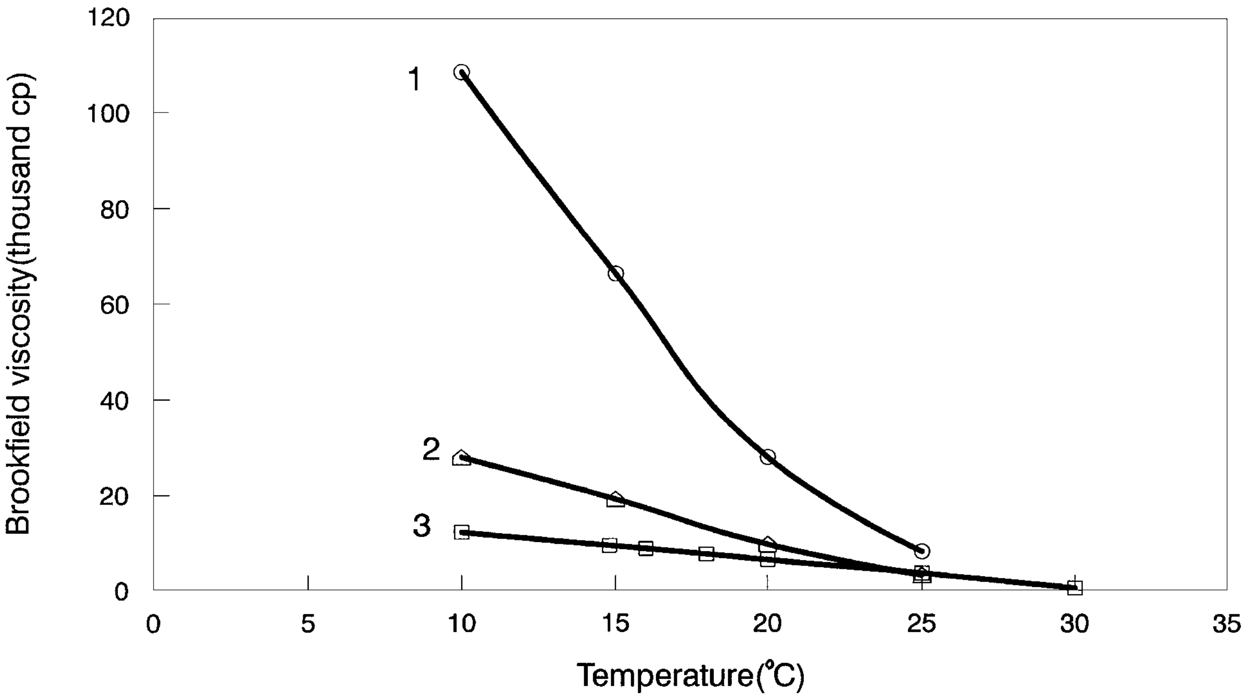

Figure 2. Viscosity dependence of solutions of B copolymers on temperature: curve 1, B-14-4 (2.5%); curve 2, B-13-4 (2.2%); curve 3, B-13-3 (4.1%).

the corresponding dodecyl acrylate copolymer with a much higher molar comonomer content of 1.5% but for which the onset of association is not visible below 5 wt% (curve 1). The viscosity of 5% solutions of the B-FX-13-2 and the B-FX-14-2 copolymers both containing about 0.1 mol% comonomer is essentially the same as that of the dodecyl acrylate copolymer with a 15 times greater comonomer content of 1.5 mol% (Table 3).

The above viscosity increases are much larger than seen for the FX-13 copolymers of poly(*N*,*N*-dimethylacrylamide) (PDMA) of similar molecular weights.[15] For instance, the low shear ($0.40\,s^{-1}$) viscosities of 5.0 wt% B-13-4 copolymer solutions ($M_w = 230\,000$) or a similar B-14-4 copolymer ($M_w = 110\,000$) with comonomer contents of 0.39 mol% and 0.49 mol%, respectively are found to be in excess of 2×10^5 cps (Table 3). The corresponding 5 wt% PDMA copolymer solution with a comparable MW and an FX-13 comonomer content of 0.40 mol% has a viscosity on the order of only 400 cP and the PDMA copolymer with a comonomer content of 0.20 mol% has a viscosity of only 20 cP.[15] The greater hydrophobicity of the NIPAM copolymer may play a role in this (Discussion). As illustrated in Fig 1, the B-14-3 copolymer seems to be somewhat more strongly associated than the corresponding B-13-3 copolymer having about the same MW and comonomer content. The opposite was shown to be the case for the PAM copolymers.[9,10]

Temperature effects

As shown in Fig 2, the viscosity of a 2.5 wt% solution of a B-FX-14-4 copolymer that is 108 400 cP at 10 °C is about 28 000 cP at 20 °C and is less than about 6000 cP at 25 °C. These viscosity decreases with temperature are much larger than observed for the PNIPAM homopolymer (typical decrease of only about 2 or 3 cP when heating 20 °C) and are fully reversible. Upon heating above 20 °C the copolymer solutions first become turbid and then insoluble at the LCST. In the presence of perfluorocarbon surfactants, the viscosity decreases with temperature are even larger (see below).

Clearly these changes are related to collapse of the chains near the LCST which appears to interfere with R_F–R_F interactions. These large viscosity decreases upon warming are very different from the temperature responses of solutions of the PAM or PDMA copolymers of FX-13. For instance, upon heating solutions of FX-13 PAM copolymers there is first a modest viscosity decrease (factor of three) as the temperature is raised from 25 °C to about 40 °C, followed by a roughly twofold viscosity increase to a maximum at about 60 °C and then a threefold decrease as the temperature is increased to 80 °C.[9,10] Similar behaviour was demonstrated for the corresponding PDMA copolymer solutions.[15]

Effects of shear

Aqueous solutions of fluorocarbon-modified PAM and PDMA copolymers are generally shear-thinning pseudoplastic fluids.[9,10] However, the B-14 or B-13 copolymers with comonomer contents below about 0.30 mol% or the B-LA copolymers containing 1.5 mol% dodecyl acrylate show all Newtonian behaviour between 0.40 and about 10 s^{-1}. The B-series copolymer solutions with a fluorocarbon content of 0.40 mol% or higher show dilatant properties above a shear rate of about $2.50\,s^{-1}$ (Fig 3). This behaviour is

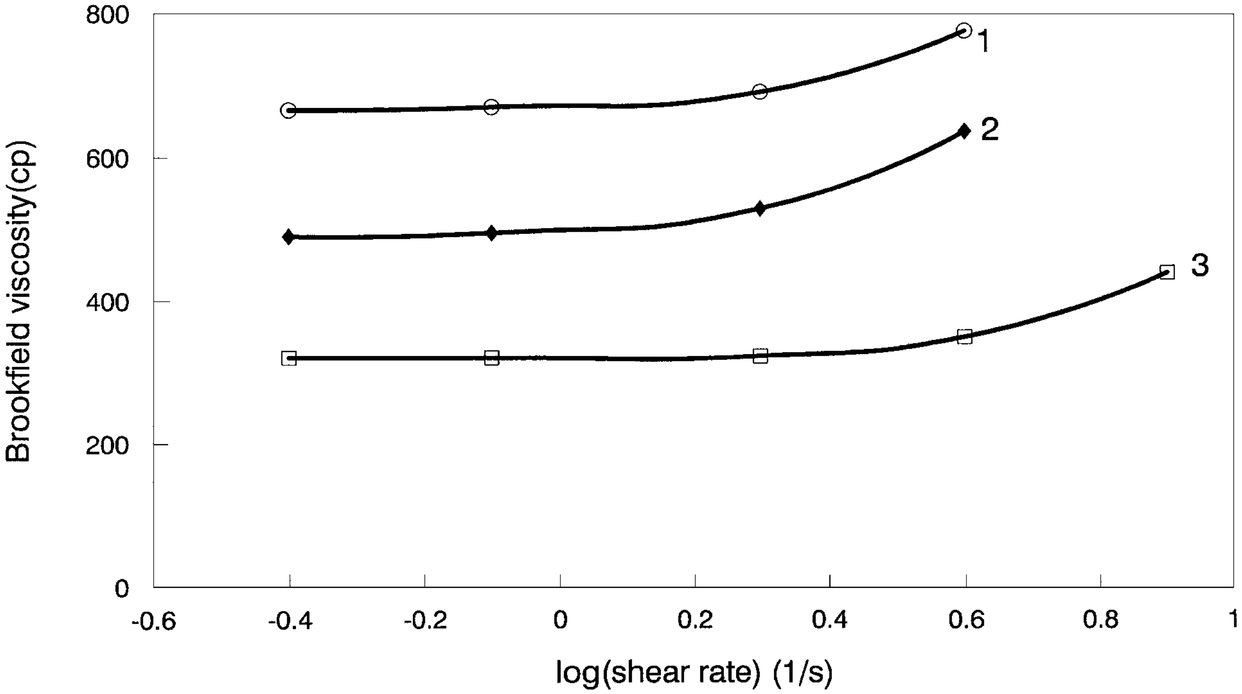

Figure 3. Viscosity dependence of copolymers on shear: curve 1, B-13-4 (1.5 wt%, 20 °C); curve 2, B-14-4 (1.3 wt%, 10 °C); curve 3, B-14-4 (1.3 wt%, 10 °C).

completely different from that observed for the PAM or PDMA copolymers which are highly pseudoplastic at all shear rates in excess of 0.40 s^{-1} (see Discussion).[9–15]

Effect of additives

The presence of NaCl in aqueous solutions of the perfluorocarbon-modified PAM and PDMA copolymers has been demonstrated to increase hydrophobic association.[9–15] A similar increase in hydrophobic association is observed for the NIPAM copolymers. For example, at 10 °C in the presence of 4.0 wt% NaCl, the low shear viscosity of a 5.0 wt% B-14-2 copolymer solution was increased from 5300 cP to 51 500 cP, and a similar increase was seen for a 5.0 wt% B-13-2 copolymer solution (Fig 4). However, the situation is different at 20 °C in which case the solution viscosity of the B-FX-13-2 copolymer was

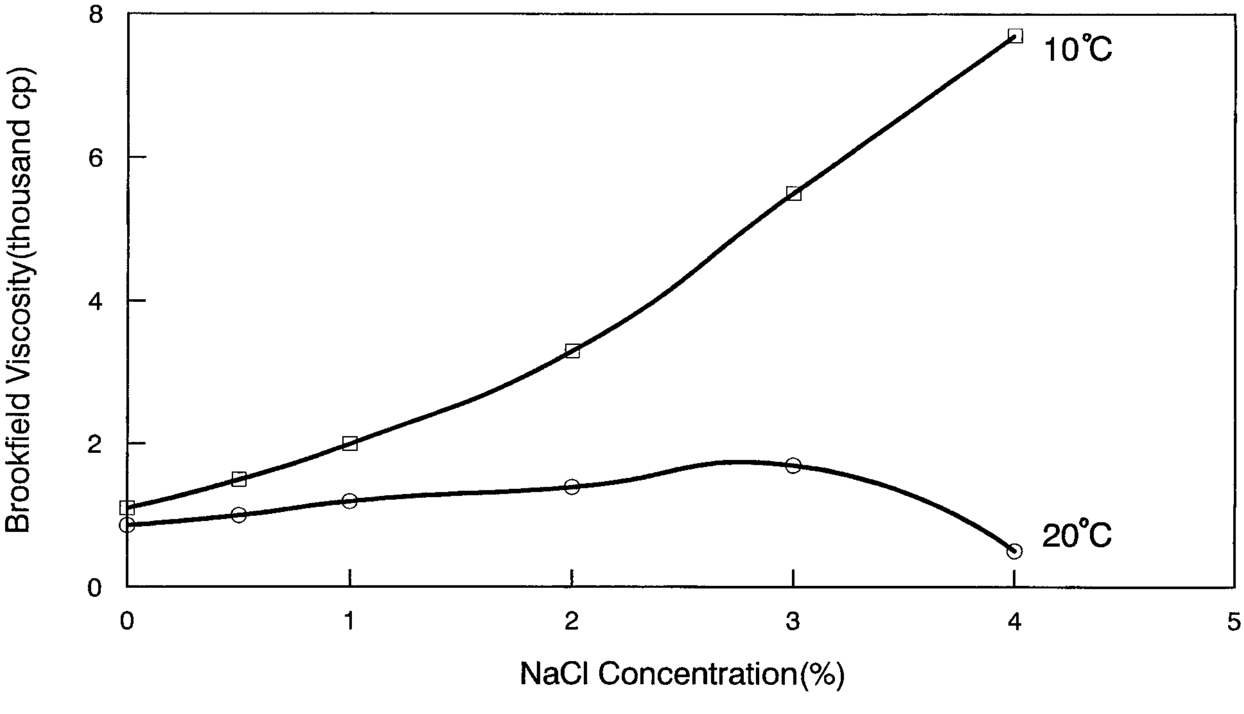

Figure 4. Effect of NaCl on the viscosity of 5.0 wt% solutions of B-13-2.

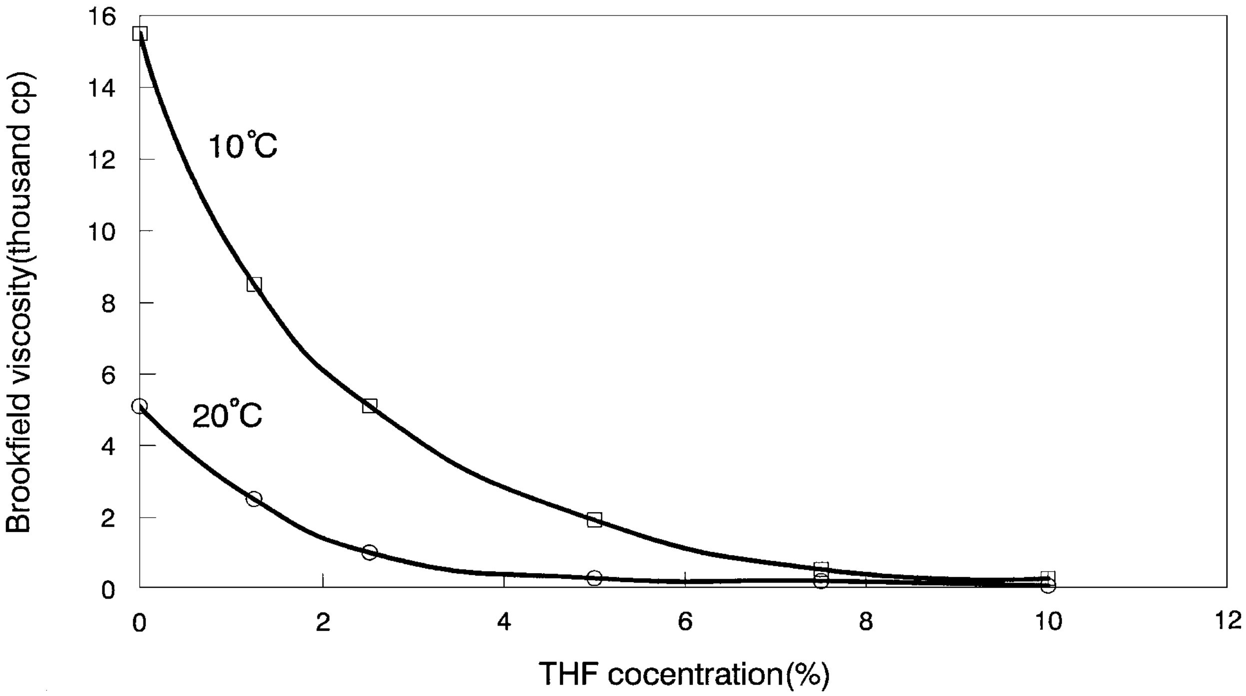

Figure 5. Effect of addition of THF on the viscosity of 2.0wt% solutions of B-13-4.

increased slightly as the NaCl concentration was increased to 3%, and then decreased as the NaCl concentration was increased to 4.0%. Most probably this latter decrease is related to the collapse of the chain due to the lower value of the LCST resulting from the presence of the salt (see below).

Addition of relatively small amounts of THF (a good solvent for PNIPAM) is effective in decreasing the viscosity of the NIPAM copolymer solutions (Fig 5). This type of behaviour is quite typical for hydrophobically modified copolymers containing both R_F and R_H groups.[11,15] However, at 10°C the viscosity of a 2.0wt% B-13-4 solution is decreased by a factor of about 100 as the THF content is increased to only 10vol%. Addition of only 1wt% THF to a 2.0wt% solution of B-13-4 at 10°C results in a 50% viscosity decrease.

As shown in Fig 6, addition of potassium perfluoro-octanoate to a 5.0wt% solution of the B-13-2 copolymer at 10°C increases the viscosity by as much

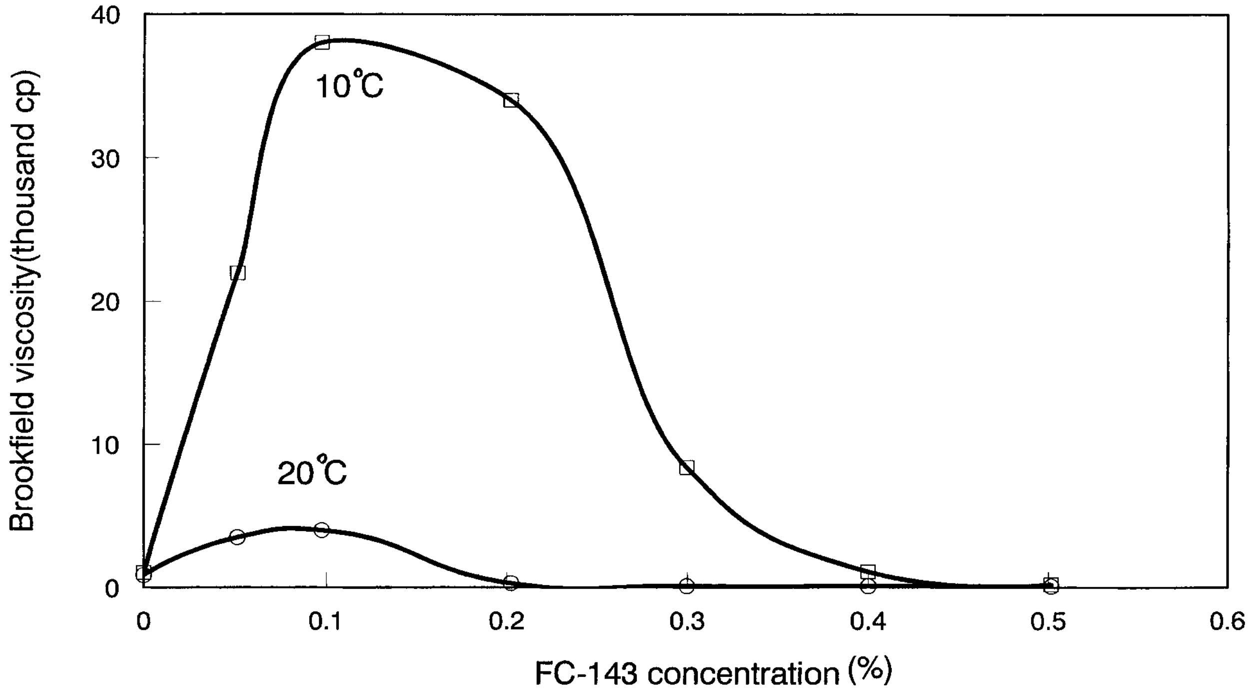

Figure 6. Effect of addition of potassium perfluoro-octanoate on the viscosity of 5.0wt% solutions of B-13-2.

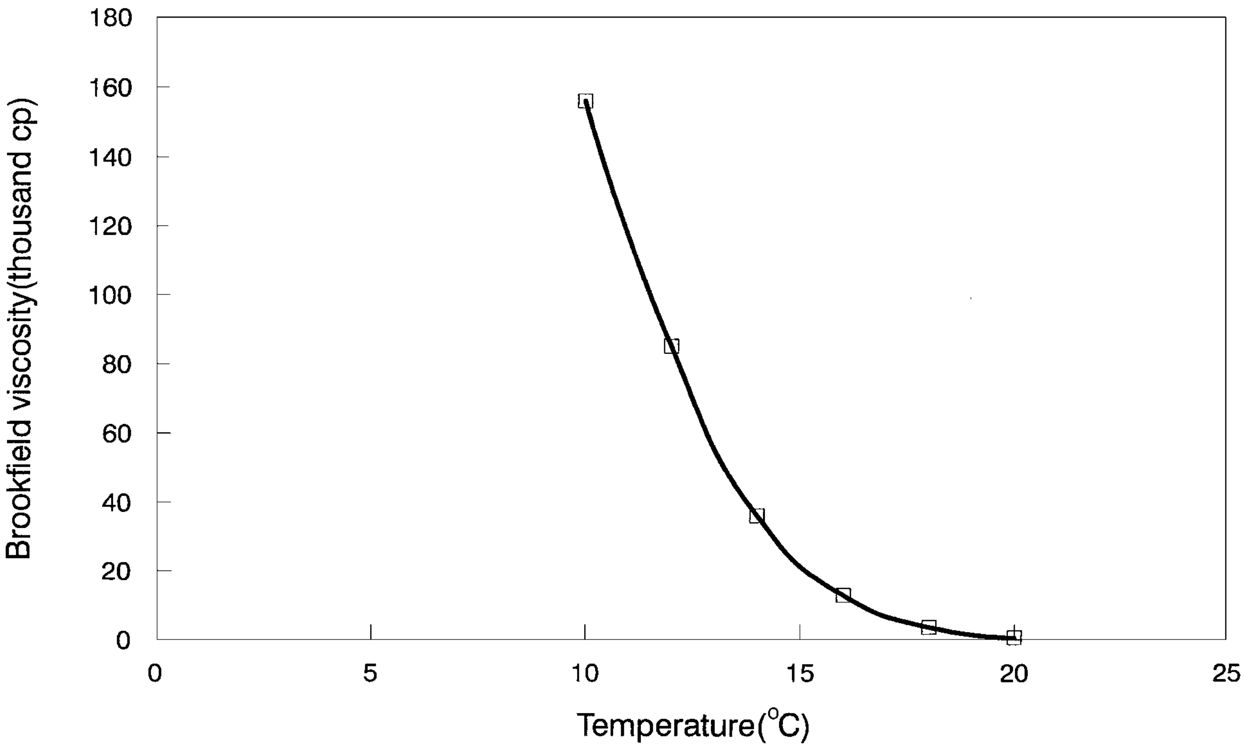

Figure 7. Effect of temperature of a 3.2 wt% solution of copolymer B-14-3 in the presence of 0.30 wt% potassium perfluoro-octanoate.

as a factor of about 40. Further surfactant addition decreases the viscosity and gives very low values at 0.5 wt% surfactant, producing the familiar bell-shaped curves as also seen by others for hydrocarbon modified water soluble polymers and for the FX-13-modified PAM[9,10] and PDMA[15] copolymers.[32–35] Thus the viscosity maximum at about 0.1 wt% potassium perfluoro-octanoate decreases by about one order of magnitude as the temperature is raised from 10 °C to 20 °C. This is not unexpected because at the higher temperature the system is closer to the LCST at which point R_F–R_F association tends to be much reduced (see above). As shown in Fig 7, the decrease in apparent viscosity with a 10 °C rise in temperature (from 10 to 20 °C) of a 3.20 wt% solution of copolymer B-14-4 in the presence of 0.30 wt% potassium perfluoro-octanoate is very large, being more than 1000-fold. This dramatic effect is not unexpected because in this case we appear to see the combined effect of the disruption of both R_F association (Fig 2) and micellar bridging (Fig 6).

Copolymer solubilities

Above about 1 mol% comonomer content the copolymers are insoluble in water. The LCST (33.0 °C) of the D-homopolymer was found to be slightly higher than that of the B homopolymer (32.6 °C), presumably because of its lower molecular weight. As expected, the incorporation of FX-13 into PNIPAM is seen to reduce the LCSTs (between 0.3 and 3.2 °C) as shown in Table 4. A similar effect has been demonstrated for the corresponding hydrocarbon-modified NIPAM copolymers.[22–24] The LCST reductions in the D series are larger than in the B series. For example, the reduction of the LCST of the D-14-4 copolymer ($\Delta T = 1.7$ °C) is slightly larger than that of B-14-4 ($\Delta T = 1.1$ °C) having an approximately equal fluorocarbon content. The effect is even larger for the D-14-5 and the B-14-5 copolymers ($\Delta T = 3.2$ °C and 1.4 °C, respectively). The reductions in LCST are significant, especially given the low fluorocarbon contents of the copolymers. Ringsdorf and co-workers[25,26] synthesized copolymers of NIPAM containing 0.5 mol% of *N*-decyl, *N*-lauryl and *N*-octadecyl acrylamide as hydrophobic comonomers and have interpreted LCST increases/decreases as due to the

Table 4. LCST of R-PNIPAM copolymers

Sample	*LCST(°C)*	*ΔT(°C)*
Homo-D	33.0	–
D-14-1	32.7	−0.3
-4	31.3	−1.7
-5	29.8	−3.2
Homo-B	32.6	–
B-14-1	32.3	−0.3
-2	32.2	−0.4
-3	31.9	−0.7
-4	31.5	−1.1
-5	31.2	−1.4
B-13-1	32.2	−0.4
-2	32.1	−0.5
-3	31.8	−0.8
-4	31.5	−1.1
-5	31.3	−1.3

hydrophobicity of the hydrocarbon groups. A similar interpretation may apply in this case because of the apparently higher effective hydrophobicity of the perfluorocarbon compared to the hydrocarbon groups.

DISCUSSION

Comonomer sequence

The kinetics of the solution and bulk copolymerizations of FX-13 and AM or DMA have been shown to be consistent with random comonomer incorporation, and this is also reflected in the association behaviour of the corresponding copolymers.[11–15] In dioxane, the NIPAM copolymerizations are homogeneous and the documented reactivity ratios of acrylamides and acrylates would predict random distributions.[36] There is no evidence in the above data that is inconsistent with a random comonomer distribution and in the following discussion such distributions will be assumed.

Association detected by light scattering

The comonomer contents of the most strongly viscosifying B and D copolymers are similar (comonomer content between 2 and 5 wt%) and slightly higher than for the FX-13 and FX-14 PAM and PDMA copolymers reported earlier.[9–11,15] However, the molecular weights of the NIPAM copolymers are typically about an order of magnitude lower than that of the PAM or PDMA copolymers prepared by emulsion polymerization, presumably because of chain transfer. As a result the number of R_F groups per chain is much lower (0.2–7.9) than for the higher MW copolymers of AM or DMA with similar comonomer contents. Thus the higher comonomer contents of the strongly associating PNIPAM copolymers are not surprising.

The light scattering data in THF indicate that, with a few exceptions, the molecular weights are generally larger for the B than for the D series homo- and copolymers, possibly because chain transfer in dioxane is expected to be larger than in benzene.[37] Furthermore, the occurrence of hydrophobic association of the R_F-modified NIPAM copolymers, especially the D series, in water is reflected by increases in apparent molecular weights as determined by light scattering (Table 1). Apparently the driving force towards hydrophobic association is strong, although at the concentrations used the degrees of association are low and the apparent light scattering MW of the aggregates indicates that the degrees of polymer association appear not to exceed three (Table 1). For sample D-13-2, the overall concentration of the perfluorocarbon groups at $1\,\mathrm{g\,L^{-1}}$ is very low, being of the order of $1\times10^{-5}\,\mathrm{M}$, and the number of R_F groups per chain is about unity. The MW of this copolymer determined by light scattering is about two (Table 1). This would suggest a dimerization constant on the order of about $10^5\,\mathrm{M^{-1}}$, the same order of magnitude as reported for the dimerization of well defined PEO chains containing one perfluoroheptyl end-group.[16] For the NIPAM copolymers with less than an average of one R_F group per chain, weak association is not surprising.

As indicated above for the D series, the apparent molecular weight determined by light scattering initially increases as comonomer content increases, consistent with intermolecular hydrophobic association. In particular this is the case if the number of perfluorocarbon groups per chain is between one and about five (samples D-13-2 to D-13-5, D-14-3 to D-14-5, B-14-3 and B-14-4). At higher comonomer contents in the D series (samples D-13-6, D-14-6) the apparent light scattering MW *decreases* compared to that at lower comonomer concentrations (Table 1). This behaviour is consistent with an increase in intramolecular association and thus decreased intermolecular association, as was observed earlier for the FX-13 and FX-14 copolymers of acrylamide and *N*,*N*-dimethylacrylamide. This is also illustrated by the intrinsic viscosities of D-13-4 and B-13-4 that are lower than that of the corresponding homopolymers, indicating predominantly intramolecular association in these highly dilute solutions (Table 2).

From the intrinsic viscosities of copolymer D-13-4 with 2.2 R_F groups per chain, the approximate concentration of R_F groups within the hydrodynamic volume of the chain would be estimated to be of the order of $10^{-3}\,\mathrm{M}$, about two orders of magnitude higher than estimated to be required for intermolecular association. Thus in dilute solutions of copolymers with at least two R_F groups per chain, some degree of intramolecular micellization is expected. As pointed out above, the weak residual intermolecular association of the NIPAM copolymers at low concentrations differs from that in the high MW polyacrylamide and poly(dimethylacrylamide) copolymers ($\mathrm{MW} > 10^6$) of FX-13 and FX-14 where the numbers of R_F groups per chain are much higher and where strong residual intermolecular (as well as intramolecular) association has been demonstrated by light scattering below 100 ppm.[12]

The greater variability in MW and other factors, such as the heterogeneous polymerization in the B series, makes interpretation more difficult. For the B-14 copolymers significant association, as measured by light scattering at the low concentrations used, is only apparent for sample B-14-4 well above two hydrophobes per chain (Table 1). Possibly, for the case of the B-13 series the comonomer contents were either too low or too high to observe association at the low concentrations used in the light scattering (0.2–0.5 wt%). Another factor was the lack of homogeneity in the B series during the polymerizations. This may have influenced the results. Unfortunately the rather large gap in comonomer contents in the B-13 series between 1.6 and 7.9 R_F groups per chain did not allow an assessment with regard to association observable by light scattering.

Viscosities

The significant association of most of the R_F-modified compolymers is also evident from large increases in the Huggins[1] constants compared to the that of the homopolymers, even at the very low concentrations used in the viscosity experiments (Table 2). Intermolecular aqueous association appears to be more pronounced for B-13-4 than for D-13-4 as indicated by the higher Huggins' constant (Table 2). This is not unreasonable because, for the higher molecular weight B copolymer (Table 1), there are a larger number of R_F groups capable of forming intermolecular hydrophobic associations.

As illustrated in Fig 1 and Table 3, the increases of viscosity with comonomer content below about 0.4–0.5 mol% are consistent with the above. At the higher comonomer contents the overall concentrations of the R_F groups apparently are large enough to allow increases in intermolecular association. For 5.0 wt% solutions of B-13-2 and B-13-3, the calculated overall concentrations of the R_F groups are about 1.2×10^{-4} M and 2.4×10^{-4} M, respectively, well above the estimated minimum concentration of perfluorocarbon groups necessary for association. Thus this competing intermolecular association is expected to become a dominant factor.

Unfortunately, solubility problems precluded the synthesis of copolymers having greater comonomer contents. It is worth noting that the FX-14 comonomer appears to be more effective in conferring associative properties to the copolymers. The opposite was observed for the corresponding copolymers of the polyacrylamide and poly(*N,N*-dimethylacrylamide) copolymers. The reason for this difference is not clear. It is conceivable that the intermolecular interaction between the R_F groups and the hydrophobic portion of the copolymers at least below the LCST plays a role in the viscosification. A similar effect has been noticed in R_F end-functionalized poly(ethylene glycol)s.[16]

The viscosity of semiconcentrated solutions of the FX-13 and the FX-14 copolymers of acrylamide and *N,N*- dimethylacrylamide was shown to decrease as the comonomer content increased above about 0.10 and 0.20 mol%, and this was attributed to increased intramolecular association at higher comonomer contents.[9,10] However, it is clear the FX-13 or FX-14 comonomer contents corresponding to PNIPAM copolymer viscosity maxima are well above that for the high MW PAM and PDMA copolymers. The lower MW NIPAM copolymers with MWs in the 100 000 range would require higher comonomer contents for extensive intermolecular association to occur.

It is interesting to note that the viscosities of the PNIPAM copolymers of FX-13 have much higher viscosities compared to the corresponding PDMA copolymers of comparable MW.[15] For instance, the 5 wt% PDMA copolymer solutions with a comparable MW and a FX-13 comonomer content of 0.20 and 0.40 mol% have viscosities of the order of only 20 cP and 400 cP, respectively. The comparable viscosities in Table 3 are approximately 1000-fold higher. It is possible that these differences are due to the greater stiffness of the PNIPAM backbone resulting from the presence of the large isopropyl group. This would lead to a reduced tendency towards intramolecular association. The greater hydrophobicity of this copolymer may also play a role (see below).

The remarkable viscosifying power of the R_F-modified NIPAM copolymers compared to the corresponding low MW PDMA derivatives is of interest, particularly because the opposite may have been expected. At a comonomer content of only 0.10 mol% and below the LCST there is a 1000-fold excess of isopropyl groups giving rise to potentially large numbers of hydrocarbon domains that may accommodate perfluorocarbon groups. This would be expected to be a formidable barrier to R_F–R_F association. However, as pointed out above, it is possible that below the LCST, intermolecular association of the R_F groups with such regions contributes to copolymer aggregation. This would also explain the greater effectiveness of the FX-14 compared to the FX-13 comonomer, and would help to explain the precipitous viscosity decreases near the LCST where such association would be expected to be intramolecular. Given the relatively low average numbers of fluorocarbons per chain for many of the copolymers listed in Table 1, the extent of intermolecular copolymer association in dilute or semidilute solutions is remarkable.

The LA-PNIPAM copolymer is an especially ineffective viscosifier giving comparable viscosities at much higher (about 15 times) comonomer contents (Table 3). This is not surprising because this has been shown previously for both the PAM and the PDMA copolymers of FX-13 and/or FX-14. In this case, the lack of association is especially pronounced near the LCST, presumably because of the compatibility of the dodecyl and the hydrophobic domains formed by the PNIPAM backbone and the isopropyl groups. Thus pronounced hydrophobic association is expected of the dodecyl pendent groups with the domains of the collapsed R_H-modified PNIPAM copolymers. However, even at lower temperatures and at high concentrations, association is weak as illustrated in Fig 1, and Table 3. Thus, the association of the B-LA copolymer containing about 10 dodecyl groups per chain is similar to that of copolymer B-FX-13-2 with a 15 times lower hydrophobe content.

One of the remarkable properties of the above systems is the very rapid decrease of viscosity near the LCST as shown in Fig 2. As suggested by Schild and Tirrell,[23] a PNIPAM copolymer containing pendent hydrocarbon groups may exist as a hydrophobic core formed by several hydrophobic groups with the hydrophilic PNIPAM surrounding the core. A disruption of this type appears to take place near the LCST of the R_F-modified NIPAM copolymers, and this appears to account for the large decreases in the viscosity of the copolymer solutions upon raising the temperature without *but especially in* the presence of the perfluorocarbon surfactant as shown in Fig 2 and 7. Thus, close to the LCST the collapsed conformation presumably would not be conducive to intermolecular R_F–R_F or R_F–R_H interactions or to micellar bridging because of the restrictions imposed by the collapsed chains. The unusually steep viscosity decrease near the LCST would be consistent with the incorporation of R_F groups in the hydrocarbon micellar domains. Although fluorocarbons and hydrocarbons are relatively incompatible, mixed hydrocarbon–perfluorocarbon micelles are known.[38,39]

The great sensitivity to the presence of small amounts of organic solvents such as THF (Fig 5) may be due in part to the changed structure of the aqueous environment resulting in a smaller driving force in the formation the R_F aggregates. It is also possible that the unusually large viscosity, decrease is due to the partitioning of THF into the hydrophobic domains resulting in their destabilization.

As shown in Fig 6, the increase in viscosity at 20 °C of the NIPAM copolymers upon addition of potassium perfluorooctanoate is similar but somewhat smaller in magnitude than observed for the FX-13-modified PAM[4,10] and PDMA[15] copolymers. These effects are known to be due to micellar bridging at low surfactant concentration and to micellar mediated dissociation at the higher surfactant concentrations.[32–35] The viscosity maximum at about 0.1 wt% potassium perfluoro-octanoate decreases by about one order of magnitude as the temperature is raised from 10 °C to 20 °C. This is not unexpected because at the higher temperature the system is closer to the LCST at which point R_F–R_F association should be much reduced (see above).

Shear effects

The slightly dilatant rheology illustrated in Fig 3 appears to typify the more strongly associating R_F-containing NIPAM copolymer, and all have a relatively large number of R_F groups per chain as seen in Table 1. It is interesting that this is not observed for the R_F-containing high MW ($MW > 10^6$) PAM or PDMA copolymers, both of which show pronounced shear thinning.[9–15] In this case, the sizes of the polymer aggregates at the concentrations used are very large, with typical PAM-FX-13 aggregate hydrodynamic sizes of the order of 10^5 nm for the most strongly associating polymers.[12] Such aggregates are expected to show pronounced pseudoplastic behaviour. The low MW PDMA FX-13 copolymers (prepared in bulk) having intrinsic viscosities close to that of the B-series copolymers are also somewhat shear thinning.[15] It should be noted that the R_F content of the most strongly associating NIPAM copolymers with dilatant behaviour is higher than the corresponding PAM or PDMA R_F copolymers. In these copolymers, the R_F groups are spaced more closely than in the PAM or PDMA copolymers, and this is turn is expected to lead to more intramolecular association competing with intermolecular association.[40,41] The shearing of the resulting polymer assemblies is now expected to lead to the stretching of the coils, disrupting intramolecular association and thereby leading to enhanced intermolecular association. A similar process has been proposed to account for dilatant behaviour of other hyrdrophobically modified copolymers.[35] In solutions of the corresponding AM or DMA copolymers with low R_F comonomer contents, such effects would be small, so that dilatant effects are absent. It is interesting to note that solutions of the PNIPAM-LA copolymer containing a relatively high comonomer content (1.50 mol%) are still Newtonian. This is additional evidence for the much stronger association between the fluorocarbon groups under these conditions compared to that of hydrocarbons.

CONCLUSIONS

The NIPAM copolymers of FX-13 and FX-14 show several interesting differences with the corresponding AM or DMA copolymers. The first of these is the enormous decrease of solution viscosity when the temperature is raised near the LCST of PNIPAM. This behaviour is completely different from the corresponding AM and DMA copolymers that show viscosity increases with temperature in the 40–60 °C range. Another and unexpected difference is the very strong association of the PNIPAM copolymers compared to the corresponding PDMA copolymers of comparable MW. Furthermore, the rheology of the semidilute solutions shows either Newtonian or dilatant rheology in contrast to the AM or DMA copolymers that are pseudoplastic.

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