Synthesis and solution properties of fluorocarbon-modified poly(N,N-dimethylacrylamide)

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Abstract: Poly(N,N-dimethylacrylamide) (PDMA) containing perfluoro-octyl pendent groups was prepared by solution polymerization of N,N-dimethylacrylamide in benzene with 0.16 –1.25 mol% 2-(N-ethylperfluoro-octane sulfonamido) ethyl acrylate (FX-13) or 2-(N-ethylperfluoro-octane sulfonamido) ethyl methacrylate (FX-14). The copolymer intrinsic viscosity strongly decreases with increasing comonomer content due to intramolecular association. However, the Huggins constant increases more than 40-fold with increasing comonomer content, indicating that intermolecular association increases with increasing comonomer content. Strong Brookfield viscosity enhancements are observed above a critical copolymer concentration varying between 0.5 and 2.0 wt% depending on comonomer type and content. Some of the copolymers show pseudoplastic behaviour whereas others show shear-thickening or both types of behaviour. These observations are consistent with competing inter- and intramolecular micellar association. Fluorescence studies using a perfluorocarbon-substituted pyrene as a probe indicate the formation of hydrophobic microdomains formed by the association of perfluorocarbon groups.

INTRODUCTION

Hydrophobically modified water-soluble polymers have received increasing attention over the last decade due to their unique rheological properties and industrial importance. For instance, hydrophobic association of polycrylamide copolymerized with dodecylacrylate, dodecylmethacrylate or N-alkyl acrylamides has been studied. Also water-soluble copolymers containing pendant perfluorocarbon groups were synthesized by copolymerization of perfluorocarbon acrylates such as FX-13 (Scheme 1) and acrylamide and similar comonomers or by grafting of perfluorocarbon groups onto hydroxethylcellulose. Such copolymers, because of the more pronounced hydrophobic character of the fluorocarbon groups, give much higher solution viscosities than the copolymers functionalized with hydrocarbons with the same carbon number. Poly(N,N-dimethylacrylamide) (PDMA) is a well known water-soluble polymer that is widely used in the paper, textile and coating industries. Recently, Xie and Hogen-Esch reported the synthesis and solution properties of FX-13-modified PDMA by perfluorocarbon surfactant-mediated emulsion copolymerization and bulk copolymerization. The aqueous viscosities of the emulsion copolymers formed were found to be much higher than those of the bulk PDMA copolymers, partly because of the lower molecular weights of the bulk copolymers. Other possible reasons include differences in comonomer sequence distribution. For the case of acrylamide (AM) copolymerizations with hydrocarbon acrylates or N-alkylacrylamides the reasons for such differences, in particular the occurrence of ‘blocky’ comonomer sequences deduced from compositional drift and other observations, have been proposed by a number of authors.

For the case of the perfluorocarbon surfactant-mediated emulsion copolymerizations of FX-13\textsuperscript{1} with both AM and N,N-dimethylacrylamide (DMA), the copolymerization kinetics indicated the absence of comonomer compositional drift consistent with simple copolymerization kinetics predicted by the reactivity ratios of the monomer pairs. However, the occurrence of random comonomer sequence distributions, or lack thereof, remains to be tested.

In the following, we report the synthesis and solution viscometric properties of FX-13\textsuperscript{1} copolymers of poly(N,N-dimethylacrylamide) synthesized in benzene solution by 2,2'-azobisisobutyronitrile (AIBN) initiated copolymerizations. In this case the polymerization is largely homogeneous and the reported reactivity ratios of DMA and acrylates would predict random comonomer sequence distributions.\textsuperscript{19} This, in turn, could be expected to affect copolymer solution rheology. Here we report the association behaviour of these copolymers monitored by viscometry. We also report the fluorescence of aqueous solutions of the copolymers in the presence of perfluorocarbon pyrene derivatives.

**EXPERIMENTAL**

**Materials**

DMA, (Aldrich) was purified by distillation under reduced pressure. The perfluorocarbon acrylates 2-(N-ethylperfluoro-octane sulfonamido) ethyl acrylate (FX-13) and 2-(N-ethylperfluoro-octane sulfonamido) ethyl methacrylate (FX-14) obtained from 3M Co. were recrystallized twice from methanol. Small amounts of perfluorocarbon impurities are present in these monomers.\textsuperscript{13-17} 1-Perfluoro-octanoyl pyrene (PFOP) was synthesized as reported earlier.\textsuperscript{15,16} AIBN (analytical grade) was also recrystallized twice from methanol. Benzene (analytical grade) was redistilled before use, while absolute ethanol was used as received. Deionized water was purchased from the Shanghai Institute of Plant Physiology, Chinese Academy of Sciences.

**Polymerizations**

DMA (2g) and various amounts of FX-13 or FX-14 and 20mg AIBN were dispersed in a 50ml capped round-bottomed flask containing 20ml benzene. After purging the solution with 99.99% pure nitrogen for 30min, the flask was placed in an oil-bath at 50°C and the polymerization was continued for 24h. The polymerization was stopped by cooling the mixture to room temperature and exposing it to air. The product was precipitated in diethyl ether and filtered. The dried copolymer was redissolved in 30ml acetone, precipitated in diethyl ether and dried under vacuum at 25°C for 24h. Copolymerization yields determined gravimetrically were quantitative within experimental error.

**Characterization of copolymers**

The comonomer content of the copolymers was determined by anion fluoride chromatography using a Dionex 2100I instrument as reported earlier.\textsuperscript{15} Viscometric measurements were carried out as reported previously.\textsuperscript{15,16} Concentrated stock solutions of the copolymers were prepared with magnetic

### Table 1. Copolymerization of FX-13 and FX-14 with DMA in benzene\textsuperscript{a}

| Sample | FX-13 (3-) or FX-14 (4-) in feed (mol %) | Fluorine content\textsuperscript{b} (wt %) | Comonomer content\textsuperscript{b} (mol %) | $[\eta]$\textsuperscript{c} (dL g\textsuperscript{-1}) | $[\eta]$\textsuperscript{d} (dL g\textsuperscript{-1}) | $K_H$\textsuperscript{c} | $K_H$\textsuperscript{d} | $M_v$\textsuperscript{e} $\times 10^{-6}$
<table>
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<td>POMA</td>
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<td>0.38</td>
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<td>co-3-1</td>
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<td>0.27</td>
<td>0.08</td>
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<td>2.63</td>
<td>0.47</td>
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<td>0.17</td>
<td>1.75</td>
<td>3.17</td>
<td>2.27</td>
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<tr>
<td>co-3-3</td>
<td>0.32</td>
<td>1.10</td>
<td>0.34</td>
<td>1.42</td>
<td>2.60</td>
<td>3.08</td>
<td></td>
<td>1.36</td>
</tr>
<tr>
<td>co-3-4</td>
<td>0.64</td>
<td>1.95</td>
<td>0.62</td>
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<tr>
<td>co-3-5</td>
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<td>3.27</td>
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<tr>
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<tr>
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<td>0.40</td>
<td>0.12</td>
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<td>–</td>
<td>–</td>
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<tr>
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<td>0.21</td>
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<tr>
<td>co-4-4</td>
<td>0.64</td>
<td>1.27</td>
<td>0.40</td>
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<td>3.12</td>
<td>1.02</td>
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\textsuperscript{a} co-3 and co-4 copolymers refer to FX-13 and FX-14 comonomers, respectively.

\textsuperscript{b} Calculated from fluorine content measured by anionic chromatography.

\textsuperscript{c} Measured by capillary viscometry in water at 25°C.

\textsuperscript{d} Measured by capillary viscometry in methanol at 25°C.

\textsuperscript{e} Calculated from $[\eta]$ in methanol with $K = 17.5 \times 10^{-5}$ dL g\textsuperscript{-1}, $a = 0.68$,\textsuperscript{30} expressed in g mol\textsuperscript{-1}.
stirring at least 24h before use. Solutions of the desired concentration were obtained by dilution of appropriate stock solutions with deionized water. The effect of shear rates or temperature was investigated by increasing the shear rate or temperature stepwise.

**Fluorescence measurements**

After dilution of copolymer solutions with deionized water, a small amount of PFOP solution in acetone was added to each sample with a microsyringe to give a final PFOP concentration of 2×10⁻⁶ mol L⁻¹ and an acetone concentration of 0.1 vol%. All samples were sonicated for 15 min and then left for 24h at room temperature before measurement. Steady-state fluorescence measurements were recorded at a wavelength of 340 nm with a Perkin-Elmer LS50 luminescence spectrometer.

**RESULTS AND DISCUSSION**

As shown in Table 1, comonomer FX-13 is essentially quantitatively incorporated into the copolymers. The degree of incorporation of FX-14 into the 4-series copolymers is somewhat lower than observed earlier and this is consistent with the greater steric hindrance of the FX-14 methacrylate during copolymerization.13–17 The actual reactivity ratios of FX-13 and FX-14 with respect to DMA are unknown. However, the reactivity ratios \( r_1 \) and \( r_2 \) of DMA(1) and MMA(2) have been reported to be 0.57 and 2.15 for the solution copolymerization of DMA and MMA.19 Using \( Q \) and \( e \) values for DMA (0.49 and 0.09) and assuming similar \( Q \) and \( e \) values for FX-13 and methacrylate \((Q = 0.42 \text{ and } e = 0.60)\) the calculated reactivity ratios \( r_1 \) and \( r_2 \) for DMA/FX-13 become 1.22 and 0.63, respectively. These values seem to be consistent with the data in Table 1. Thus, the probability for the formation of FX-13 or FX-14 comonomer diads at the low comonomer fractions employed is expected to be close to zero. Given the reaction conditions this would be expected to lead to random comonomer incorporation into the PDMA copolymers.

The reduced viscosity plots in water of samples co-3-1 and co-3-5 having comonomer contents of 0.08 and 1.07, respectively, are shown in Fig 1 along with that of PDMA homopolymer. The plots for the other copolymers are similar and show good linearity below about 0.3 g dL⁻¹. The reduced viscosities of co-3-1 and the homopolymer appear to be quite similar and give roughly the same apparent intrinsic viscosities of about 2.6 dL g⁻¹. The slopes are also similar, with Huggins constants of 0.49 and 0.47 for the PDMA and sample co-3-1, respectively. This similarity indicates that for solutions below 0.5 wt%, the case of co-3-1, hydrophobic association is too small to affect dilute solution viscosities.

However, for samples co-3-2 to co-3-5 the aqueous intrinsic viscosities decrease strongly with increasing perfluorocarbon content. The intrinsic viscosity of 0.38 dL g⁻¹ for sample co-3-5 is almost seven times smaller than that of PDMA homopolymer and co-3-1. However inspection of Table 1 suggests that the aqueous intrinsic viscosities do not reflect molecular weights. Thus the intrinsic viscosities of samples co-3-1 to co-3-5 in methanol, in which hydrophobic association is expected to be absent, are roughly of the same order of magnitude. The intrinsic viscosities indicate viscosity average molecular weights \( (M_v) \) of about 1×10⁶ g mol⁻¹. They are lower than the \( M_v \) values of the emulsion copolymers \((M_v = 2 \times 10^6\)–5×10⁶ g mol⁻¹) prepared in water by ammonium persulfate initiated polymerization of DMA and FX-13 at 50°C.14 However they are higher than that of the AIBN initiated PDMA–FX-13 copolymers \((M_v = 3 \times 10^5\)–7×10⁵ g mol⁻¹) obtained by bulk copolymerization.14 The lower aqueous intrinsic viscosities of co-3-2 to co-3-5 would seem to be consistent with increasingly strong intramolecular association of the perfluorooctyl groups as the comonomer content increases from 0.08 to 1.07 mol%.7

An estimation of the concentration of perfluorocarbon groups within the polymer coils is of interest. For instance, given the intrinsic viscosity of co-3-4 of 0.83 dL g⁻¹, the concentration of DMA units within the coil would be of the order of 0.12 mol% and the concentration of perfluorocarbon groups of 0.62 mol% would then be of the order of 10⁻³ mol L⁻¹. This would be well in excess of the concentration of perfluorocarbon groups \((10^{-4} \text{ mol L}^{-1})\) required for association to occur in the case of polyethylene glycol end-functionalized with perfluorohexyl groups.20 For co-3-5 this intracoil concentration of perfluorocarbon groups would be about 3×10⁻³ mol L⁻¹. Thus the apparent contraction of the coils at higher comonomer concentrations is not surprising.

The Huggins constants of co-3-1 to co-3-5 in water show dramatic increases with increasing perfluorocarbon content. Thus, the Huggins constant of co-3-5 \((R_g = 1.07 \text{ mol%)}) is about 40 times larger than that of
the homopolymer and 10 times that of co-3-2 ($R_F = 0.17 \text{mol%}$). These increases in Huggins constant with increasing comonomer content are similar to that observed for the FX-13 copolymers of N-isopropylacrylamide and are not surprising; however, it should be kept in mind that the Huggins constants are calculated from apparent intrinsic viscosities that are in turn affected by intramolecular association. This would apply particularly to copolymers with higher perfluorocarbon contents. Thus, as the concentration increases, intermolecular association increases, and this may be expected to decrease intramolecular associations and increase the intrinsic viscosities; as a result, the Huggins constants may have been overestimated. However, in this case the increase of intrinsic viscosity with concentration should lead to upwardly sloping reduced viscosities and this is not observed.

The reduced viscosities of 0.5wt% solutions of PDMA and co-3-1, co-3-2, co-3-3, co-3-4 and co-3-5 are 4.1 dL g$^{-1}$, 4.3 dL g$^{-1}$, 5.2 dL g$^{-1}$, 4.5 dL g$^{-1}$, 3.7 dL g$^{-1}$, and 1.9 dL g$^{-1}$, respectively. These viscosities go through a maximum with increasing comonomer content. This was observed previously for the higher molecular weight emulsion PDMA/FX-13 copolymers and for the FX-13 and FX-14 acrylamide copolymers of this type. This behaviour is consistent with the increasing association of progressively contracted coils as the comonomer content increases.

The Brookfield viscosity–concentration profiles of Fig 2 and 3 also indicate that at a given concentration intermolecular association increases as the perfluorocarbon content goes from 0.08 to 1.07mol%. As shown in Fig 2, the increases in viscosity in going from PDMA to co-3-1 are not large and are seen only above about 2.0 g dL$^{-1}$, consistently with the very low perfluorocarbon content of co-3-1. However, the viscosity increases in going from co-3-1 to co-3-2 from co-3-2 to co-3-3 and from co-3-3 to co-3-4 are particularly large, with increases of 1–2 orders of magnitude between each incremental doubling in comonomer content. Note again, that in this case, the viscosity versus comonomer content at a polymer concentration of about 1% gives a maximum at a comonomer content of 0.62 mol% of co-3-4.

Flynn and Goodwin defined a ‘critical hydrophobic comonomer content’ beyond which the number of intermolecular associations increases dramatically as reflected by the measured viscosities. From the above, we estimate this critical hydophobe concentration for the 3-series copolymers to be between 0.10 and 0.20 mol%. As shown in Fig 3, there is an actual viscosity decrease in going from co-3-4 to co-3-5. This is again consistent with the above and earlier data on these systems indicating that the viscosity increases due to increasing intramolecular association caused by greater comonomer content are offset by increasing intramolecular association which eventually dominates as the comonomer content increases.

As expected, the onset of association occurs at lower polymer concentrations as the comonomer content increases. Thus the concentration at which significant association occurs decreases with increasing comonomer content, as shown in Fig 2 and 3. It is unlikely that these effects are strongly correlated with molecular weights as the data in methanol indicate. It is also worth noting that the viscosities of co-3-2–co-3-4 level off at higher concentrations, giving sigmoidal viscosity–concentration profiles. This interesting behaviour has not been observed previously for these systems.

The viscosity versus concentration profiles of the FX-14 copolymers are shown in Fig 4. In this case too, the increases in viscosity with comonomer content are particularly large in going from co-4-1 to co-4-2 from co-4-2 to co-4-3 and from co-4-3 to co-4-4. The effects of increasing intramolecular association at higher comonomer content are again visible because the viscosity of co-4-5 is lower than that of co-4-4 below 2.5 wt%.

It is worth noting that the viscosities of the FX-14 copolymers with a high comonomer content are appreciably lower than those of the FX-13 copolymers. For instance, the viscosity of 1.0 wt% solution of co-3-4 is about 20000 cP at a shear rate of 0.4 s$^{-1}$, whereas the viscosity of a 1.0 wt% solution of co-4-4

Figure 2. Brookfield viscosity as a function of polymer concentration for PDMA and FX-13 copolymers co-3-1 and co-3-2 in water at 25°C (Shear rate=0.36 s$^{-1}$).

Figure 3. Brookfield viscosity as a function of polymer concentration for FX-13 copolymers co-3-3, co-3-4 and co-3-5 in water at 25°C (Shear rate=0.4 s$^{-1}$).
under the same conditions is at least 100-fold lower. Similar effects have been observed for FX-13 and FX-
14 polyacrylamide copolymers. The reason for these
differences is not clear. It is possible that the FX-14
units, having a greater hydrocarbon content and thus
being more lipophilic and hence perhaps less fluoro-
philic, are less effective in promoting association. It is
also possible that there are steric reasons for the lower
apparent hydrophobicity of the FX-14 unit arising
from a lower flexibility of the FX-14 units. This issue
remains to be clarified.

Compared to the PDMA-FX-13 emulsion copoly-
mers synthesized by Xie and Hogen-Esch,14 the
aqueous viscosities of the present 3-series copolymers
are lower at the same comonomer content. For
instance, the solution viscosity of 0.5 wt% solutions
of the FX-13/PDMA emulsion type copolymers with a
comonomer content of 0.10 mol% gives solution
viscosities of about 10000 cP at a shear rate of
0.4 s$^{-1}$, whereas the corresponding copolymers of the
3-series have lower solution viscosities. However, the
present 3-series copolymers are strongly viscosifying,
although at somewhat higher comonomer concentra-
tions. Thus 1 wt% solutions of co-3-4 attain a viscosity
in excess of 10000 cP (Figure 3) whereas the most
strongly viscosifying emulsion PDMA-FX-13 copoly-
mer reaches this viscosity at 0.5 wt%.14 Some of this
difference is probably due to the lower molecular
weights of the present copolymers, as pointed out
above. Furthermore, the emulsion copolymers, even
after repeated precipitation and dialysis, contain small
but significant amounts of surfactants that are difficult
to remove completely. The presence of surfactants has
been documented to increase viscosities dramatically
by micellar bridging.23-27 Thus comparisons are not
straightforward even at the same molecular weights.
As pointed out above, the higher viscosifying power of the
emulsion copolymers having molecular weights
that are roughly three times higher than the present
copolymers is not unexpected because the number of
perfluorocarbon groups per chain, and thus its
tendency to associate with other chains, increases with
chain length. Also at the same copolymer concentra-
tion and the same comonomer content (the overall
solution concentration of R$_f$ groups being identical)
the same degree of intermolecular association of the
perfluorocarbon groups for higher molecular weight
copolymers is expected to give rise to larger copolymer
clusters (also see below). Thus it is possible that the
effect of molecular weight alone could account for the
observed viscosity differences. These molecular weight
effects are better illustrated by the comparison of the
bulk and solution PDMA-FX-13 copolymers, because
surfactant effects are absent. For instance, the viscosity
average molecular weights of the bulk copolymers are
of the order of $2 \times 10^6 - 6 \times 10^6$ g mol$^{-1}$ which is lower
than that of the present copolymers having viscosity
average molecular weights of the order of $1 \times 10^6\n- 2 \times 10^6$ g mol$^{-1}$. For instance, the viscosity of a
5.0 wt% solution of the PDMA bulk copolymer with
an FX-13 content of 0.40 mol% under otherwise
identical conditions was found to be only 450 cP
compared to a value of about 20000 cP for a 3.0 wt%
solution of co-3-3 with an FX-13 content of
0.32 mol%. Therefore, unless undiagnosed and un-
precedented comonomer sequence effects are present,
molecular weight effects are important, and the
present data on the above FX-13/PDMA systems do
not appear to support the presence of blocky co-
monomer sequences proposed for hydrocarbon modi-
fied polacrylamides.9-12

Temperature effects
As shown in Fig 5 solutions of the 3-series copolymers
all show reversible decreases with increasing tempera-
ture, indicating the physical nature of the association
processes. This behaviour is different from that
observed by Xie and Hogen-Esch14 who reported
small (about 30%) viscosity increases of 1.0 wt%
solutions of emulsion PDMA-FX-13 copolymers in
the 30-40°C range followed by viscosity decreases at
higher temperatures. The present co-3-5 suggests this
type of behaviour because its viscosity does not appear
to change between 45 and 50°C. These effects hint at
changes in the balance between inter- and intramol-
ecular hydrophobic association, but their source is not
clear and more work is needed to elucidate these results.

**Shear rate effects**

The viscosity dependence on shear rate is rather complex (see Figs 6–8). Solutions (5wt%) of the homopolymer and co-3-1 show virtually no shear rate dependence. However, solutions of co-3-2 show pseudoplastic behaviour in the range 0–2.0 s$^{-1}$ but little dependence at higher shear rates. For higher comonomer content co-3-3 and co-3-4, an increase of shear rates above 1 s$^{-1}$ gives rise to viscosity increases the rate of increase being much steeper for co-3-4. For co-3-5 a viscosity maximum is observed around 2 s$^{-1}$.

The viscosity of the 4-series copolymers is affected somewhat differently, as shown in Fig 8. Solutions of co-4-1 are almost unaffected by shear rate and thus resemble that of PDMA and co-3-1. With increasing comonomer content, both shear thinning and shear-thickening behaviour were observed. Thus the viscosity of co-4-2 and co-4-3 showed a shallow minimum at about 0.3 s$^{-1}$ and then increased about twofold as the shear rate increased to 12 s$^{-1}$. Co-4-4 behaved somewhat similarly, but in this case the shear thickening was more pronounced. Surprisingly, the rheology of co-4-5 showed only pronounced pseudoplastic behaviour.

From the above, it would appear that the shear thinning and shear thickening behaviour is correlated with the balance between inter- and intramolecular association of the perfluorocarbon groups. In the limit of very low comonomer content there is a shear thinning behaviour that was observed many times for FX-13 and FX-14 acrylamide copolymers. In the following we argue that this balance is affected not only by shear but also by molecular weight. We assume that the Mark–Houwink equation for PDMA homopolymer is applicable to the present copolymers. For unassociated monodisperse copolymers at concentrations below the overlap concentration ($c^*$) the hydrodynamic volume ($V_h$) of one mole of copolymer with a molecular weight $M$ and an intrinsic viscosity $[\eta]$ is given by

$$V_h = [\eta]M = KM^{1+a}$$  \(1\)

where $K$ and $a$ are the Mark–Houwink constants describing the relationship between molecular weight and intrinsic viscosity. The concentration of perfluorocarbon ($R_F$) groups within this volume is given by

$$[R_F] = \frac{N_x}{[\eta]M} = \frac{x}{(mKM^a)}$$  \(2\)

where $N_x$ and $x$ are the number of hydrophobes per mole of chains and the mole fraction of hydrophobes in the chain, respectively, and $m$ is the mass per monomer unit. From eqn (2), at a constant value of $x$ the concentration of hydrophobic groups within the domain of the coil and thus intramolecular association will decrease with increasing molecular weight (proportional to $M^{-a}$). For example for a Mark–Houwink $a$ value of 0.81, indicated for PDMA in water, a tenfold increase of MW will decrease the $[R_F]$ value by a factor of about seven. This predicts that small coils will be collapsed to a much larger degree than large coils with the same comonomer content. This association mediated intramolecular collapse is expected to lead to a further increase in effective $R_F$ concentration.
Thus in the case of very high molecular weight copolymers, the balance between inter- and intramolecular association would be shifted to intermolecular association. Hence, in this case predominantly pseudoplastic behaviour is plausible.

In the case of the present PDMA copolymers, the MW of which is about one order of magnitude lower than that of the emulsion PDMA copolymers, intramolecular association is expected to be much more important. This would explain why for the lower molecular weights of the present copolymers effective association requires an increased $R_F$ content compared with higher molecular weight copolymers. However, this increase is expected to lead to further chain contraction caused by intramolecular association. The shear induced stretching of the chains is expected to disrupt intramolecular association, leading to increasing concentrations of free $R_F$ groups available for intermolecular association. This could account for shear thickening. At higher comonomer content this shear induced disruption may begin to become more important, and this is consistent with what is observed for co-3-3 and co-3-4. Because of its higher comonomer content, this effect would be expected to be more important for co-3-4 where the increase in shear rate from $1.0$ to $2.0 \text{ s}^{-1}$ gives rise to a viscosity that is about an order of magnitude higher than for co-3-3. For co-3-2 the effect may be obscured, but it is interesting that between about 2 and $8 \text{ s}^{-1}$ there is little change in viscosity. For co-3-5 the viscosity increase with shear is indeed even larger but is only visible over a very small shear rate interval ($0.4$ to about $2 \text{ s}^{-1}$). Above a shear rate of about $2 \text{ s}^{-1}$ the intermolecular assemblies in this case are apparently large enough to be pulled apart by shearing and the solutions become pseudoplastic. A similar rationale has been advanced by Candau and co-workers\textsuperscript{6,7} to account for the shear thickening behaviour of hydrophobically modified polyacrylamides. The 4-series copolymers show predominantly pseudoplastic behaviour (Fig 8). The reason for this difference is not clear, but it may be linked to the higher copolymer concentrations shifting intramolecular to intermolecular association.

Fluorescence studies

In studies of the hydrophobic association of hydrocarbon modified polymers, pyrene is a widely used probe.\textsuperscript{28} Fluorocarbon microdomain formation has been studied only recently by fluorescence, using PFOP which was shown to have a strong affinity for the perfluorocarbon domains formed by copolymer assembly and is therefore a useful probe for fluorocarbon association.\textsuperscript{15,16,29}

Figure 9 shows the emission spectra of PFOP ($2 \times 10^{-6} \text{ mol L}^{-1}$) in solutions of co-3-4 in the $0.32$ to $10.0 \text{ g dL}^{-1}$ concentration range. At low polymer concentration (spectra a and b), the fluorescence spectrum is characteristic of self-aggregation of PFOP in water, ie a weak ‘monomer’ band with a maximum at $373 \text{ nm}$ without fine structure and a strong broad band around $530 \text{ nm}$ associated with excimer emission. Above a polymer concentration of about $1 \text{ g dL}^{-1}$ the monomer emission intensity increases considerably, and near-UV fine structure is visible with maxima at $373, 390$ and $410 \text{ nm}$. The near-UV emission increases and the relative intensity of the excimer emission decreases with increasing polymer concentration, and almost disappears at the highest polymer concentration. These changes coincide with a sharp increase in viscosity above about $1 \text{ g dL}^{-1}$ due to intermolecular association (Fig 3). It seems likely, therefore, that the emission increase is due to interpolymer association. For co-3-4 at a concentration of $1 \text{ g dL}^{-1}$ the concentration of DMA units is of the order of $0.10 \text{ mol L}^{-1}$, and with a comonomer content of $0.62 \text{ mol\%}$ the concentration of $R_F$ groups is about $6.2 \times 10^{-4} \text{ mol L}^{-1}$. The number of $R_F$ groups per interpolymer micelle is not known, but assuming this to be equal to about $10$ to $100$ the estimated order of magnitude of both inter- and intramolecular micelles would be of the order of $6 \times 10^{-2}$ to $6 \times 10^{-6} \text{ mol L}^{-1}$. Thus even complete PFOP partitioning into the micelles would not give more than one PFOP group per micelle and is consistent with the virtual absence of excimer emission in the more concentrated solutions of co-3-4.

As shown in Fig 9, below about $1 \text{ g dL}^{-1}$ of co-3-4 there is no noticeable increase in near-UV emission. This is of interest because the low intrinsic viscosity ($0.83 \text{ dL g}^{-1}$) of this copolymer (Table 1) hints at significant intramolecular micellization (see above). At an average molecular weight of about $1 \times 10^{6} \text{ g mol}^{-1}$, the average number of perfluorocarbon groups per chain is about six. Thus, either the size or concentration of these micelles is too small to allow micellar partitioning of the PFOP probe.

Figures 10 and 11 show the monomer emission intensity ($I_m$) and the ratio of monomer to excimer emission ($I_m/I_e$) as a function of concentration of co-3-2 to 3-3, 3-4, and co-3-5. For the case of co-3-2, $I_m$ and $I_m/I_e$ are almost concentration independent below about $3 \text{ g dL}^{-1}$, but at higher comonomer contents
these quantities increase with concentration, especially for co-3-4 and co-3-5. These increases appear to reflect the partitioning of PFOP from the aqueous to the hydrophobic regions of the perfluorocarbon micellar domains. As shown in Fig 11, co-3-5 with a higher comonomer content than co-3-4 actually gives a lower monomer/excimer ratio. This observation would track the corresponding viscosity versus concentration plot of co-3-4 and co-3-5 (Fig 3) and would thus be consistent with intermolecular association being the primary factor in the increases in PFOP emission with polymer concentration. We estimate the approximate critical association concentration (CAC) by intersection of two straight line segments through the data points at low concentration in the rapidly rising portion of the curves. The resulting CAC values for co-3-3, co-3-4 and co-3-5 were found to be 1.4 g dL$^{-1}$, 1.3 g dL$^{-1}$ and 0.9 g dL$^{-1}$ respectively.

It should be noted that the greater PFOP partitioning into the micelles at higher polymer concentration would also be driven by higher micelle concentrations. Thus, even for the case of intramolecular micelles, the concentration of these micelles should increase with increasing copolymer concentration so that greater PFOP partitioning into the intramolecular micelles is expected.

CONCLUSIONS

Copolymers of fluorocarbon containing acrylates (FX-13) or methacrylates (FX-14) and $N,N$-dimethylacrylamides were synthesized by copolymerization in benzene and were systematically studied by viscometry and fluorescence using 1-perfluoro-octanoyl pyrene. The results indicate the occurrence of mainly intramolecular association below a concentration of about 0.50 g dL$^{-1}$. In semidilute solution, viscosities increase dramatically when the concentration exceeds a critical value, and this increase becomes more significant with increasing comonomer content, indicating strong intermolecular hydrophobic association between fluorocarbon groups. Copolymer viscosities are shown to decrease with increasing temperature. The copolymers also display complex shear-dependent behaviour. Copolymers with a lower comonomer content show pseudoplastic behaviour. Copolymers containing a greater comonomer content are shear thickening. For the case of co-3-5 with the highest comonomer content a maximum appears in its viscosity–shear-rate curve. FX-14 copolymers generally show the same behaviour as that of FX-13 modified PDMA, but co-4-5 having the greatest comonomer content shows only pseudoplastic behaviour.

Association is also demonstrated by monomer emission (373 nm) increases and excimer emission (530 nm) decreases with both comonomer content and copolymer concentration. Thus, plots of $I_{373}$ and $I_{373}/I_{530}$ versus copolymer concentration rise sharply as the polymer concentration is increased above a critical value which decreases with increasing comonomer content.

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