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Poly(*N*,*N*-dimethylacrylamide)s with Perfluorocarbon Pendent Groups Connected through Poly(ethylene glycol) Tethers Give Physical Gels in Organic Solvents

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ABSTRACT: The synthesis is reported of copolymers of *N*,*N*-dimethylacrylamide (DMA) and methacrylates containing 1,1-dihydroperfluorononyl groups separated from the methacrylate by long PEG tethers (between 1000 and 14 000 Da). The copolymers with macromonomer contents of 1 mol % or less give gels in organic solvents such as dioxane, THF, or methanol, as well as in water, at copolymer concentrations between 1 and 8 mol %. Copolymer gel formation is enhanced in the presence of longer PEG tethers and higher comonomer contents and copolymer concentrations. These factors also increase polymer association, as indicated by steady shear viscosities. This is consistent with fluorophilic association mediated by liquid crystalline domains involving very small numbers of perfluorocarbon groups.

Introduction

Hydrophobically modified (HM) associating polymers have attracted interest due to their unique rheological properties.[1−12] In particular, water-soluble vinyl copolymers formed by radical copolymerization of water-soluble monomers and hydrophobic but dispersable comonomers have been the subject of extensive studies.[5−10]

Substitution of hydrocarbon with C-7 or C-8 perfluorocarbon groups has resulted in HM polymers with much stronger fluorophilic association and greater surface activities compared with the corresponding hydrocarbon groups.[10−16] Thus, well below the critical concentration, which is on the order of the inverse of the intrinsic viscosity and above which polymer coils will begin to overlap, these copolymers tend to associate strongly but reversibly through hydrophobic/fluorophilic interactions. Thus, in aqueous media and often below the critical polymer concentration, these copolymers tend to associate strongly but reversibly through hydrophobic/fluorophilic interactions. The resulting large polymer clusters give rise to viscosity increases that are much greater than those for the corresponding HM polymers with pendent hydrocarbon groups with the same carbon number.[10−12] Furthermore, the perfluorocarbon content, optimized for efficient association, is lower than that of similar hydrocarbon-modified copolymers.

Hydrophilic poly(ethylene glycol) (PEG) “tether” groups between the pendent hydrophobic groups and the main chain have been shown to promote the formation of hydrophobic domains. For instance, this was demonstrated for hydrophilic polymers with hydrocarbon[9,17,18] and perfluorocarbon (RF)[12,19] pendent groups. Thus, polyacrylamide copolymers having acrylate units with C_7F_{15} or dodecyl pendent groups linked through oligoethylene oxide tethers show 10−50-fold increases in association when the tether lengths were increased from zero to three EO units. This was proposed to arise from entropic effects through decoupling of the motions of the associated hydrophobic groups and the hydrophilic chains.[12] However, although 10-fold increases were observed by insertion of a single EO unit, the effect of increasing the number of EO units from one to three was rather small, with viscosities increasing 3- to 5-fold. Thus, it seemed to be of interest to examine such effects for much longer PEG tether chains.

Here we report that poly(*N*,*N*-dimethylacrylamide) (PDMA) copolymers[20,21] having pendent 2,2′-dihydroperfluorodecanoyl groups connected to the polymer backbone via poly(ethylene glycol) chains having between 23 and 336 EO units, surprisingly, associate strongly not only in water but in organic solvents such as dioxane, benzene, methanol, and THF and other organic solvents.[22] For instance, in dioxane, strong interpolymer association is shown by steep viscosity−concentration profiles, with association occurring at concentrations well below 0.1 g/dL for some copolymers. At higher polymer concentrations (as low as 5 wt %) gels are formed that are capable of dissolving by incremental addition of small amounts of dioxane. Furthermore, as shown by the viscosity versus concentration profiles and rheology data, the copolymers with longer PEG tethers give stiffer gels confirming stronger association. Some of these gels are surprisingly robust with high elastic moduli (see below). To our knowledge, this is the first report of gels formed in organic solvents exclusively through association of pendent perfluorocarbon groups.[22]

Experimental Section

The comonomer, 2-(*N*-ethylperfluorooctanesulfonamido)ethylacrylate (FOSA) donated by the 3M Co. was recrystallized in ethanol (mp 36−42 °C). The synthesis and characterization of macromonomers **1**−**4** (Scheme 1) was carried out by potassium *N*,*N*-dimethylsilyl amide-initiated anionic polymerization of ethylene oxide in THF at room temperature.[23] This was followed by reaction with methacrylic anhydride, deprotection of the *N*,*N*-dimethylsilylamino group, and reaction with 1,1-dihydroperfluorodecanoyl chloride as shown in Scheme 1. Thus, a typical EO polymerization was carried out under high vacuum in a 50 mL polymerization flask by introduction from an ampule of 2 mL of a 0.5 M. solution (1 mmol) of potassium bis(trimethylsilyl)amide (BTMSAK) in toluene followed by evaporation of toluene and introduction of EO (136 mmol) dissolved in 20 mL of THF. The MW of PEG was controlled by the molar ratio of ethylene oxide and BTMSAK. The

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Scheme 1. Structure of FOSA and Synthesis of R_F-PEG Macromonomers 1−4

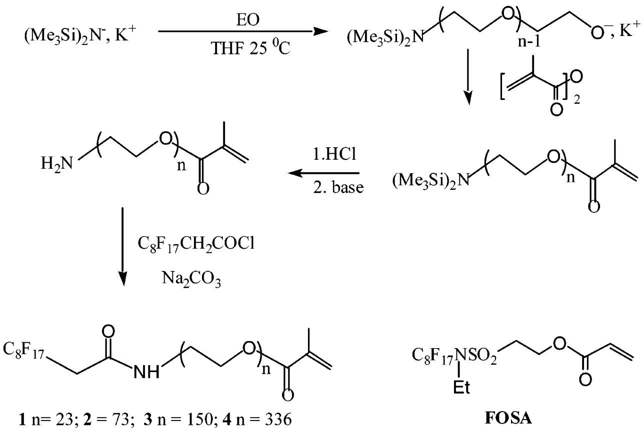

Table 1. R_F-PEG Macromonomer Synthesis

sample code[a]	reaction time (h)	M_n[b] ($\times 10^{-3}$) (calc)	M_n[c] ($\times 10^{-3}$)	M_n[d] ($\times 10^{-3}$)	MWD[d]
FPEG1K	48	1.0	1.0	1.0	1.17
FPEG3K	48	3.0	3.0	3.2	1.22
FPEG6K	48	6.0	6.5	6.6	1.14
FPEG14K	72	14.0	14.5	14.8	1.12

[a] 1K, 3K, 6K, and 14K refer to approximate molecular masses of the PEG tethers. [b] From the EO/initiator molar ratio. [c] By ^{1}H NMR integration (see text). [d] By SEC using PEG standards.

polymerization solution was stirred at 20 °C for 48 h (72 h for FPEG14K, Table 1) followed by addition of 0.23 g (1.5 equiv, 1.5 mmol) of methacrylic anhydride for 4 h at 0 °C and 15 h more at room temperature. The reaction mixture was treated with 1 mL of 1.0 M HCl for 4 h to deprotect the trimethylsilyl group, and the macromonomer intermediate was precipitated in a 20-fold excess of diethyl ether (DEE), washed with diethyl ether, and dried in vacuo.

Five grams of this amino end functionalized methacryloyl PEG (PEG1K, 5 mmol) was then reacted with 3.72 g (1.5 equiv) of 2,2′-*H*,*H*-perfluorooctanoyl chloride[24] in the presence of 2.5 g (5 equiv) of Na_2CO_3 in dicholomethane for 3 h. The reaction mixture was then filtered and precipitated in a 20-fold excess of diethyl ether and dried in vacuo. Proton NMR (500 MHz, $CDCl_3$) gave the following chemical shifts: δ (ppm) 6.1−5.5 (2H, s, $CH_2{=}C{-}$), 4.3 (2H, t, $-CO-O-CH_2-$), 3.6 (92−1272H, m, $(CH_2CH_2O)_n$), 3.2 (2H, t, $-NH-CO-CH_2-$), 1.9 (3H, s, $-CH_3$). ^{19}F NMR (500 MHz, $CDCl_3$) δ (ppm): −81.2 (3F, $-CF_3$), −112.3 (2F, $-CF_2-CH_2-CO-$), −122, −127 (12F, $-(CF_2)_6-$).

Copolymerizations in dioxane were carried out with 0.5 g of DMA (5.0 mmol) and varying amounts (0.25−1.0 mol %) of the R_F-PEG macromonomer dissolved in dioxane and were initiated by AIBN (0.1 g) in a round-bottomed flask (25 mL) capped with a rubber septum at 60 °C. Using two syringe needles as gas inlet and outlet, a stream of ultrapure grade argon (99.99%) was introduced into the flask for 30 min to remove oxygen. The flask was then placed in a mineral oil bath kept at 60 °C, and the polymerization was allowed to proceed at 60 °C for 24 h. The polymerizations were terminated by opening the flask to the air. Homopolymerizations were carried out in a similar manner.

The ^{19}F NMR spectra were recorded on a Bruker AMX-500 FT-NMR spectrometer operating at 500 MHz in $CDCl_3$ at 30 °C. The chemical shifts of ^{19}F signals are referenced to $CFCl_3$. The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-500 FT-NMR spectrometer operating at 500 MHz in $CDCl_3$ at 30 °C. The compositions of the copolymers was determined by proton NMR integration of the PEG and the DMA methyl groups at 3.65 and 2.8−3.3 ppm, respectively. The compositions of the FOSA copolymers (FOSA-025) were determined by ^{19}F NMR using CF_3CH_2OH as internal standard.

Table 2. Copolymerization of DMA and R_F-PEG Macromonomers at 60 °C in Dioxane

sample[a]	comonomer (mol %) calcd	comonomer (mol %) obsvd[b]	R_F content (wt %)	M_w[c] ($\times 10^{-4}$)	MWD[c]
PDMA	0	0	0	9.3	3.13
1K-025	0.25	0.33	1.3	5.7	2.43
3K-025	0.25	0.28	1.1	10.5	3.39
6K-025	0.25	0.29	1.0	7.9	2.71
14K-025	0.25	0.30	0.9	8.1	2.52
FOSA-025	0.25	0.23[d]	1.0	8.3	3.31
1K-100	1.00	0.95	3.5	10.7	3.06
6K-100	1.00	*e*	*e*	*e*	*e*
14K-100	1.00	*e*	*e*	*e*	*e*

[a] 1K, 3K, 6K, and 14K refer to the M_n of PEG tethers in R_F-PEG macromonomers; the last three digits divided by 100 give the comonomer content in mole percent. [b] From ^{1}H NMR; see Experimental Section. [c] Determined by SEC in THF/MeOH/Et_3N using PS standards; see Experimental Section. [d] From ^{19}F NMR; see Experimental Section. [e] Insoluble gels.

SEC measurements were performed on a Waters high-pressure liquid chromatography system consisting of a Water 600E multisolvent delivery system, a PLgel 10 μm precolumn filter (Polymer Laboratories), three columns connected in series with 10 μm particle size and 500, 10^4, and 10^6 Å pore sizes (Plgel, Polymer Laboratories), and a Water 410 differential refractometer. Molecular weights of polymers were determined by SEC measurements in THF (macromonomers) or THF/methanol/triethylamine (85/10/5) mixtures (copolymers) at 35 °C using PEG and PS standards, respectively.

Brookfield and capillary viscometry measurements were carried out as reported elsewhere.[11,12,20] The rheology of the copolymers was measured on a Carri-Med CSL^{2}100 controlled stress rheometer using a 4 cm, 1.59° cone and plate. Oscillatory flow measurements were conducted to obtain the dynamic viscoelastic properties. All experiments were performed within the linear viscoelastic regime, where the dynamic storage modulus (G') and loss modulus (G'') are independent of applied stress. Minimum concentrations needed for gel formation ($C_{\min}$) were determined by repeating copolymerizations in 1 g/dL increments until gel formation was found to occur.

Results and Discussion

Macromonomers **1**−**4**, having PEG number average molecular weights (MWs) of about 1000, 3000, 6000, and 14 000, respectively, were synthesized by the potassium bis(trimethylsilyl)amide (BTMSAK) initiated anionic polymerization of EO as reported by Yokayama et al.[23] This was followed by reaction with methacrylic anhydride, deprotection of the *N*,*N*-dimethylsilylamino group, and reaction with 1,1-dihydroperfluorodecanoyl chloride as shown in Scheme 1. The macromonomers were isolated by precipitation in diethyl ether and dried in vacuo. The SEC MWs determined in THF using PEG standards corresponded well with the MWs calculated from the EO/initiator ratio (Table 1), and the structures were supported by ^{1}H NMR and ^{19}F NMR (Table 1).

The copolymer samples are indicated by the approximate MW of the PEG tether (i.e. 1K refers to PEG tether with a number average MW of 1000) followed by three digits indicating the macromonomer molar content in mole percent multiplied by 100 (Table 2). Thus, 6K-025 is the copolymer made in dioxane containing 0.25 mol % of the R_F-PEG comonomer having a PEG tether with a number average MW of 6000.

To avoid complications from comonomer micellization in water, copolymerizations of DMA and macromonomers **1**−**4** at various total monomer/comonomer concentrations between 1 and 12 wt % were initiated with AIBN in dioxane.[2−9] Copolymerization yields, determined gravimetrically, were quantitative. (Table 2).

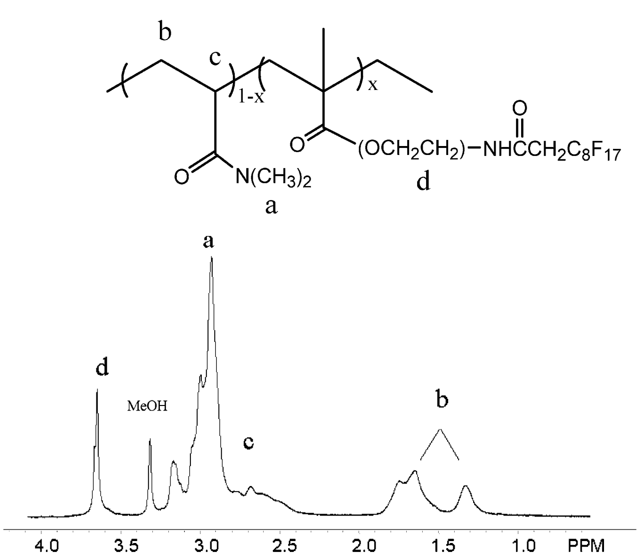

Figure 1. ^1H NMR spectrum (500 MHz) of 3K-025 in CD_3-OD.

As shown in Figure 1 the proton NMR spectrum of copolymer 3K-025 shows the PEG methylenes at 3.65 ppm and a dimethylamino multiplet of the PDMA backbone at 2.8−3.2 ppm with the fine structure due to PDMA stereochemistry.[21] The methine and methylene protons are seen at 2.4−2.8 and at about 1.3−1.8 ppm, respectively. The resonances between 1.3 and 3.2 and at 3.65 ppm were used to calculate the comonomer contents (estimated error of about 10%) and were in reasonable agreement with the calculated values, indicating near quantitative macromonomer conversions, and thus consistent with gravimetry.

Apparent SEC weight average MWs, determined in THF/MeOH/Et_3N using polystyrene standards, were found to be between 50 000 and 110 000 and are on the same order of magnitude as that of the PDMA homopolymer, consistent with the absence of copolymer association during SEC elution. The absence of association in THF under SEC elution conditions was also shown by the fact that the elution volumes were independent of the amounts of injected polymer. From the copolymer mass, the volume of the injection loop, and the elution volume interval, these concentrations were estimated to be between 5 and 20 mg/L.

Surprisingly, at concentrations of between 1 and 8 wt % the copolymerizations of macromonomers **1**−**4** in dioxane and in several other organic solvents gave gels. This was not seen for the PDMA/FOSA copolymers. The approximate minimum concentrations (C_{min}) at which gelation was observed empirically sharply decreased with increased comonomer content and tether lengths for the 1K, 3K, and 6K comonomers (Figure 2). Several of these gels, especially at the lower copolymer concentrations, could be dissolved by multiple additions of small amounts of dioxane, indicating that the cross-linking was physical.

The apparent reduced viscosity versus concentration plots of the copolymer of 1K-025 (0.25 mol % of comonomer **1**) in dioxane and that of the PDMA homopolymer in this solvent were essentially identical (Figure 3). However, at the same comonomer molar content, the reduced viscosity and Brookfield viscosity plots of PDMA copolymers 3K-025, 6K-025, and 14K-025 in dioxane indicate greatly enhanced association (Figure 3a and b)-with increased tether lengths. The increases in the reduced (Figure 3a) and Brookfield (Figure 3b) viscosities of the 6K-025 compared with the 3K-025 copolymer are especially pronounced. Thus, the Huggins constants for copolymers 3K-025 and 6K-025, estimated from the slopes of the reduced viscosity plots assuming an intercept equal to that of the homopolymer, were about 2.0 and 30.0, respectively, with both being far in excess of that found for the homopolymer. Copolymer 14K-025 shows an especially strong association in dioxane, even below 0.05 g/dL. This is all the more remarkable, as perfluorocarbon contents at constant molar content of the comonomer decrease somewhat with increasing PEG lengths.

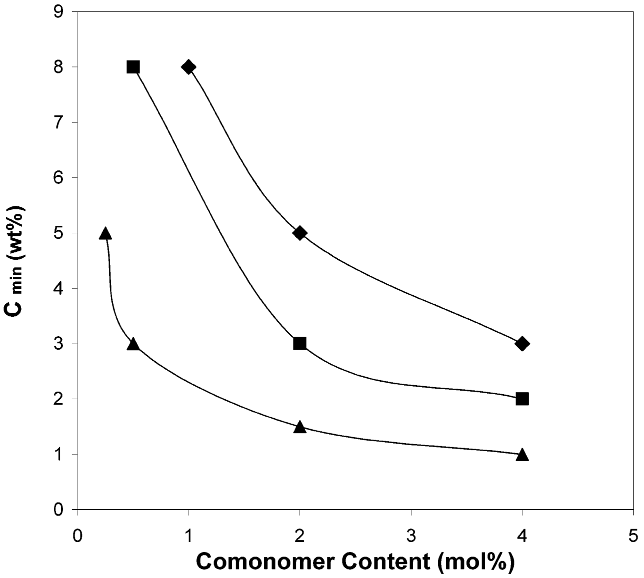

Figure 2. Effect of comonomer tether lengths on the minimum polymer concentration at which gelation occurs (C_{min}) in dioxane: 6 K (▲); 3 K (■); 1 K (◆).

At 12 g/dL the 6K-100 and 14K-100 copolymers formed relatively stiff and highly elastic gels in dioxane, indicating a high density of mechanically active network junctions, that is, the perfluorocarbon aggregates that are active in interpolymer cross-linking (see below). Lower concentrations (<1 wt %) gave viscous solutions.

Figure 4 shows the storage (G') and loss (G'') moduli of polymer gels measured within the linear viscoelastic regime. The G' curves are rather flat and have higher values than the G'', and both moduli increase with increasing PEG tether length, indicating greater densities of mechanically active junctions (Figure 4). As shown in Figure 2, the lowest concentrations at which gel formation is observed decrease with increasing comonomer contents. To our knowledge the above appears to be the first case of a hydrophilic polymer where gel formation is due to tether-mediated interpolymer perfluorocarbon/solvophobic interactions.[22]

The above DMA copolymers of **1**−**4**, moreover, show association at very low RF contents in solvents such as benzene, dioxane, THF, and methanol. For instance, as shown in Figure 3a, the 6K-025 and 14K-025 copolymers show significant association in dioxane at concentrations below about 0.05 g/dL, corresponding to RF concentrations on the order of about 1×10^{-5} M. In water, similar but somewhat lower limiting concentrations are observed that are of the same order of magnitude as those reported for C_7F_{15} end-capped PEGs (MW of 5000).[25,26] In this case, the association at these very low concentrations was shown to be dimeric in the 10^{-3} to 10^{-5} M

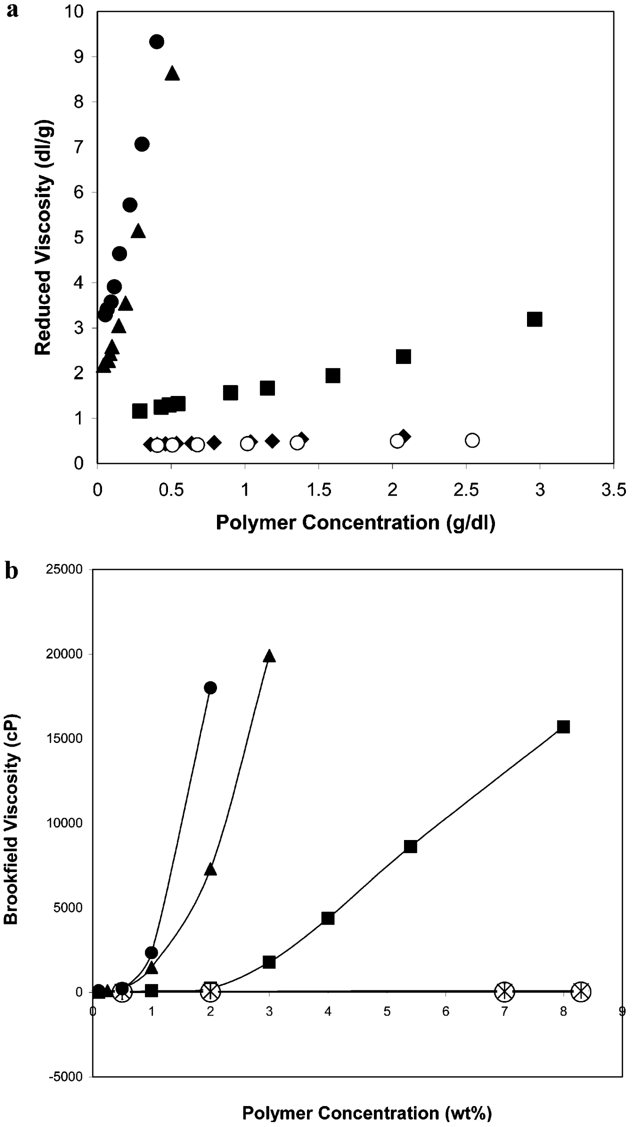

Figure 3. Effect of PEG lengths on reduced viscosity (a) and Brookfield viscosity at 0.6 s^{-1} (b) of PDMA-D and D-025 copolymers at 25 °C in dioxane: PDMA (○); FOSA-025 (∗); 1K-025 (◆); 3K-025 (■); 6K-025 (▲); 14K-025 (●).

range. Given the extraordinarily low RF contents of the D-025 copolymers that correspond to only 1−3 RF units per chain, the data are also consistent with a dimeric association in the present case. Larger numbers of RF groups per junction are possible at higher concentrations.

The important role of the long tethers is surprising, as the RF content of the copolymers at constant comonomer content undergoes a slight relative decrease with increasing tether lengths. The enhanced association in the presence of longer PEG tethers is probably not caused by decoupling of the motions of the RF and that of the main chain proposed earlier for much shorter PEG tethers.[12] It is more plausible that the long tethers mitigate the excluded volume effects that are expected to hinder the formation of intercoil association. The association of the terminal RF groups may also be favored by the incompatibility of PDMA and PEG that should favor the formation of interpolymer PEG domains.[27] The concentration of the RF groups in these domains should be increased accordingly. The strong perfluorocarbon-mediated association in organic solvents would appear to be consistent with the formation of very small, possibly liquid crystalline domains, given the very low numbers of RF groups/chain.[28−35] The associations in organic solvents, judged by the viscosity−concentration profiles, are only somewhat weaker than those in water.[36] The low mobilities of the RF groups in the viscous dioxane solutions or gels are also consistent with broad fluorine-19 resonances that are somewhat wider in water than in organic solvents.

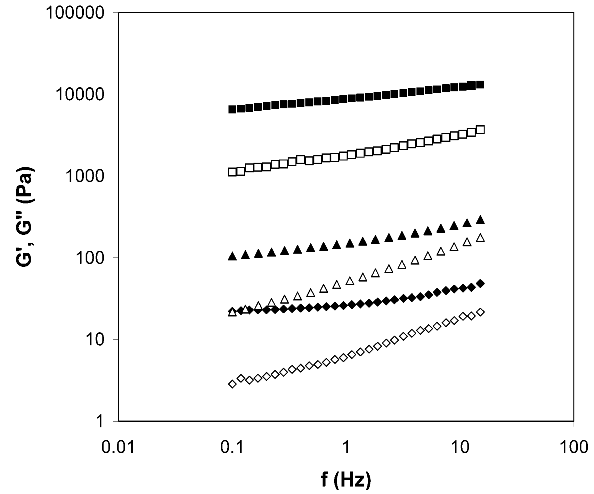

Figure 4. Storage (G', closed symbols) and loss (G'', open symbols) moduli of PDMA-D and D-100 copolymers at 12.0 wt % in dioxane at 25 °C: 1K-100 (◆, ◇); 6K-100 (▲, △); 14K-100 (●, □).

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References and Notes

(1) *Hydrophilic Polymers, Performance with Environmental Acceptance*; Glass, J. E., Ed.; Advances in Chemistry Series 240; American Chemical Society: Washington, DC, 1996.

(2) *Polymers as Rheology Modifiers*; Schulz, D. N., Glass, J. E., Eds.; ACS Symposium Series 462; American Chemical Society: Washington, DC, 1991.

(3) McCormick, C. L.; Bock, J.; Schulz, D. N. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1989; Vol. 17, p 730.

(4) *Polymers in Aqueous Media: Performance through Association*; Glass, J. E., Ed.; Advances in Chemistry 223; American Chemical Society: Washington, DC, 1989.

(5) Chang, Y.; Lochhead, R. Y.; McCormick, C. L. *Macromolecules* **1994**, *27*, 2145.

(6) (a) Candau, F.; Regalado, E. J.; Selb, J. *Macromol. Symp.* **2000**, *150*, 241. (b) Candau, F.; Selb, J. *Adv. Colloid Interface Sci.* **1999**, *79*, 149.

(7) (a) Lundberg, D. J.; Glass, J. E.; Eley, J. E. *J. Rheol.* **1991**, *35*, 1255. (b) Dualeh, A. J.; Steiner, C. A. *Macromolecules* **1991**, *24*, 112. (c) Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 912. (d) Tae, G.; Kornfield, J. A.; Hubbell, J. A.; Johannsmann, D.; Hogen-Esch, T. E. *Macromolecules* **2001**, *34*, 6409.

(8) (a) Yekta, A.; Duhamel, J.; Brochard, P.; Adiwidjaja, H.; Winnik, M. A. *Macromolecules* **1993**, *26*, 1829. (b) Kopperud, H. M.; Hansen, F. K.; Nystrom, B. *Macromol. Chem. Phys.* **1998**, *199*, 2385. (c) Nilsson, S.; Thuresson, K.; Hansson, P.; Lindman, B. *J. Phys. Chem. B* **1998**, *102*, 7099.

(9) Schulz, D. N.; Kaladas, J. J.; Maurer, J. J.; Bock, J.; Pace, S. J.; Schulz, W. W. *Polymer* **1987**, *28*, 2110.

(10) Zhang, Y.-X.; Da, A.-H.; Hogen-Esch, T. E. *New Fluorocarbon-Containing Hydrophobically-Associating Polyacrylamide Copolymers*; ACS Symposium Series No. 467: Water-Soluble Polymers; Shalaby, S., McCormick, C. L., Butler, G. B., Eds.;

American Chemical Society: Washington, DC, 1991; Chapter 10, pp 159−174.

(11) (a) Zhang, Y.-X.; Da, A.-H.; Butler, G. B.; Hogen-Esch, T. E. *J. Polym. Sci., Polym. Lett.* **1990**, *28*, 213. (b) Zhang, Y.-X.; Da, A.-H.; Hogen-Esch, T. E.; Butler, G. B. *J. Polym. Sci., Chem. Ed.* **1992**, *30*, 1383.

(12) Hwang, F. S.; Hogen-Esch, T. E. *Macromolecules* **1995**, *28*, 3328.

(13) Su, Z.; McCarthy, T. J.; Hsu, S.; Stidham, H. D.; Fan, Z.; Wu, D. *Polymer* **1998**, *19*, 4655.

(14) Berlinova, I, V.; Nedelcheva, A. N.; Samichikov, V.; Ivanov, Y. *Polymer* **2002**, *43*, 7243.

(15) Riess, J. *Tetrahedron* **2002**, *58*, 4113.

(16) Zhou, H.; Song, G.-Q.; Zhang, Y.-X.; Chen, J.; Jiang, M.; Hogen-Esch, T. E.; Dieing, R.; Ma, L.; Haeussling, L. *Makromol. Chem. Phys.* **2001**, *202*, 3057.

(17) Noda, T.; Hashidsume, A.; Morishima, Y. *Macromolecules* **2001**, *34*, 1308.

(18) Tam, K. C.; Farmer, M. L.; Jenkins, R. D.; Bassett, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 2275.

(19) Zhang, Y.-X.; Liu, S.; Du, L.; Zhuang, D.; Chen, J.; Jiang, M.; Hogen-Esch, T. E.; Wu, S.; Swift, G. *J. Appl. Polym. Sci.* **2002**, *84*, 1035.

(20) Xie, X.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 1734.

(21) Xie, X.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 1746.

(22) There has been a report of gel formation in perfluorocarbon end-capped telechelic poly(AMPS) or similar copolymers of AMPS with hydrocarbon or vinylsilane comonomers: Sawada, H.; Katayama, S.; Nakamura, Y.; Kawase, T.; Hayakawa, Y.; Masanori, B. *Polym. Commun.* **1998**, *3*, 743.

(23) Yokoyama, M.; Okano, T.; Sakurai, Y. *Bioconjugate Chem.* **1992**, *3*, 275.

(24) Achilefu, S.; Mansuy, L.; Selve, C.; Thiebaut, S. *J. Fluorine Chem.* **1995**, *70*, 19.

(25) Zhang, H.; Pan, J.; Hogen-Esch, T. E. *Macromolecules* **1998**, *31*, 2815.

(26) Hogen-Esch, T. E.; Zhang, H.; Xie, X. In *Associative Polymers in Aqueous Solutions*; ACS Symposium Series Vol. 765; Glass, J. E., Ed.; American Chemical Society: Washington, DC, 2000; Chapter 11, pp 179−203.

(27) Da, J.; Hogen-Esch, T. E. Unpublished results.

(28) Volkov, V. V.; Plate, N. A.; Takahara, A.; Kajiyama, T.; Amaya, M.; Murata, Y. *Polymer* **1992**, *33*, 1316.

(29) Percec, V.; Lee, M. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 723.

(30) Wilson, L. M.; Griffin, A. C. *Macromolecules* **1994**, *27*, 1928.

(31) Beyou, E.; Babin, P.; Bennetau, B.; Dunogues, J.; Teyssie, D.; Boileau, S. *J. Polym. Sci., Part A: Chem. Ed.* **1994**, *32*, 1673.

(32) Krupers, M.; Moller, M. *Macromol. Chem. Phys.* **1997**, *198*, 2163.

(33) Wang, J.; Ober, C. K.; Kramer, J. E. *Macromolecules* **1997**, *30*, 1906.

(34) Bracon, F.; Guittard, F.; Taffin de Givenchy, E.; Cambon, A. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4487.

(35) Xiang, M.; Li, X.; Ober, C. K.; Char, K.; Genzer, J.; Sivaniah, I.; Kramer, E. J.; Fischer, D. A. *Macromolecules* **2000**, *33*, 6106.

(36) Da, J.; Hogen-Esch, T. E. Submitted for publication.

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