Phase separation phenomena in aqueous solutions of amphiphilic poly(ethylene oxide) star polymers

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Three- and four-armed star polymers with poly(ethylene oxide) arms capped with hydrophobic end-groups were synthesized from nonylphenoxypoly(ethylene glycol)s and well defined tri- and tetraisocyanates. The latter were hydrosilylation products of *m*-isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI). In aqueous solution the arm ends associate, and above a critical star concentration the mixture phase separates into a dilute phase and a condensed gel phase. Their respective polymer concentrations remain constant as long as the two phases coexist, their volume fractions being proportional to the total polymer concentration. Brookfield viscosity measurements confirm the formation of the gel phase which resembles an amphiphilic hydrogel. It exhibits a high affinity for hydrophobic compounds.

(Keywords: amphiphilic star polymers; poly(ethylene oxide); associative polymers)

INTRODUCTION

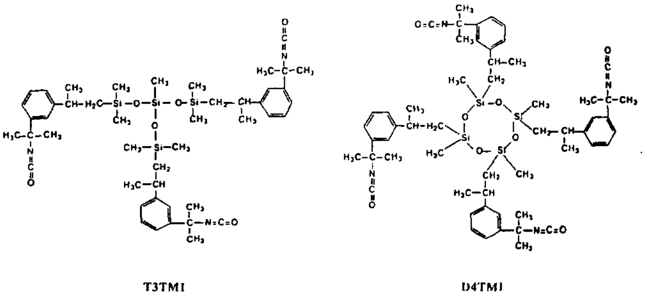
Water-soluble amphiphilic polymers have been explored for such uses as rheology modifiers, polymeric surfactants and drug carriers[1–13]. Hydrophobically modified cellulosics or poly(acrylamide)s, and block or graft copolymers with hydrophobic and hydrophilic segments are just a few examples of such macromolecules. Amphiphilic star polymers generally consist of a more or less hydrophobic core and a number of hydrophilic or amphiphilic arms[2,6,10–12,14–16]. Particularly interesting are stars in which the arms are end-capped with hydrophobic moieties. Such polymers can function as associative thickeners, as demonstrated by Brown and Glass[14] for star-type urethane-ethoxylate polymers endowed with nonylphenoxy end-capped arms. Phase separation has also been observed in these systems.

The reaction of a multifunctional isocyanate with methoxy(polyethylene glycol)s (MPEGs) or with a hydrophobically end-capped polyethylene glycol (e.g. the Igepals with octyl- or nonylphenoxy end-groups) is a simple method for the preparation of amphiphilic star polymers. However, many of the commercially available isocyanates (e.g. the Desmodurs) have average functionalities deviating from a whole number[17,18]. Their use is likely to produce a mixture of star polymers each with a different number of arms. We recently reported the synthesis of well defined, multifunctional aliphatic isocyanates obtained in essentially quantitative yield by the bulk hydrosilylation of *m*-isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI) with linear and cyclic hydrogen methylsiloxanes[19,20]. Two of the structures, abbreviated as T3TMI and D4TMI, are shown in *Scheme 1*. Both compounds were employed recently as crosslinking agents in the synthesis of poly(ethylene oxide) (PEO) networks for use as gel polymer electrolytes[21] and amphiphilic hydrogels[22]. They were also used as precursors for PEO-type star polymers[23]. This paper gives a detailed account of the synthesis and associative properties of star polymers with a T3TMI or D4TMI core and nonylphenoxypoly(ethylene glycol) (NPPEG) arms. Interesting phase separation phenomena are observed as a function of polymer structure and concentration.

EXPERIMENTAL

Materials

T3TMI and D4TMI, both colourless liquids, were synthesized as previously described[20]. The four NPPEGs, acquired from Aldrich, were Igepal CO-210, 720, 890 and 990, the stated molecular weights (MWs) being 308, 749, 1982 and 4625, respectively. From ^1H n.m.r. data (nonyl *versus* oxymethylene groups) the respective MW values for the latter three Igepals were found to be 718, 1920 and 3920, or an average of 11.0, 38 and 84 ethylene oxide



Scheme 1 Structures of tri- and tetraisocyanates

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(EO) units. The Igepals were dried azeotropically or freeze-dried with benzene. Solvents used in the experiments were distilled from CaH_2. Dibutyltin dilaurate (DBTDL) and *N*,*N*-tetramethylethylene diamine (TMEDA) were products from Aldrich. Star solutions were made in doubly distilled water. Salts were used without further purification. The Amicon membranes YM2 (>1000 MW), YM5 (>5000 MW) and YM10 (>10 000 MW) were used for ultrafiltration of the star polymers.

Synthesis of star polymers

In a typical reaction, 1 g of D4TMI (0.96 mmol) was added to a solution of 39.2 g (10 mmol) Igepal CO-990 in 40 ml dry toluene. After adding a few drops of DBTDL or TMEDA, the mixture was allowed to react for 3 h at 25°C, then for at least 3 h more at 70°C until no isocyanate i.r. absorption at 2260 cm^{-1} could be detected. The star polymer, abbreviated as D4TMI–IG990, and excess Igepal CO-990 were precipitated in cold hexane to remove the catalyst. The polymer mixture was freeze-dried from dioxane to remove traces of toluene, then dissolved in a 300 ml mixture of ethanol and distilled water (3:2 v/v) and ultrafiltrated through an Amicon YM10 membrane. Water was removed by rota-evaporator and by freeze-drying from benzene (or azeotropically, depending on the MW of the Igepal used). Reactions with Igepal CO-210 and 720 did not require an excess of these compounds.

Measurements

I.r. spectra were obtained with a Perkin-Elmer 1310, and ^1H n.m.r. spectra on a Bruker AMX 300 spectrometer. D.s.c. measurements were carried out on a Perkin-Elmer DSC-4 at a heating rate of 10°C min^{-1}. Gel permeation chromatograms were obtained with a Waters GPC1A using ultrastyragel columns of 500, 10^4 and 10^5 Å. Star polymer concentrations were determined by silicon analysis of water-soluble stars using an ICP-FMA03 emission spectrometer. A Brookfield RVT viscometer was employed to obtain low-shear viscosities of the stars in aqueous solution.

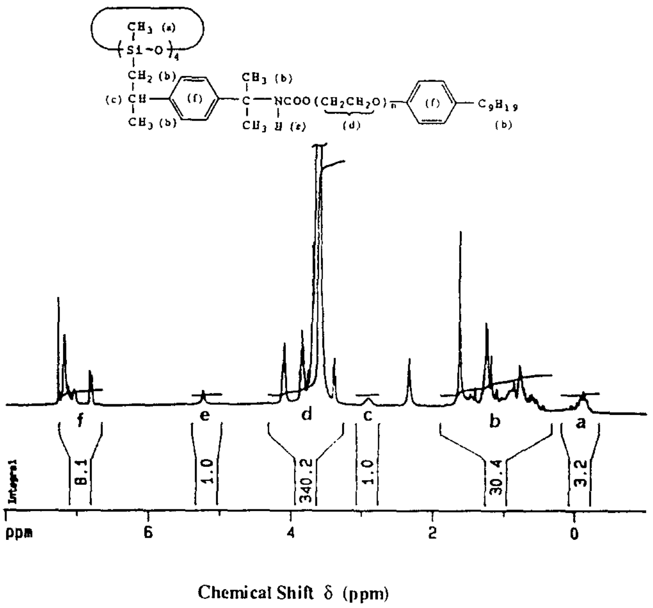
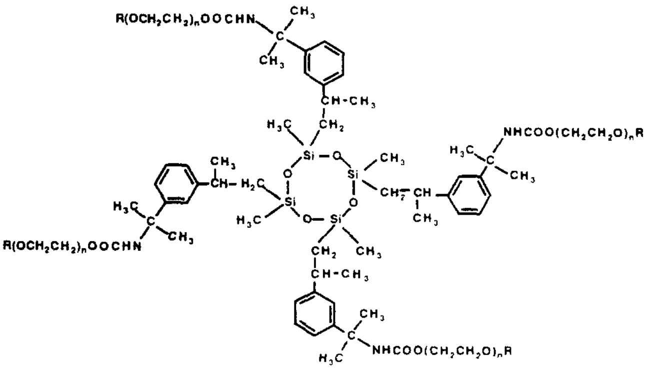


Figure 1 300 MHz ^1H n.m.r. spectrum of D4TMI–IG990 in $CDCl_3$ at 25°C



R = $C_6H_4C_9H_{19}$ n = 2, 11, 38, 84

Scheme 2 Star polymers from D4TMI and nonylphenoxypoly(ethylene glycol)s

RESULTS AND DISCUSSION

The hydrosilylation of *m*-TMI by linear and cyclic hydrogen methylsilanes has been shown to proceed quantitatively with exclusive β-addition to the isopropenyl group[20]. Well defined di-, tri-, tetra- and pentaisocyanates are obtained, two of which (T3TMI and D4TMI) are shown in *Scheme 1*. Since the reactivity of the aliphatic NCO group in *m*-TMI is impeded by the adjacent isopropyl group[24], it was necessary in the synthesis of star polymers of T3TMI or D4TMI with MPEG arms to use temperatures of 70–80°C to complete the reactions in reasonable time[23]. Also, the use of equivalent amounts of NCO and OH groups (or a slight excess of OH) resulted in the formation of small amounts of higher-molecular-weight species due to the allophanate reaction at the elevated temperatures. To avoid this, a larger excess of the MPEG was used. This also speeds up the conversion to star polymer. G.p.c. data and silicon analysis of these stars clearly show only one species[23,25]. The excess MPEG was removed by ultrafiltration in water. This works well for the MPEG star polymers since the latter were shown by surface tension measurements to be aggregated while MPEG itself is not. In purifying the Igepal star polymers by ultrafiltration in aqueous solution we found that neither the Igepal nor the star passed the membrane. This is not surprising since the Igepals are non-ionic surfactants and strongly aggregated in water. However, the Igepal aggregates break down on adding ethanol, and with 60 vol% ethanol Igepal CO-990 passes through the YM10 membrane while the bulk of the D4TMI–IG990 remains behind.

The 300 MHz ^1H n.m.r. spectrum of the star polymer D4TMI–IG990 is given in *Figure 1*. It confirms the proposed four-arm structure of this compound, the general structure of which is shown in *Scheme 2*. G.p.c. tracings before and after ultrafiltration (*Figure 2*) show that the excess Igepal CO-990 has been effectively removed. The number-average molecular weight of the star molecules was calculated from their ^1H n.m.r. spectra by assuming that T3TMI and D4TMI were pure starting materials. Some of the star properties are shown in *Table 1*, including their melting points (T_m) and number of arms, *f*, where *f*=(MW of the star − MW of the core)/(MW of the arm). The T_m values, all of which were taken at the maximum of their respective d.s.c. tracings, appear to be independent of the core structure. For the IG990 stars the T_ms are 6 to 7°C below that of IG990 itself ($T_m = 57$°C) and for the IG890 star the T_m is 11°C lower than that found for IG890 ($T_m = 47$°C). Also listed in *Table 1* are the hydrophile–lipophile balance (*HLB*) values calculated from the expression $HLB = 20\,M_H/(M_H + M_L)$, M_H and M_L being the respective formula weights of the hydrophilic and lipophilic segments of the stars[26].

Solubility and phase separation

When D4TMI or T3TMI stars with IG890 or IG990 arms are shaken with water and then left standing, the system separates into two liquid phases. The upper layer has a low polymer concentration and is transparent. The lower phase of high polymer concentration has the appearance of a hazy, viscous gel. Earlier studies of T3TMI and D4TMI stars with MPEG arms (i.e. without hydrophobic end-groups) revealed that for MPEGs with MW > 350, solutions up to 10 wt% star were stable[23]. However, the star molecules were aggregated. Surface tension measurements yielded critical micelle concentrations (*CMC*) varying from 9×10^{-5} M for D4TMI–MPEG 350 to 3.0×10^{-4} M for D4TMI–MPEG 1900. In contrast, the Igepal stars, through their hydrophobic arm end-groups, are expected to associate into a more or less network-like structure. Hence, the occurrence of phase separation in these systems above a certain critical concentration is not surprising. D4TMI–IG210 (4 EO units per star arm) is insoluble in water, while D4TMI–IG720 (11 EO units per arm) gives a translucent upper phase. This may not be surprising since their *HLB* number is less than 13 (*Table 1*). Non-ionic surfactants are predicted to give clear solutions only when their *HLB* number exceeds 13[26].

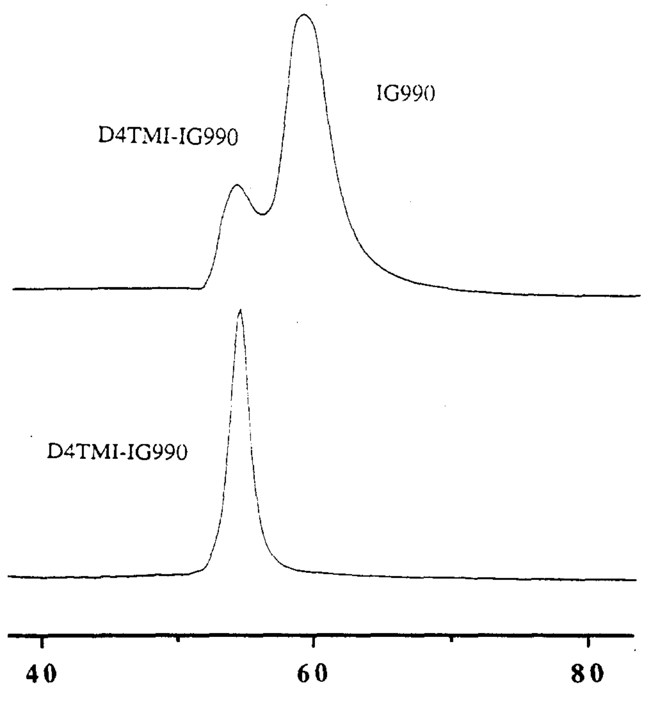


Figure 2 G.p.c. tracings of D4TMI–IG990 before and after removal of IG990 by ultrafiltration

The two-phase formation was studied in more detail for T3TMI–IG990, D4TMI–IG990 and D4TMI–IG890. The respective volumes V_u and V_l of upper and lower layer were carefully measured as a function of the total star concentration, C_t. The star concentration in the upper phase, C^*, was determined by i.c.p. silicon analysis. The mass conservation law gives

$$C_t V_t = C^* V_u + C_l V_l \tag{1}$$

where $V_t = V_u + V_l$ and C_l is the star concentration in the condensed lower phase. The volume fractions v_u and v_l of upper and lower layer are given by

$$v_u = \frac{V_u}{V_t} = \frac{C_l - C_t}{C_l - C^*} \quad \text{and} \quad v_l = \frac{V_l}{V_t} = \frac{C_t - C^*}{C_l - C^*} \tag{2}$$

Our data at room temperature show that C^* and C_l are constant as long as the two phases coexist. Hence, a plot of v_u (or v_l) *versus* C_t should be linear. *Figure 3* shows that this is indeed the case. The polymer concentration in the condensed phase, C_l, was calculated from equation (1). It also equals the intercept of the v_u *versus* C_t plot at $v_u = 0$, where $C_t = C_l$. The conclusion is that only one phase exists when the total polymer concentration $C_t < C^*$ or $C_t > C_l$. For $C^* < C_t < C_l$ two phases coexist in equilibrium, with constant concentrations of C^* and C_l, respectively, and their volume fractions depending on the total polymer concentration. A partition coefficient $k = C_l/C^*$ can be defined and is a measure of how the polymer is partitioned between the condensed and dilute phases. The relevant data are collected in *Table 1* which also lists the ratio of water molecules to EO units and the water content (in wt%) in the gel phase.

The critical star concentration C^* above which phase separation occurs appears to be higher than the *CMC* of comparable MPEG stars. The latter can be calculated from the expression $\ln CMC = -11.65 +$

Table 1 Properties[a] of associative star polymers

Star polymer	MW	f	T_m (°C)	*HLB*	$10^3 C^*$ (M)	$10^3 C_l$ (M)	C_l/C^* (k)	H_2O/EO (gel phase)	H_2O (wt%) (gel phase)
T3TMI–IG990	12 300	2.9	49	17.7	0.32	11.0	34	17.4	86.5
D4TMI–IG990	16 300	3.9	50	17.8	0.55	7.8	14	18.5	87.3
T3PM–IG990[b]	10 700	2.7	49	18.4	0.17	10.4	61	18.6	87.4
D4TMI–IG890	8900	4.1	36	15.7	1.07	22.1	21	13.2	80.3
D4TMI–IG720	4050	4.0		10.8					

[a] MW from ^{1}H n.m.r. spectra; f = number of star arms = (MW star − MW core)/MW arm; C^* = critical star concentration in dilute upper phase; C_l = star concentration in gel phase

[b] The core T3PM refers to tris(*p*-isocyanatophenyl)methane (see Discussion)

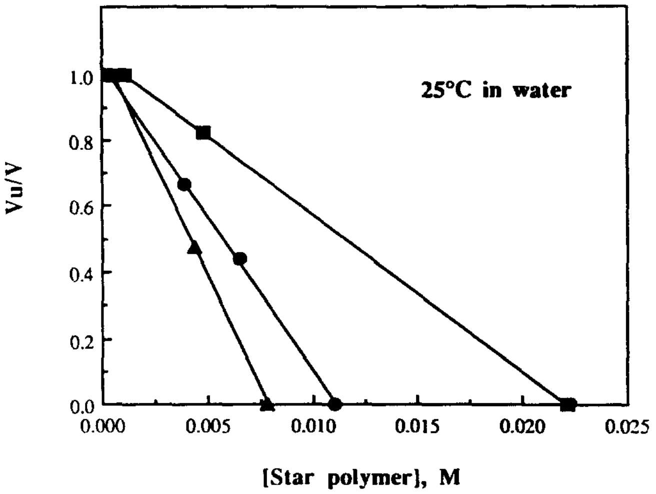


Figure 3 Phase separation of associative PEO-type star polymers in water at 25°C. Plots of V_u/V (volume fraction of dilute upper phase) *versus* C_t (total polymer concentration): (▲) D4TMI-IG990; (■) D4TMI-IG890; (●) T3TMI-IG990

0.20 *HLB* recently found from surface tension measurements of a series of D4TMI–MPEG star polymers[25]. The *CMC* of a D4TMI–MPEG star with 86 EO units (almost the same number of EO units as in D4TMI–IG990) is calculated to be 3.65×10^{-4} M. The value for the T3TMI homostar analogue is 3.55×10^{-4} M. An experimental *CMC* of 3.3×10^{-4} M was found for IG990 itself[27]. This is close to a calculated value of 3.13×10^{-4} M using the expression $\ln CMC = -13.36 + 0.28\,HLB$ ($HLB = 18.9$ for IG990) recently found by us for C_9-Igepals[25].

At the critical concentration $C^* = 5.54 \times 10^{-4}$ M where D4TMI–IG990 starts to form two phases, the concentration of nonylphenoxy arm end-groups is 2.2×10^{-3} M, nearly seven times the *CMC* of IG990. For T3TMI–IG990 the C^* equals 3.21×10^{-4} M, i.e. phase separation occurs at an end-group concentration of 9.63×10^{-4} M, about three times the *CMC* of IG990. Apparently, for the same arm structure, the tristar starts to phase separate at a lower nonylphenoxy concentration than the four-armed star. This may be due to an increased probability of intramolecular association between the hydrophobic end-groups or between end-groups and core in the four-armed star molecule relative to the tristar. We believe that formation of the gel phase is chiefly caused by the intermolecular association of the nonylphenoxy end-groups. Below C^* intramolecular association is dominant, while above C^* the star molecules start to overlap and intermolecular association becomes prevalent. Core–core interactions responsible for the formation of aggregates in solutions of stars with MPEG arms are probably less important in aqueous solutions of Igepal stars since the cores are partially shielded by the hydrophobic arm end-groups. This appears to be confirmed by our results with Igepal-armed star polymers containing tris(*p*-isocyanatophenyl)methane (T3PM) as the hydrophobic core[28]. On the one hand, and not surprisingly, the *CMC*s of MPEG homopolymer stars with the relatively small T3PM core are about ten times higher than those of comparable stars containing the large D4TMI or T3TMI core[28]. On the other hand, an aqueous solution of a T3PM star with IG990 arms separates into two liquid phases above $C^* = 8 \times 10^{-5}$ M, that is, at a nonylphenoxy concentration of 2.4×10^{-4} M. This is close to the *CMC* of IG990 but far below that of the T3PM–MPEG stars. It is also interesting to note that the water content of the gel phase of the three IG990 stars is very similar, the values at 25°C being 87.3 wt% for D4TMI–IG990, 86.5 wt% for T3TMI–IG990 and 87.4 wt% for T3PM–IG990. The respective ratios of H_2O molecules to EO units in these gels are 18.5, 17.3 and 18.6. Swelling in PEO networks is chiefly determined by the crosslinking density. We are presently studying in more detail the relationship between water content of the gel phase and the EO content of the associative star polymer. Preliminary data for T3PM–Igepal stars show a rapid decrease in the amount of water for Igepals with less EO units. In the physically associated hydrogels of our stars the hydrophobic domains function as crosslinks. However, the average number of nonylphenoxy end-groups in such a domain (i.e. the average domain size) has not yet been determined.

Brookfield viscosities

Results of Brookfield viscosity measurements for the star T3TMI–IG990 at a shear rate of $2\,s^{-1}$ are shown in *Figure 4* and *Table 2*. Included are data for the homopolymer star T3TMI–MPEG5000 and for the linear polymers IG990 and MPEG14000. The latter has an MW close to that of the two stars. *Figure 4* reveals that the viscosity of the hydrophobically modified T3TMI–IG990 and that of the homopolymer star rapidly increase above 10 wt%. The viscosity of the Igepal star solution can only be measured above 11.1 wt% since below this concentration a two-phase system exists. The homopolymer tristar solution remains homogeneous over the entire concentration range although the solutions are cloudy.

No dramatic increase in the Brookfield viscosity is observed for the linear polymers MPEG14000 and IG990, in spite of micelle formation with the latter. In a 40 wt% aqueous ethanol solution, association between the hydrophobic arm end-groups of stars such as D4TMI–IG990 is absent, as shown by the low Brookfield viscosity (*Figure 4*) and by the fact that no phase separation occurs in this system (in water, the C_t for the gel phase of this star is 10.6 wt%). It is interesting that

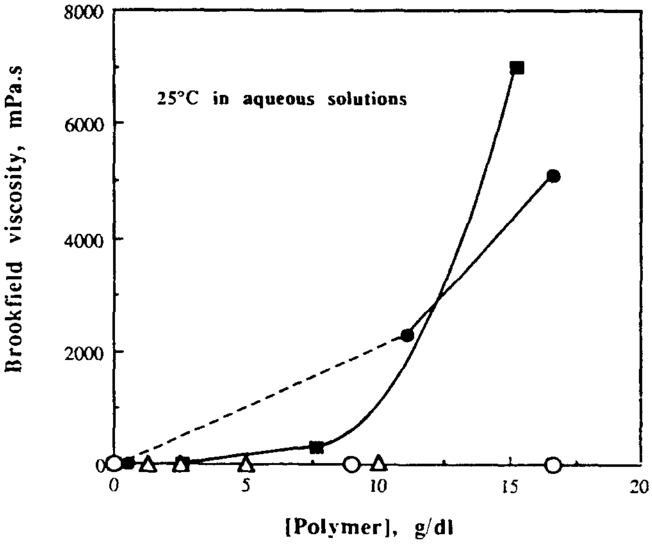


Figure 4 Brookfield viscosities in water at 25°C ($2\,s^{-1}$ shear rate): (●) T3TMI-IG990; (■) T3TMI-MPEG5000; (○) MPEG14000; (△) D4TMI-IG990 in ethanol–water (2:3 v/v)

Table 2 Brookfield viscosities of star polymers (25°C, shear rate $2 s^{-1}$)

Polymer	MW	Solvent	[Polymer] (wt%)	η (mPa)
MPEG14000	14600	H_2O	16.7	12
IG990	3900		4.0	2
			10.0	7
			16.7	36
T3TMI–IG990	12300		11.1	2300
			16.7	5100
D4TMI–IG990	16300	$3 H_2O/2C_2H_5OH$ (v/v)	2.5	3
			5	7
			10	22
T3TMI–MPEG5000	15300	H_2O	15.2	6750

the star homopolymer T3TMI–MPEG5000 also exhibits a rapid increase in viscosity, its value being 6700 mPa for a 15.5 wt% solution, even higher than for the associative star (*Figure 4*). The high viscosity is probaby caused by clustering of star micelles resulting from chain entanglement. A similar phenomenon was reported in concentrated solutions of linear non-ionic block copolymer surfactants[5,29]. Partial crystallization of PEO arms may also contribute to the increased viscosity of these star solutions.

Sorption of hydrophobic molecules in the associated gel

We reported recently that water-swollen amphiphilic PEO networks with T3TMI or D4TMI crosslinks exhibit an unusually high affinity for hydrophobic compounds such as dodecyl sulfate, tetraphenylboron, picrate, bromophenol blue and 8-anilinonaphthalene sulfonate (ANS)[22]. The binding sites are the large hydrophobic T3TMI and D4TMI crosslinks. The gel phase of our Igepal stars resembles an amphiphilic hydrogel. Therefore, an initial exploration was made on the partitioning of some of these hydrophobic compounds between the dilute and condensed phase of an aqueous T3TMI–IG990 star solution. The following observations were recorded. After equilibration of 1 ml of a 0.0013 M sodium picrate solution with 1 ml of the T3TMI–IG990 hydrogel, 90% of the picrate had transferred to the gel phase which turned intensely yellow. Mixing 3 ml of a 0.001 M NH_4ANS solution with 2 ml of the gel phase left only 8% ANS in the dilute upper phase. Under u.v. light the 2 ml ANS-enriched gel phase showed a deep-blue fluorescence, implying that the ANS is bound to the hydrophobic associative domains[30]. Adding comparable quantities of sodium tetraphenylboron displaces the picrate or ANS molecules from the gel due to a stronger affinity of the gel for BPh_4^- ions[22]. Dodecyl sulfate also accumulates in the gel phase. This causes the gel to take up water from the dilute upper phase and eventually the two-phase system reverts to a homogeneous solution.

The observed phenomena parallel those found for the permanently crosslinked amphiphilic hydrogels[22] and also resemble results reported earlier for the binding of hydrophobic species to polysoap-type polystyrenes with pendent crown ethers or oligo-oxyethylene chains[31].

Hydrodynamic volume of the stars

If we make the assumption that the star molecules are spherical in shape and that on reaching the critical concentration C^*, the hydrodynamic volumes, V^*, of the stars begin to overlap, it is possible to arrive at an estimate of the star radius and the amount of water per EO unit, N_{H_2O}, in the swollen star molecules of the dilute phase. The same parameters were calculated recently by Xu *et al.*[5] for micelles of the block copolymer poly(styrene-*b*-ethylene oxide) for which they adopted a star model. If Z denotes the number of star molecules in a total volume V_t, then the volume of the swollen star is given by $V^* = KV_t/Z$ where K is the packing density. Since in our system $Z = C^*$, the radius r_s of the star is given by $r_s = (3K/4\pi C^* N_A)^{1/3}$, N_A being Avogadro's number. The core radius, assuming it is spherical and water-impenetrable, equals $r_c = (3M/4\pi\rho N)^{1/3}$ where M is the molecular weight and ρ the density of the core. The mean volume occupied by water and star arms can be computed from the thickness, $r_s - r_c$, surrounding the core. This in turn provides us with the number of water molecules per EO unit (N_{H_2O}) in the swollen star[5] using the known volumes of an EO unit (64.6 Å^3) and a water molecule (30.0 Å^3). Values for r_s, r_c and N_{H_2O} thus calculated are shown in *Table 3*. K was taken as 0.74, the value for a close-packing model. Included in *Table 3* are the calculated lengths for elongated PEO star arms, based on either the fully extended zigzag model for PEO or the meander model in which the PEO chain is an expanded helical coil[32]. For comparison, values of similar parameters for a poly(styrene-*b*-ethylene oxide) micelle[5] with PEO arms comparable to those of our stars are also listed in *Table 3*.

The data reveal that the thickness, $r_s - r_c$, of the solvent-swollen shell surrounding the star molecules in the dilute phase is considerably less than the calculated values of either r_{zigzag} or $r_{meander}$. This implies that the PEO star arms emanating from the core are not fully elongated, a conclusion also reached by Xu *et al.*[5] for poly(styrene-*b*-ethylene oxide) micelles. The PEO arm length appears to be highest for the star with the smallest hydrophobic core (T3PM), probably as a result of decreased intramolecular interaction between core and arm ends. The ratio H_2O to EO units in the gel phase (*Table 1*) is 10 to 50 times less than in the dilute phase (N_{H_2O} of *Table 3*), depending on the structure of the star. Preliminary d.s.c. tracings of the gel phase clearly reveal the presence of bound water (melt peak around −13°C), similar to what we reported for water-swollen hydrogels[22]. Also, the ratio N_{H_2O} in both gel and dilute phase (and, therefore, C^* and C_1), as well as the volume

Table 3 Hydrodynamic parameters of associative PEO star polymers in the dilute aqueous phase

Sample	C^* (M)	r_s (Å)	r_c (Å)	N_{H_2O}	r_{zigzag} (Å)	$r_{meander}$ (Å)
T3TMI–IG990	3.21×10^{-4}	97	7.0	505	293	159
D4TMI–IG990	5.54×10^{-4}	80	7.5	211	293	159
D4TMI–IG890	1.07×10^{-3}	65	7.5	247	134	72
T3PMI–IG990	1.70×10^{-4}	120	5.3	958	293	159
PS–PEO micelle[a]		120	38	263	367	200

[a] Data for poly(styrene-*b*-ethylene oxide) triblock copolymer from ref. 5

fractions of the two phases changes dramatically as a function of temperature and added salt. Although without salt the gel phase for all star polymers was always the lower of the two phases, this can be reversed in the presence of salts. For example, on adding sufficient NaF, NaH_2PO_4 or Na_2SO_4, the gel phase acquires a lower density than the dilute phase and floats on top of the latter. Results of these measurements will be published elsewhere.

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