

SELF-ASSEMBLING AMPHIPHILIC POLYELECTROLYTES AND THEIR NANOSTRUCTURES

Yotaro Morishima*

*Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka,
Osaka 560-0043, Japan*

Abstract The self-assembling behavior of random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) and hydrophobic comonomers possessing dodecyl groups linked by various spacer bonds was discussed with a focus on the effect of the spacer. The characterization of association behavior of such polymers in water using quasielastic light scattering, capillary electrophoresis, NMR relaxation, various fluorescence, and viscoelastic methods was described. These copolymers form a variety of self-assembled nanostructures depending on the type of the spacer. Random copolymers of AMPS and *N*-dodecylmethacrylamide show a strong preference for intrapolymer self-association even in concentrated aqueous solutions forming single-macromolecular self-assemblies (unimolecular micelles). In contrast, random copolymers of AMPS and dodecyl methacrylate are prone to undergo interpolymer associations yielding multipolymer micelles. In random copolymers of AMPS and a methacrylate substituted a nonionic surfactant ($\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{25}\text{C}_{12}\text{H}_{25}$) ($\text{C}_{12}\text{E}_{25}$), dodecyl groups are much less restricted by the polymer backbone because they are linked via a long, flexible hydrophilic spacer. Thus, the polymer-bound $\text{C}_{12}\text{E}_{25}$ surfactant moieties form micelles similar to those formed by discrete surfactants, but they are bridged by polymer chains forming a network structure.

Keywords Self-assemblies, Hydrophobically-modified polyelectrolytes, Nanostructures, Hydrophobic association, Unimolecular micelles, Multipolymer micelles, Transient network, Viscoelasticity, Shear thickening, Shear thinning.

INTRODUCTION

In the past decades, self-assembling hydrophobically-modified water-soluble polymers have attracted considerable interest of chemists in both academia and industry because of their relevance to biological macromolecular systems and also to industrial applications^[1-3].

Macromolecular self-associations are driven by non-covalent interactions such as electrostatic, hydrogen bonding, van der Waals and hydrophobic interactions. Hydrophobic interactions are the major driving force for the self-assembling of hydrophobically-modified water-soluble polymers in aqueous media.

A commonly employed synthetic method for such polymers is copolymerization of hydrophilic and hydrophobic monomers with a block, alternating, or random sequence distribution. In particular, random copolymers have received a great deal of interest because of their relative ease of synthesis and a wide range of monomer selections comparable to the case of block copolymers. As can be found in some recent reviews^[4-6], micelle formation by amphiphilic random copolymers in aqueous media has been extensively studied.

An important starting point for understanding the self-assembling behavior of hydrophobically-modified water-soluble polymers is to know whether polymer-bound hydrophobes associate within the same polymer chain or among different polymer chains. Two fundamental structures that are formed by intra- and interpolymer hydrophobic associations are loops and crosslinks, respectively. A loop can be formed by association between closest neighboring hydrophobes or between hydrophobes far apart from each other on the same polymer chain.

* Corresponding author: Yotaro Morishima, E-mail: morisima@chem.sci.osaka-u.ac.jp

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The latter case may result in a contraction of the polymer chain and hence a decrease in solution viscosity. Hydrophobically-modified polymers possessing a small number of hydrophobes may form a “flower-like” micelle along a polymer chain, consisting of hydrophobic cores and hydrophilic loops surrounding the cores (Fig. 1a). This type of micelle has been theoretically predicted for the self-organization of sequential multiblock copolymers in selective solvents^[7-9]. As the number of hydrophobes on a polymer chain is increased, the size of the interior core increases whereas the size of the exterior hydrophilic loop decreases. Hence, the flower-like micelle (a “second-order” structure) may collapse into a third-order structure due to secondary association of the hydrophobic cores, yielding a highly compact assembly as conceptually illustrated in Fig. 1b.

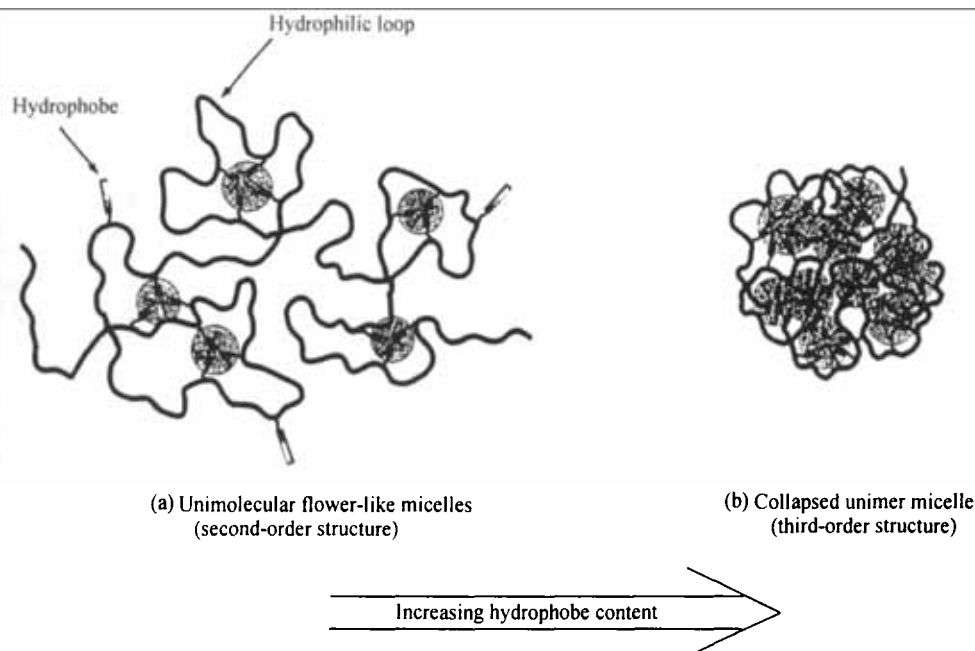


Fig. 1 Schematic illustration of completely intrapolymer hydrophobic associations: a unimolecular flower-type micelle with a second-order structure (a) and a collapsed unimolecular micelle with a third-order structure (b)

On the other hand, the formation of an interpolymer crosslink would result in a large increase in the size of associated structures depending on the extent of the crosslinking. When the number of hydrophobes linked to one polymer chain is small, interpolymer hydrophobic associations may lead to a situation where several polymer chains are crosslinked together, giving rise to a large increase in solution viscosity. As the number of polymer-bound hydrophobes is increased, an infinite network may be formed, resulting in gelation or bulk phase separation of the sample.

Most of hydrophobically-modified random copolymers reported so far undergo both intra- and interpolymer associations concurrently. In the case where intrapolymer associations are dominant but a portion of hydrophobes undergo interpolymer association, intermolecularly bridged flower-like micelles may be formed, and the extent of such micelle bridging normally depends on the content of hydrophobes in the polymer as well as the polymer concentration.

EFFECTS OF STRUCTURAL VARIATIONS OF AMPHIPHILIC POLYELECTROLYTES ON ASSOCIATION BEHAVIOR

Hydrophobically-modified polyelectrolytes are among the amphiphilic polymers that have been extensively studied in the past decades^[10-25].

A characteristic of hydrophobic self-associations in hydrophobically-modified polyelectrolytes is that hydro-

phobic associations compete with electrostatic repulsions, showing a marked tendency of intra- and interpolymer hydrophobe associations strongly depending on macromolecular architectures.

Our group has been investigating associative properties of random copolymers of various electrolyte monomers, including sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS), (meth)acrylic acid, and quaternary ammonium type monomers, and hydrophobic comonomers, including methacrylamides or methacrylates substituted with various types of hydrophobes via various types of spacer bonds (Fig. 2)^[5, 23–32]. It has been established, from these studies, that some of the structural parameters determining a preference for intra- or interpolymer hydrophobe association include a) the type of hydrophobes, b) their content in a polymer, c) the sequence distribution of electrolyte and hydrophobic monomer units in a polymer chain, and d) the type of spacer bonding between hydrophobes and the polymer backbone. Among them the spacer between hydrophobes and the polymer backbone is a critical structural parameter that controls the associative behavior of polymer-bound hydrophobes. This is due to the fact that in the process of the self-association of polymer-bound hydrophobes, polymer chains would impose steric constraints to the hydrophobes and thus affect the motional freedom of the hydrophobes^[33]. In addition, the sequence distribution of charges and hydrophobic units along the polymer chain is an important structural factor to determine whether the hydrophobic self-association occurs in an intra- or interpolymer fashion^[18, 34, 35]. Polymers with blockwise hydrophobe distributions show a tendency for interpolymer association, whereas random and alternating distributions exhibit a propensity for intrapolymer association.

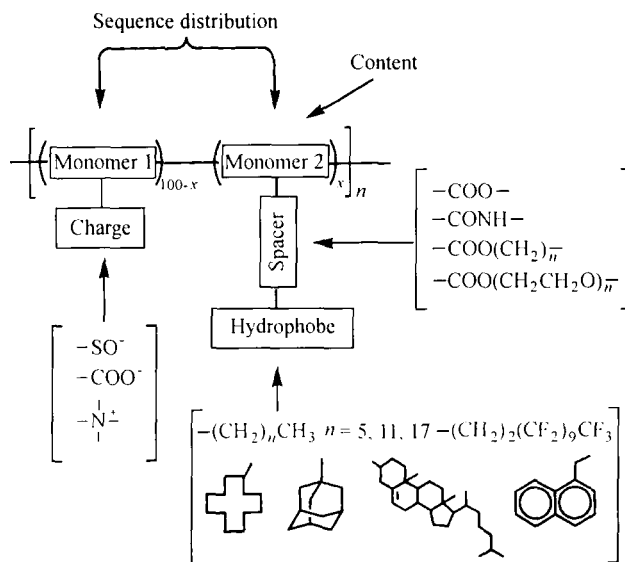
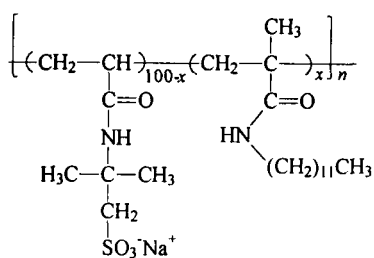
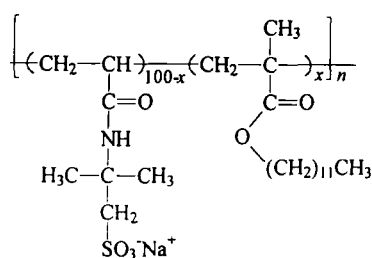


Fig. 2 Structural variations of random copolymers of electrolyte and hydrophobic monomers

As will be discussed in the following sections, associative properties of hydrophobes linked to a polyelectrolyte via amide and ester spacer bonds are remarkably different^[29–31]. Amide-linked hydrophobes exhibit a strong tendency for intrapolymer association whereas ester-linked hydrophobes are prone to undergo interpolymer association. For example, random copolymers of AMPS and *N*-dodecylmethacrylamide (DodMAm) (Chart 1) show a strong preference for intrapolymer self-association even in concentrated aqueous solutions, leading to the formation of single-macromolecular self-assemblies (unimolecular micelles)^[26, 31, 32]. In contrast, random copolymers of AMPS and dodecyl methacrylate (DMA) (Chart 1) are prone to undergo interpolymer association, yielding multipolymer micelles^[30]. Moreover, the solubility of AMPS copolymers having amide-linked hydrophobes is markedly different from that of AMPS copolymers having ester-linked hydrophobes.

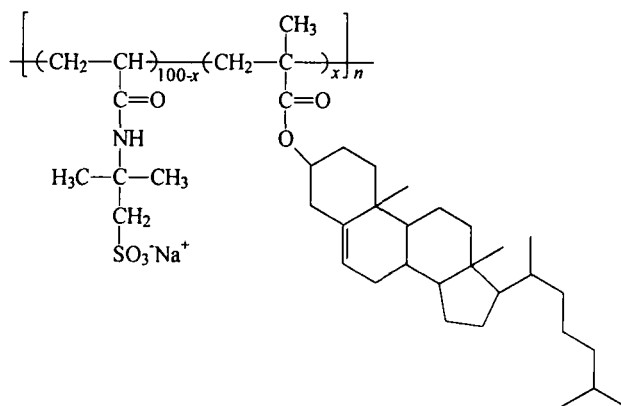


AMPS-DodMAM copolymer



AMPS-DMA copolymer

Chart 1



AMPS-CholMA copolymer

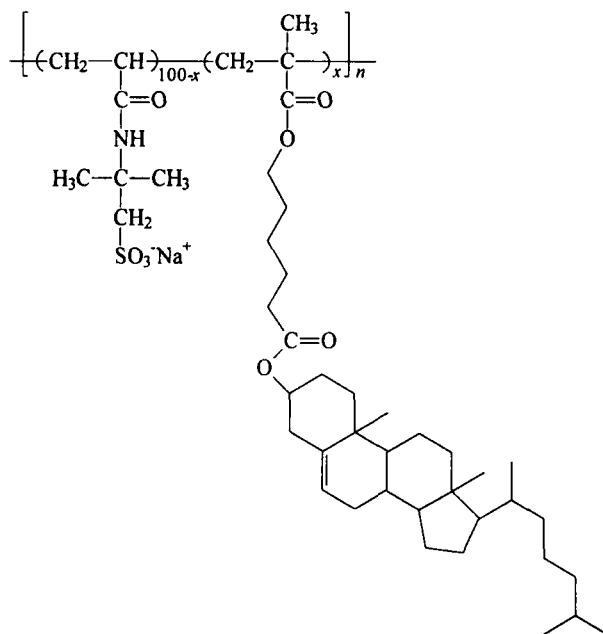
AMPS-Chol-C₅-MA copolymer

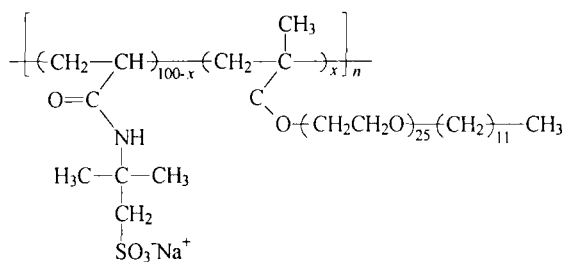
Chart 2

AMPS-DodMAM copolymers (Chart 1) are soluble in water up to ca. 60 mol% hydrophobe content^[32],

whereas AMPS-DMA copolymers (Chart 1) are soluble in water only when the hydrophobe content is lower than 15 mol%^[30].

Interpolymer association occurs more favorably if hydrophobes are linked via a longer spacer bond. For example, cholesterol moieties in random copolymers of AMPS and cholesteryl 6-methacryloyloxyhexanoate (Chol-C₅-MA) (Chart 2) show a stronger tendency for interpolymer association than those in random copolymers of AMPS and cholesteryl methacrylate (CholMA) (Chart 2)^[29]. In AMPS-Chol-C₅-MA copolymers, cholesterol moieties are linked to the polymer backbone via a (CH₂)₅ spacer whereas in AMPS-CholMA copolymers, cholesterol moieties are connected to the polymer backbone via an ester bond. The (CH₂)₅ spacer-linked cholesterol moieties form intermolecularly-bridged micelles even if the cholesterol content in the copolymer is lower than 5 mol%^[29].

The association properties of random copolymers of AMPS and a methacrylate bearing a nonionic surfactant (HO(CH₂CH₂O)₂₅C₁₂H₂₅) (C₁₂E₂₅) (Chart 3) are greatly different from those polymers mentioned above, arising from the fact that hydrophobes are much less restricted by the polymer backbone because they are linked via a long, flexible hydrophilic spacer^[36, 37]. The polymer-bound C₁₂E₂₅ surfactant moieties form micelles via intra- and interpolymer associations that are bridged by polymer chains, thus forming a network structure.



AMPS-DE25MA copolymer

Chart 3

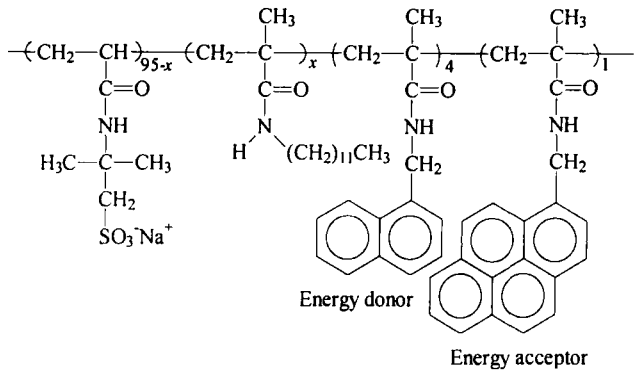
In this article, we will focus on self-assembling AMPS copolymers with hydrophobic comonomers possessing dodecyl groups linked by various spacer bonds. These copolymers would form a variety of self-assembled structures such as a) unimolecular micelles, b) multipolymer micelles and c) “transient” networks of polymer-bound surfactant micelles.

UNIMOLECULAR MICELLES FORMED BY AMIDE-LINKED HYDROPHOBES

The associative behavior of random copolymers of AMPS and *N*-dodecylmethacrylamide (DodMAM) (Chart 1) depends strongly on the DodMAM content (f_{Dod}) in the copolymer, as characterized by viscometry, quasielastic light scattering (QELS), capillary electrophoresis (CE), NMR relaxation, and various fluorescence techniques^[31, 32]. For fluorescence studies, the polymers that are singly-labeled with pyrene or naphthalene or doubly-labeled with pyrene and naphthalene were employed (Chart 4). The labeling of the polymer can be achieved by *co*- or terpolymerization using monomers substituted with a naphthalene or pyrene moiety.

Figure 3 shows the relaxation time distributions in QELS for the AMPS-DodMAM copolymers with varying compositions. When f_{Dod} is relatively low in the range 2.5–10 mol%, relaxation time distributions in QELS (i.e., hydrodynamic size distributions) depend on polymer concentration. The distributions are unimodal at low polymer concentrations but they become bimodal at higher polymer concentrations, the slow mode component increases with increasing polymer concentration. The fast mode is due to unimers (a single polymer state) of the polymer and the slow mode is due to intermolecular associates of the polymers. When f_{Dod} is increased beyond 10 mol%, intrapolymer hydrophobe associations become predominant yielding intrapolymer hydrophobic microdomains. The formation of intrapolymer hydrophobic microdomains would result in a considerable chain collapse. The chain collapse occurs most significantly in a range $10 < f_{\text{Dod}} < 40$ mol% in 0.05 mol/L NaCl

aqueous solutions. These intrapolymer hydrophobic microdomains are surrounded by loops of charged segments, and thus one may conjecture a flower-like unimolecular micelle where a number of hydrophobic microdomains are joined together in clusters on a polymer chain, as schematically illustrated in Fig. 1a.



AMPS-DodMAm copolymer doubly-labeled with naphthalene and pyrene

Chart 4

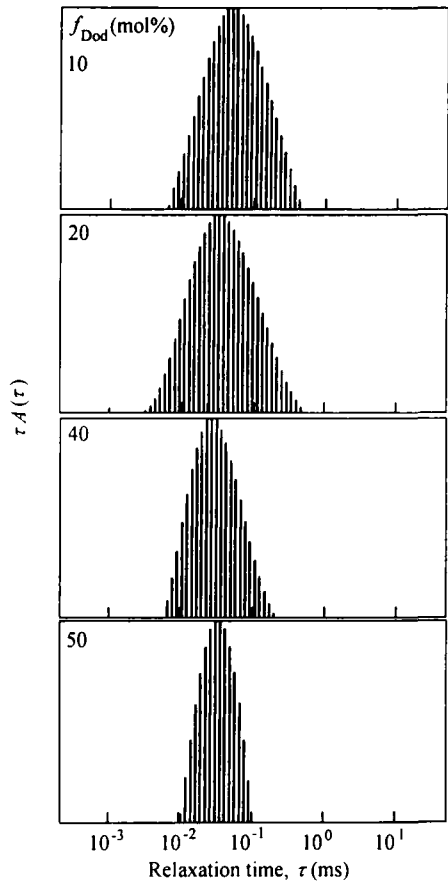


Fig. 3 Distributions of the relaxation times in QELS for AMPS-DodMAm copolymers with varying compositions
Polymer concentration: 1 g/L; [NaCl] = 0.05 mol/L

The intensity ratio of the third to first peaks in the vibrational fine structures in pyrene fluorescence spectra (I_3/I_1) is a useful indicator for the micropolarity where pyrene exists, the I_3/I_1 ratio being larger in less polar microenvironments^[38]. The I_3/I_1 ratio of the pyrene-labeled polymers with varying f_{Dod} increases in the region $10 < f_{\text{Dod}} < 30$ mol%, reaching a maximum at $f_{\text{Dod}} \approx 30$ mol%, indicating that hydrophobic microdomains begin to form at $f_{\text{Dod}} \approx 10$ mol% and the pyrene labels are entrapped in the hydrophobic microdomains. With an increase in f_{Dod} , the extent of the label incorporation increases, reaching a maximum extent near $f_{\text{Dod}} \approx 30$ mol%.

Intrapolymer NRET between naphthalene and pyrene, both labeled on the same polymer chain (Chart 4), provides information about changes in the microscopic chain dimension^[39]. The intensity of pyrene fluorescence emitted by the doubly-labeled polymers (Chart 4) upon excitation of naphthalene at 290 nm increases significantly with increasing f_{Dod} , arising from intrapolymer NRET from photoexcited naphthalene to pyrene labels^[31]. This is due to a decrease in the average separation between the naphthalene and pyrene labels in the same polymer chain. That is, with increasing f_{Dod} , increasing fractions of naphthalene and pyrene labels come close to each other within the Förster radius (2.86 nm ^[40]). This decrease in the donor-acceptor distance results from an increase in the extent of the intrapolymer association of dodecyl groups with increasing f_{Dod} . The intensity of pyrene fluorescence relative to the intensity of naphthalene fluorescence ($I_{\text{Py}}/I_{\text{Np}}$) with selective excitation of naphthalene at 290 nm can be used as a measure of an NRET efficiency. As shown in Fig. 4, with increasing f_{Dod} , the $I_{\text{Py}}/I_{\text{Np}}$ ratio increases slightly at $f_{\text{Dod}} < 10$ mol% but more significantly in the range $10 < f_{\text{Dod}} < 50$ mol%, reaching a plateau near $f_{\text{Dod}} \approx 50$ mol %, indicating that the compaction of the polymer size occurs over a range of $10 < f_{\text{Dod}} < 50$ mol% and saturates near $f_{\text{Dod}} \approx 50$ mol%. These results are practically consistent with those of the I_3/I_1 ratio^[31].

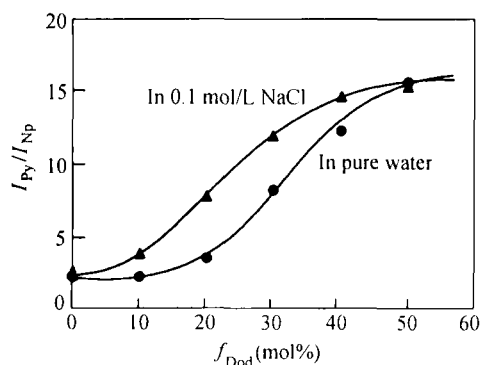


Fig. 4 Relationship between the $I_{\text{Py}}/I_{\text{Np}}$ ratio and f_{Dod} for AMPS-DodMAM copolymers in pure water and in 0.05 mol/L NaCl aqueous solutions
Excited at 290 nm; monitored at 344 nm

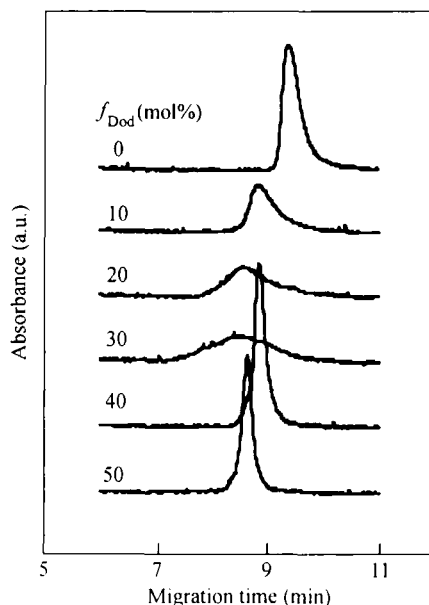


Fig. 5 Electropherograms for AMPS-DodMAM copolymers with varying compositions
Polymer concentration: 1 g/L; pH = 9
Ionic strength: 0.05

As f_{Dod} is increased to 40 mol% or higher, the polymers form compact unimolecular micelles where polymer chains are highly collapsed, arising from secondary association between the surfaces of hydrophobic microdomains within the same polymer chain. The flower-like unimolecular micelles formed in the range $10 < f_{\text{Dod}} < 30$ mol % may be viewed as a second-order structure of the polymer, as schematically illustrated in Fig. 1a.

At $f_{\text{Dod}} > 40$ mol %, however, the second-order structure is folded into a third-order structure comprised of an aggregated cluster of hydrophobic microdomains, as illustrated in Fig. 1b. The collapse of the second-order structure into the third-order structure can be experimentally observed by capillary electrophoresis (CE) (Fig. 5). The width of electropherograms becomes broader as f_{Dod} is increased up to 30 mol%, implying that the distribution of the hydrodynamic volumes (i.e., the conformational distributions) for the second-order structure of these copolymers becomes broader with increasing f_{Dod} up to 30 mol%. When f_{Dod} is increased to 40 mol%, however, the band abruptly becomes very narrow, an indication of the collapse of the second-order structure into the third-order structure of the unimolecular micelle.

An important feature of these copolymers is that such unimolecular micelles with a third-order structure are formed even at high polymer concentrations in the order of 100 g/L.

MULTIPOLYMERIC MICELLES FORMED BY ESTER-LINKED HYDROPHOBES

The association properties of AMPS-DMA copolymers (Chart 1) are dramatically different from those of AMPS-DodMAM copolymers despite the fact that the only difference in these two types of copolymers is the spacer bond (i.e., the ester vs. amide bond) connecting dodecyl groups to the polymer backbone.

The association properties of AMPS-DMA copolymers with the hydrophobe content (f_{MDA}) varying from 1 to 15 mol% have been investigated by fluorescence and QELS techniques in 0.1 mol/L NaCl aqueous solutions^[30]. Aggregation numbers (N_{agg}) of dodecyl groups in the copolymers have been determined employing a fluorescence technique based on the excimer formation of pyrene molecules solubilized in the hydrophobic microdomains of the polymers. For the calculation of N_{agg} , pyrene monomeric fluorescence decay data were fitted to the Infelta-Tachiya equation^[41–43], which assumes that all pyrene probes are randomly distributed over the micelles according to a Poisson distribution and that distributions of fluorophores and quenchers over the micelles are frozen on the time scale of the fluorescence lifetime. For the copolymer with $f_{\text{MDA}} = 9$ mol%, an N_{agg} value of 195 has been observed. For the copolymer with $f_{\text{MDA}} = 15$ mol%, an N_{agg} value is 158, a little smaller than that for $f_{\text{MDA}} = 9$ mol%. The numbers of dodecyl groups per polymer chain are 18 and 35 for the copolymers with $f_{\text{MDA}} = 9$ and 15 mol %, respectively, as calculated from the molecular weights and f_{MDA} values for the polymers. If one assumes that one polymer micelle has one hydrophobic domain (i.e., a unimolecular micelle), the number of polymer chains participating in the formation of the micelle can be calculated to be about 11 and 4–5 for the copolymers of $f_{\text{MDA}} = 9$ and 15 mol%, respectively.

In Fig. 6 are presented the relaxation time distributions in QELS observed at 3.1 g/L polymer in 0.1 mol/L NaCl. When f_{MDA} is lower than 3 mol%, the relaxation time distribution is bimodal with fast and slow mode relaxation peaks^[30]. With an increase in the polymer concentration, the height of the slow mode peak relative to that of the fast mode peak increases. Apparent hydrodynamic radii (R_h) for the fast relaxation mode is in a range of 4–6 nm regardless of the polymer concentration. On the other hand, the R_h value for the slow mode component is ca. 70 nm at a polymer concentration of 0.5 g/L and increases to 90–100 nm as the polymer concentration is increased to 25 g/L. In addition, the component of the slow mode relative to that of the fast mode increases with increasing polymer concentration. These observations indicate that when f_{MDA} is lower than 3 mol%, some polymer chains exist as unimers with $R_h \approx 5$ nm while some other polymer chains form multipolymer aggregates, arising from “hydrophobic crosslinking” by the interpolymer association of dodecyl groups. It is a rather surprising observation that the copolymer exhibits a tendency for interpolymer association even at f_{MDA} as low as 1 mol%.

As f_{MDA} is increased to 9 mol%, the relaxation time distribution becomes unimodal and R_h values fall into a range of 10–13 nm in the polymer concentration range of 0.3–25 g/L, suggesting the formation of multipolymer micelles with an N_{agg} of ca. 195. All the polymer chains are found in the multipolymer micelles but their sizes are much smaller than those observed for the hydrophobically crosslinked polymer chains of the copolymers with $f_{\text{DMA}} \leq 3$ mol%. As f_{DMA} is further increased to 15 mol%, the unimodal distributions become narrow but R_h for the multipolymer micelle markedly increases to 70–180 nm, the size increases with increasing polymer concentration, whereas N_{agg} remains constant at ca. 158 independent of the polymer concentration. Thus, the

association behavior is completely different from that of the copolymer with $f_{\text{DMA}} = 9 \text{ mol\%}$. That is, all polymer chains form much larger aggregates and the size of the aggregates increases with the polymer concentration.

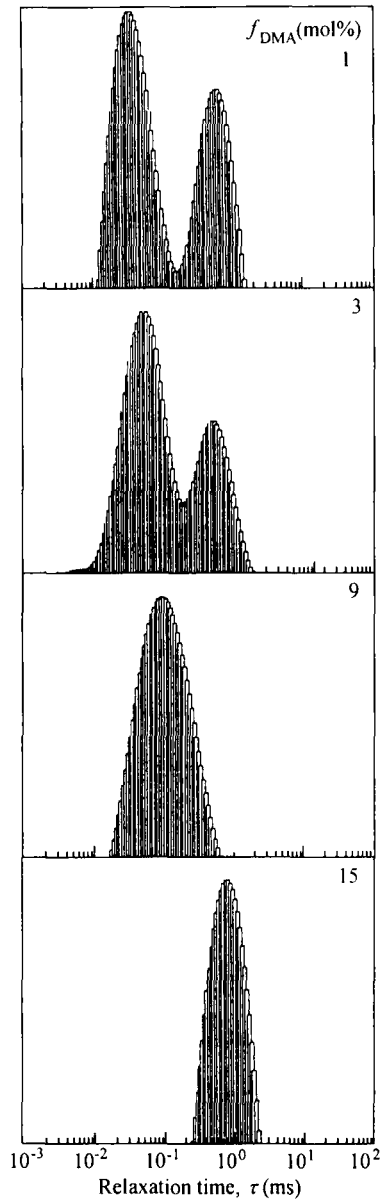


Fig. 6 Distributions of the relaxation times in QELS for AMPS-DMA copolymers with varying compositions
Polymer concentration: 3.1 g/L; [NaCl] = 0.1 mol/L

A unimodal micelle model has been proposed for the copolymer with $f_{\text{DMA}} = 9 \text{ mol\%}$, and a bridged micelle model has been proposed for the copolymer with $f_{\text{DMA}} = 15 \text{ mol\%}$. Models for these micelles are illustrated in Fig. 7 together with R_h and N_{agg} values observed. An important observation is that the distribution of the hydrodynamic sizes for the multipolymer aggregates, both the hydrophobically crosslinked chains and the polymer micelles, is monodisperse as far as we can see from QELS data (Fig. 6). This is particularly true for the micelle formed from the copolymer with $f_{\text{DMA}} = 15 \text{ mol\%}$. In other words, the number of polymer chains that can associate to form a polymer micelle is limited. This behavior is in contrast to the general behavior of so-called

hydrophobically associating “thickeners” which would form extensive hydrophobic crosslinks, leading to a large increase in viscosity with an increase in polymer concentration. Therefore, the solution behavior of the AMPS-DMA copolymer is quite different from that of ordinary associating polymers. The solution viscosities of the AMPS-DMA copolymers are very low compared to those of associating polymers.

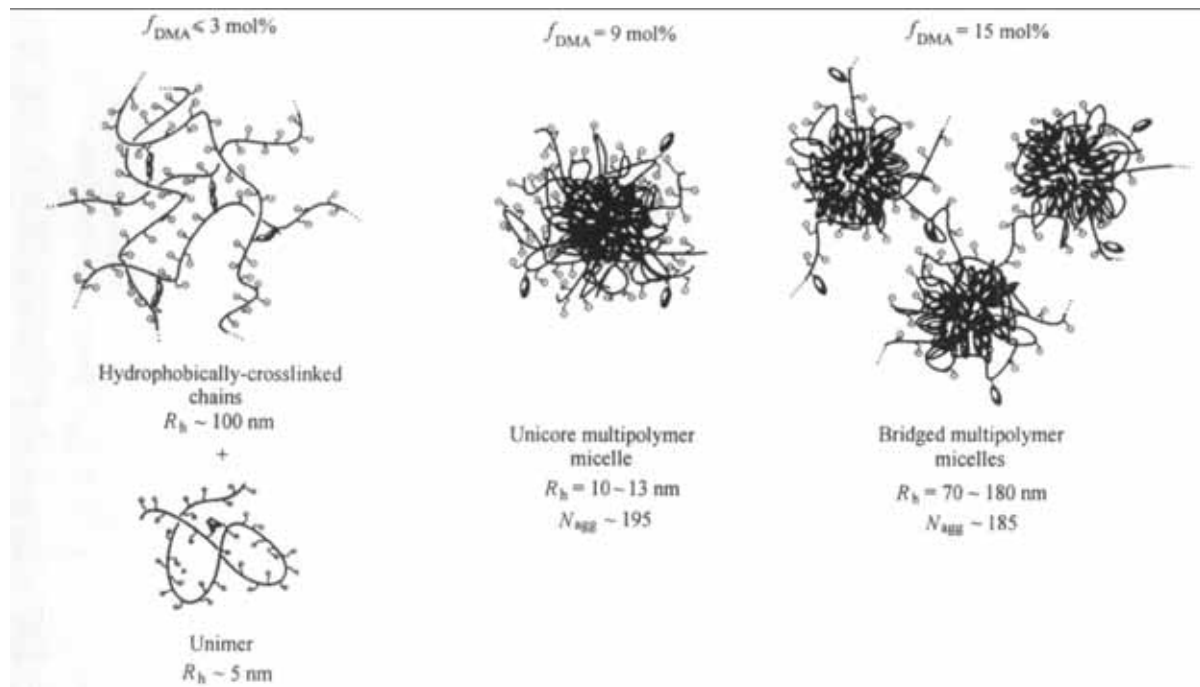


Fig. 7 Models for interpolymer associates formed by AMPS-DMA copolymers with varying compositions

TRANSIENT NETWORKS FORMED BY POLYMER-BOUND SURFACTANT MICELLES

If a flexible, hydrophilic spacer, such as a $(\text{CH}_2\text{CH}_2\text{O})_n$ spacer, is incorporated between a hydrophobe and the polymer backbone, the hydrophobe at the end of that spacer would be able to move freely and hence the hydrophobes would easily associate with other hydrophobes on the same or different polymer chains^[33]. In this section, we focus on the associative behavior of random copolymers of AMPS and a methacrylate substituted with a nonionic surfactant, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{25}\text{C}_{12}\text{H}_{25}$ ($\text{C}_{12}\text{E}_{25}$), with the content of the methacrylate-end-capped $\text{C}_{12}\text{E}_{25}$ macromonomer (DE25MA) unit (f_{DE25}) ranging from 10 to 30 mol% (Chart 3)^[36, 37]. It is expected that the polyAMPS main chain and the $(\text{CH}_2\text{CH}_2\text{O})_{25}$ spacer chain are highly hydrated in aqueous solutions and thus the dodecyl groups at the end of the spacer are microscopically phase-separated from the hydrophilic part of the polymer. In such a situation, hydrophobic associations among the dodecyl groups and hence the formation of hydrophobic domains would be greatly facilitated. The formation of hydrophobic domains is experimentally manifested by fluorescence spectra of pyrene solubilized in the polymer hydrophobic domains. Aggregation numbers (N_{agg}) of dodecyl groups in the hydrophobic domains have been determined using the same fluorescence technique as described in the previous section based on the excimer formation of pyrene solubilized in the domains. It has been found that N_{agg} values range from 53 to 68 depending on f_{DE25} . These hydrophobic domains can be regarded as cores of micelles formed by polymer-bound $\text{C}_{12}\text{E}_{25}$ surfactant moieties. The discrete $\text{C}_{12}\text{E}_{25}$ surfactants form micelles whose aggregation numbers are in the neighborhood of 40 at room temperature. Therefore, the core size (i.e., N_{agg}) of the polymer-bound $\text{C}_{12}\text{E}_{25}$ micelle is somewhat larger than that of the corresponding discrete $\text{C}_{12}\text{E}_{25}$ micelle. The polymer-bound micelle is formed from the association of the $\text{C}_{12}\text{E}_{25}$ moieties not only on the same polymer chain but also on different polymer chains. In the case of $f_{\text{DE25}} = 20$ mol%,

for example, one polymer chain possesses 15 hydrophobes while $N_{\text{agg}} = 57$. Therefore, one micelle unit is formed at least by 4 polymer chains assuming all the hydrophobes on the same polymer chain occupy the same micelle core. However, if some hydrophobes on the same polymer chain occupy different micelle cores, then the micelles are to be bridged by polymer chains.

Since the polymer-bound micelles are formed not only by intrapolymer associations but also by interpolymer associations, an apparent critical micelle concentration (CMC) was observed. Apparent CMC values for the copolymers were estimated by analysis of fluorescence excitation spectra for pyrene probes solubilized in the micelle^[36]. The apparent CMC values for the copolymers are smaller than the CMC for the discrete $C_{12}E_{25}$ surfactant by more than an order of magnitude.

In Fig. 8, low-shear viscosities of aqueous solutions of the polymer with $f_{\text{DE25}} = 20$ mol% measured at a shear rate of 0.1 s^{-1} are plotted as a function of the polymer concentration (C_p) at an added NaCl concentration of 0.10 mol/L. The solutions are Newtonian at this low shear rate and thus the viscosities are regarded as zero shear viscosities. The viscosity increases gradually with increasing polymer concentration at $C_p < 10 \text{ g/L}$, and the viscosity starts to increase sharply near $C_p \approx 10 \text{ g/L}$. When C_p is increased from 10 to 70 g/L, the viscosity increases by three orders of magnitude. These observations indicate that the extent of interpolymer associations (i.e., micelle bridging) is relatively small at $C_p < 10 \text{ g/L}$ but the number of micelle bridges considerably increases with increasing polymer concentration at $C_p > 10 \text{ g/L}$, resulting in the formation of a macroscopic network made up of the bridged micelles. A proposed model for a polymer-bound micelle network is illustrated in Fig. 9.

Micelle network formation is derived from interpolymer hydrophobic associations that occur competing with interpolymer electrostatic repulsions. Thus, the extent of the micelle bridging is dependent on the added salt. The viscosity increases with increasing salt concentration at $[\text{NaCl}] < 0.15 \text{ mol/L}$, reaching a maximum value near $[\text{NaCl}] \approx 0.15 \text{ mol/L}$, and then decreases with a further increase in $[\text{NaCl}]$. Moreover, when $[\text{NaCl}]$ is increased, N_{agg} increases whereas R_h decreases. This suggests that the interpolymer hydrophobic association (i.e., micelle bridging) is not favorable at higher salt concentrations. Therefore, two kinds of salt effects are competing in the polymer association process. When C_p is low, the extent of micelle bridging decreases with increasing $[\text{NaCl}]$. On the other hand, when C_p is high enough, where interpolymer associations are favorable, the extent of micelle bridging increases with increasing $[\text{NaCl}]$ due to electrostatic shielding of interpolymer repulsions. However, when $[\text{NaCl}]$ is increased to a certain level, polymer-bound micelles are more prone to be formed through intrapolymer associations and hence the extent of micelle bridging decreases with increasing $[\text{NaCl}]$.

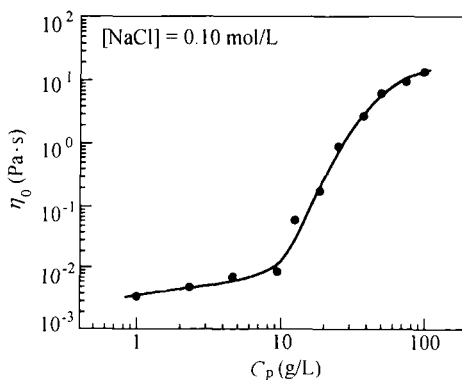


Fig. 8 Dependence of the low-shear viscosity on the polymer concentration for the AMPS-DE25MA copolymer with $f_{\text{DE25}} = 20 \text{ mol \%}$

Shear rate: 0.1 s^{-1} ; $[\text{NaCl}] = 0.1 \text{ mol/L}$; $T = 25^\circ\text{C}$

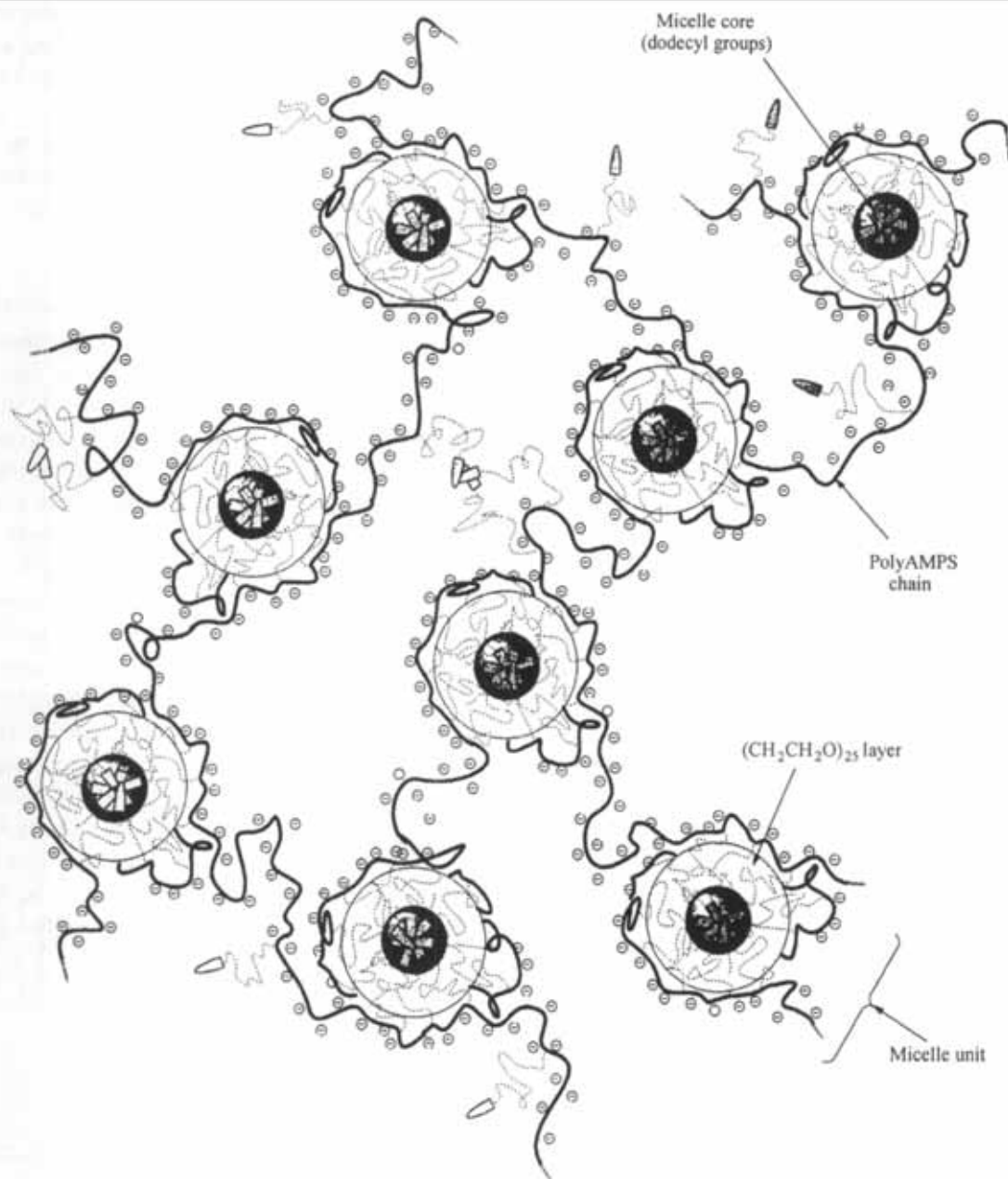


Fig. 9 A hypothetical model for polymer-bound micelles bridged by polymer chains

An important observation is that the viscosity depends strongly on shear stress when the shear rates exceed $\text{ca. } 30 \text{ s}^{-1}$. Figure 10 exhibits the shear-rate-dependent viscosities of a solution of the polymer with $f_{\text{DE25}} = 20 \text{ mol\%}$ at $C_p = 25 \text{ g/L}$ in 0.2 mol/L NaCl . The solution exhibits constant viscosities independent of the applied shear rate up to $\text{ca. } 30 \text{ s}^{-1}$. This shear-rate-independent viscosity behavior is followed by shear thickening at intermediate shear rates, and the thickening behavior persists until the shear rate is increased to $\text{ca. } 200 \text{ s}^{-1}$. When the shear rate is further increased beyond 200 s^{-1} , shear thinning is observed. In general, shear-thickening is derived from a shear-induced increase in the density of mechanically active chains. Therefore, a plausible explanation for the observed shear thickening is an increase in micelle bridging induced by applied shear stress. Namely, when shear stress is applied to the polymer-bridged micelles beyond the Newtonian region, some of the

polymer-bound surfactant moieties may be “pulled out” of the micelle and become available for associations with other surfactant moieties on different polymer chains. Such a situation may lead to an increase in the number of bridging polymer chains and hence a viscosity increases. A further increase in the shear rate may cause the interpolymer network junctions to fragment, leading to a decrease in the network structure in size and hence a decrease in the viscosity.

When the applied shear stress in a shear thinning region is removed, the viscosity goes back to the zero shear viscosity instantly, indicating that the shear-induced disruption and reformation of the micelle bridge occur reversibly^[37]. When a high shear stress is applied to the micelle network, micelle bridges are destroyed at a faster rate than their reformation, leading to a decrease in the bridge density and hence a drop in the steady shear viscosity.

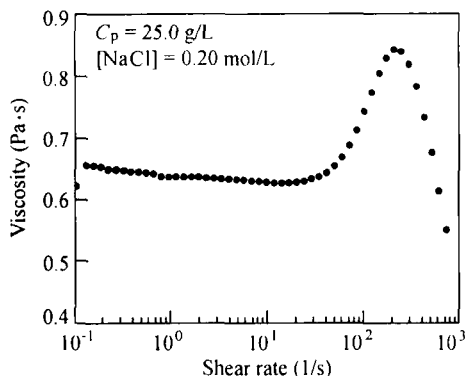


Fig. 10 Shear rate dependent viscosity profile for the AMPS-DE25MA copolymer with $f_{\text{DE25}} = 20$ mol %
Polymer concentration: 25 g/L
[NaCl] = 0.2 mol/L;
 $T = 25^\circ\text{C}$

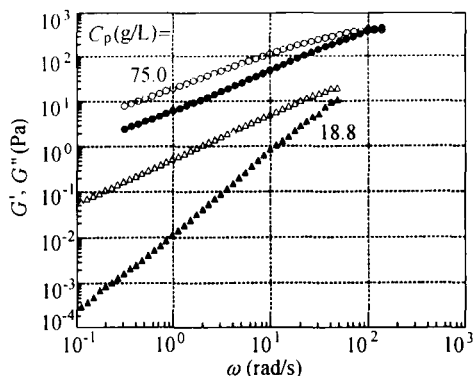


Fig. 11 Storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, as a function of angular frequency (ω) of AMPS-DE25MA ($f_{\text{DE25}} = 20$ mol %) in 0.1 mol/L NaCl at 25°C under a shear stress of 1.0 Pa
Closed and open symbols represent $G'(\omega)$ and $G''(\omega)$, respectively.

Storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, for the same polymer are plotted in Fig. 11 as a function of angular frequency (ω) at polymer concentrations of 18.8 and 75.0 g/L in 0.1 mol/L NaCl^[37]. At $C_p = 18.8$ g/L, $G''(\omega)$ is proportional to ω while $G'(\omega)$ is proportional to ω^2 , a typical feature of the second-order fluid behavior^[44]. As the polymer concentration is increased, both $G'(\omega)$ and $G''(\omega)$ values increase and the two values become close to each other. At $C_p = 75.0$ g/L, $G'(\omega)$ and $G''(\omega)$ values are of the same order of magnitude and they are nearly parallel at low and intermediate frequencies, the solutions exhibiting significant elastic properties. The magnitude of $G'(\omega)$ at a moderate ω value is related to the density of mechanically active junctions^[44]. Thus, the increase in $G'(\omega)$ indicates an increase in the number of micelle bridges caused by an increase in interpolymer associations. On the other hand, the increase in $G''(\omega)$ indicates an increase in the effective volume occupied by the network structure in solution. At $C_p = 75.0$ g/L, the slope of the $G'(\omega)$ plot is rather flat, exhibiting gel-like behavior^[44]. The elastic properties in the concentrated regime arise from a larger number of bridging polymer chains that are mechanically active.

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