Synthesis, Viscosity Behavior, and Interactions with a Surfactant of Some Amphiphilic Copolymers of Diallyldimethylammonium Chloride and Diallyldodecyl- or Diallyloctadecyl-Ammonium Chloride

Shaikh A. Ali,[1] A. M. El-Shareef,[2] H. A. Al-Muallem[1]

[1]*Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*
[2]*Department of Chemistry, Dammam Girl's College, Dammam 31113, Saudi Arabia*

ABSTRACT: The copolymerization of hydrophobic monomers, diallyldodecyl- or diallyloctadecyl-ammonium chloride, with hydrophilic monomer diallyldimethylammonium chloride in dimethyl sulfoxide using azobisisobutyronitrile (AIBN) as the initiator afforded a series of water-soluble cationic polyelectrolytes (CPE) containing various proportions (0–16 mol %) of the hydrophobes. A polymer concentration (C^*_{HA}) of 0.5 g/dL was required for the manifestation of hydrophobic associations in some of these copolymers containing the C_{18} pendents. This is a notable improvement over the C^*_{HA} values (ca. 15–17 g/dL) for the associating polymers having a $\sim C_{10} - C_{14}$ pendents. At a shear rate of 0.36 s^{-1} at 30°C, salt-free water solutions of the CPEs (4 g/dL) containing 8 mol % of the C_{12} hydrophobes and 3.6, 7.6, 15.5 mol % of C_{18} hydrophobe have apparent viscosity values of 780, 6000, 956,000, and 1,100,000 cps, respectively. Considerable increase in the viscosity values of the CPE was observed in the presence of the surfactant cetyltrimethylammonium bromide (CTAB). The superior viscosity behavior for the polymers containing the C_{18} hydrophobe in comparison with C_{12} is attributed to the longer pendent-length of the former hydrophobe, which can efficiently undergo association from a distance far enough that minimizes interchain repulsion between the like charges. The CPEs containing the hydrophobes were found to be a better inhibitor of the corrosion of mild steel in 1M HCl at 60°C. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3256–3265, 2008

Key words: viscosity; association; water-soluble polymers; polymerization; surfactants; corrosion inhibition

INTRODUCTION

Hydrophobically associating water-soluble polymers, by virtue of their interesting solution properties, are becoming increasingly important to the industries.[1,2] The copolymerization of a water-soluble monomer with a few mole percent of a hydrophobic comonomer in a homogeneous solution affords amphiphilic polymers with random distribution of the hydrophobes as isolated units. However, the micellar copolymerization systems[2] involving a hydrophilic monomer ($\sim$ 3 wt %) in a continuous water phase and hydrophobic monomer inside the micelles favor a random distribution of the hydrophobes as small blocks in the hydrophilic polymer chains.[3–7] Above a hydrophobic association concentration (C^*_{HA}), these polymers form a reversible three-dimensional physical crosslinks of polymer chains, which are responsible for the superior viscosity behavior of the microblocky polymers derived from miceller process in comparison with the random polymers that exhibit largely intramolecular associative behavior.[8–11] The shear thinning or thixotropy behavior associated with the reversible nature of these physical crosslinks led to their applications in water-borne coatings, paints, cosmetics, and enhanced oil recovery.[12–16] In contrast to polymers containing neutral hydrophilic acrylamide and neutral hydrophobic derivative of acrylamide, the presence of ionic sites of similar charges along the hydrophilic backbone of associating polyelectrolytes leads to a great variety of behaviors.[17] Ion-containing polyacrylamides usually require a higher hydrophobe content or the presence of an added salt to manifest effective interchain associations.[18–20]

The discovery of the polymerization of *N,N*-diallyl quaternary ammonium salts **1** by Butler and Ingley[21,22] via an intra- and intermolecular chain propagation through a five-membered cyclic structure and subsequently, their copolymerization with sulfur dioxide[23] led to the synthesis of an array of linear water-soluble cationic polyelectrolytes (CPE)[24] **2** and **3** of tremendous scientific and technological interest. There are reports[25–31] that describe the synthesis of associating ionic copolymers prepared by Butler's polymerization technique. Previous ki-
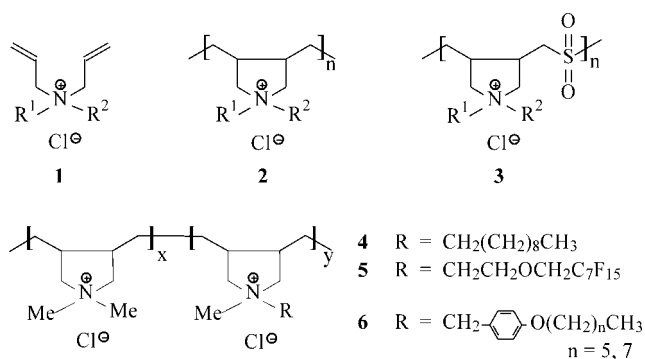
Scheme 1 Butler's polymerization technique[21] for the conversion of diallylammonium salts **1** to an array of water-soluble cationic polyelectrolytes **2** and sulfur dioxide copolymers **3**.

netic studies[32] have indicated that a monomer concentration of 50–65 wt % is required to obtain polymers with high conversion, high molecular weight, and low residual double bonds. The polymerization of hydrophilic and hydrophobic diallyl monomers in such high concentrations has been reported to yield random rather than microblocky copolymers even though the hydrophobic monomer possesses surfactant properties.[26] In a series of copolymers **6** (Scheme 1) with the hydrophobic contents 3–30 mol %, it was found that the intrinsic viscosities continuously decrease with increasing hydrophobic content, which indicates that the copolymers formed mainly intramolecular hydrophobic associations.[25] The copolymers **4** and **5** with a hydrophobe content of 8.22 mol % were found[26,27] to have an undesirable and fairly high C^*_{HA} (16 wt %) when compared with the hydrophobically associating nonionic copolymers of acrylamide (C^*_{HA} < 1%). Note that the lengths of the hydrophobic pendants in copolymers **4**, **5**, and **6** (n = 7) are equivalent to 10, 11, and 14 CC bonds, respectively. (The length of the benzene ring is considered as equivalent to four CC bonds). It is expected that an increase in the pendant-length would lead to an efficient and increased association from a distance far enough that would minimize

interchain repulsion between the like charges. In our study of ionic polymers, we report the synthesis and compare the solution properties of amphiphilic copolymers **10** and **11** derived from copolymerization of the hydrophilic monomer (M_1) **7** and comonomers (M_2) **8** and **9** having different chain length of hydrophobes (Scheme 2).

It is also one of our important objectives to study the inhibitive effect of the associating copolymers of the types of **10** and **11** for the first time on the corrosion of mild steel in acidic medium. The study of corrosion of mild steel and iron is of both theoretical and practical concern.[33,34] Corrosion inhibitors are widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing to restrain the corrosion attack on metallic materials.[35–37] It is known that polymers are adsorbed stronger than their monomer analogs;[38] the polyvinyl pyridine[39] or alkylaniline/formaldyde oligomers[40] are demonstrated to be far more superior to their monomers in corrosion inhibition. The improved performances of the polymeric materials are ascribed to their multiple adsorption sites for bonding with the metal surface. In this work, we intend to examine the effect of hydrophobic pendents, which can cover a larger area of the metal surface, on the inhibition of mild steel corrosion in acidic environment.

EXPERIMENTAL

Physical methods

Elemental analysis was carried out on a EuroVector Elemental Analyzer Model EA3000 (Milan, Italy). ^{1}H-NMR spectra of the polymers were measured in D_2O and CD_3OD (using TMS as internal standard) on a JEOL LA 500 MHz spectrometer (Tokyo, Japan). Viscosity measurements were made with an Ubbelohde viscometer (Schott-Gerate, Gmbh, Hofheim, Germany) (having Viscometer Constant of 0.005718 cSt/s at all temperatures). Digital Brookfield rotational viscometer (Middleboro, MA) with UL adaptor accessories or SC4-18 spindle accessories was
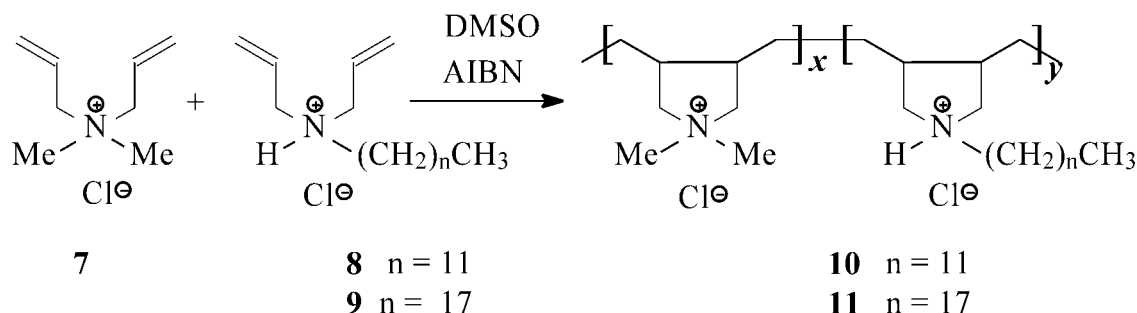
Scheme 2 The synthesis of amphiphilic copolymers **10** and **11** derived from copolymerization of hydrophilic monomer (M_1) **7**/hydrophobic comonomers (M_2) **8** and **9**.

TABLE I
Copolymerization[a] of the Monomers 7/8 and 7/9

Entry no.	Sample	DMSO (g)	7 (mmol)	8 (mmol)	9 (mmol)	Feed[b] $M_1 : M_2$	Polymer[b] $M_1 : M_2$	Yield (%)	$[\eta]$[c] (dL/g)	$10^{-4} \overline{M}_{w,app}$
1	**10**-M$_2$-0	6.5	25.0	0	–	100 : 0	100 : 0	88	0.581	6.50
2	**10**-C$_{12}$-3	6.5	23.75	1.25	–	95 : 5	97 : 3.0 (±0.3)	80	0.503	6.65
3	**10**-C$_{12}$-6.1	6.5	22.5	2.50	–	90 : 10	94 : 6.1 (±0.2)	82	0.436	6.75
4	**10**-C$_{12}$-8	6.5	21.25	3.75	–	85 : 15	92 : 8.0 (±0.4)	68	0.219	6.71
5	**10**-C$_{12}$-9.8	9.5	21.25	3.75	–	85 : 15	90.2 : 9.8 (±0.5)	52	0.0804	7.10
6	**11**-C$_{18}$-1.6	6.5	24.25	–	0.75	97 : 3	98.4 : 1.6 (±0.1)	87	0.402	6.80
7	**11**-C$_{18}$-3.6	6.5	23.5	–	1.5	94 : 6	96.4 : 3.6 (±0.3)	88	0.394	7.02
8	**11**-C$_{18}$-7.6	6.5	22.5	–	2.5	90 : 10	92.3 : 7.6 (±0.2)	85	Insoluble	7.11
9	**11**-C$_{18}$-10	6.5	21.25	–	3.75	85 : 15	90.0 : 10.0 (±0.7)	83	Insoluble	7.43
10	**11**-C$_{18}$-15.5	10.5	20.0	–	5.0	80 : 20	84.5 : 15.5 (±0.8)	76	Insoluble	7.35

[a] Polymerization reactions were carried out in DMSO in the presence of AIBN (125 mg) at 62°C for 48 h.
[b] mol % in the feed and polymer (as determined by ^{1}H-NMR).
[c] Intrinsic viscosity by extrapolation of the linear parts of the viscosity plots usually in the range 0.25–0.031% polymer solution 0.1N NaCl at 30°C (measured with an Ubbelohde viscometer ($K = 0.005718$).

used to measure apparent viscosities at various shear rates and temperatures.

Molecular weights of the samples were determined by light-scattering experiments at 21°C. Solutions of the CPE **10** containing no hydrophobe ($y = 0$) (polymer concentration range: 0.03–0.1 g/dL) were prepared in 0.5M NaCl solution; the presence of salt allows the screening of the positive charges to minimize ionic interactions and allow the polymer chains to form random coils. Methanol, which is helpful in disrupting hydrophobic associations, was used as a solvent for the hydrophobically modified polymers. Millipore disposable filters (Billerica, MA) of pore sizes 0.2 and 0.02 μm were used to remove dust particles from the polymer solutions and pure solvent, respectively. Corrections were made for the concentration of the polymer solution after filtration to account for screened polymer by the filtration media. Measurements were performed on each solution immediately after filtration. Static light scattering (SLS) experiments were performed using DAWN EOS light-scattering instrument (Wyatt Technology, Santa Barbara, CA). The system light source was a linearly polarized gallium arsenide (GaAs) laser. The laser is positioned so that the incident beam was vertically polarized. A RFM-340 Refractometer (Bellingham and Stanley, Kent, UK) was used to measure the differential refractive indices (dn/dc) of different polyelectrolyte solutions. Molecular weight determination of the hydrophobically modified polymers was complicated owing to hydrophobic associations. As a result, we can expect that the light scattering measurements lead to an apparent molecular weight, $M_{w,app}$ rather than true molecular weight.

Materials

2,2′-Azobisisobutyronitrile (AIBN) from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization from a chloroform-ethanol mixture. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64–65°C (4 mmHg). All glasswares were cleaned using deionized water. Diallyldimethylammonium chloride (**7**) (65 wt % in water), obtained from Aldrich (St. Louis, MO), was freeze-dried and crystallized (acetone/methanol). The hydrophobic monomers **8** and **9** were prepared as described.[28] t-Butylhydroperoxide (80% in ditertiarybutylperoxide) from Fluka Chemie AG (Buchs, Switzerland) was used as received.

General procedure for the copolymerization of 7/8 and 7/9 in DMSO using AIBN as the initiator

All polymerizations were carried out using conditions as described in Table I. In a typical experiment, the components were taken in a 25-cm^3 round-bottomed flask. The required amount of initiator (as listed in Table I) was then added under N$_2$ and the closed flask was stirred using a magnetic stir bar at 62°C for 48 h. The reaction mixture was homogeneous. The stir bar stopped moving after 1–3 h. Toward the end, the reaction mixture was turned into an opaque solid mass. The polymer was dissolved in methanol and precipitated (twice) in acetone. The white polymer was dried under vacuum at 55°C to a constant weight of the copolymer **10** or **11**.

Elemental analyses and apparent molecular weight of the CPEs 10 and 11

The elemental analyses supported the compositions of the copolymers as determined by ^{1}H-NMR spectroscopy (*vide infra*). The analyses for a few samples of CPEs **10**.1H$_2$O [(C$_8$H$_{18}$ClNO)$_x$(C$_{18}$H$_{38}$ClNO)$_{1-x}$] and **11**.1H$_2$O [(C$_8$H$_{18}$ClNO)$_x$(C$_{24}$H$_{50}$ClNO)$_{1-x}$] were

as follows (the numbers in parentheses represent calculated values, where $x \leq 1$): **10**-M$_2$-0: C, 53.1% (53.47%); H, 9.9% (10.10%); N, 7.6% (7.79%). **10**-C$_{12}$-8: C, 54.8% (54.60%); H, 10.0% (10.25%); N, 7.6% (7.52%). **11**-C$_{18}$-7.6: C, 54.7% (54.83%); H, 10.2% (10.28%); N, 7.6% (7.46%).

Apparent molecular weight ($M_{w,\text{app}}$) of the CPE **10** and **11** (associating polymers usually do not give true molecular weights) were determined and are listed in Table I.

Corrosion inhibition tests

Corrosion inhibition tests were performed as described[41] using coupons measuring $2.5 \times 2.0 \times 0.1$ cm^3 prepared from mild steel having the percent composition: 0.089 (C), 0.34 (Mn), 0.037 (Cr), 0.022 (Ni), 0.007 (Mo), 0.005 (Cu), 0.005 (V), 0.010 (P), 99.485 (Fe). A solution of $1M$ HCl was prepared from reagent ACS concentrated HCl (Fisher Scientific Company) using distilled water, which was deionized by passing through a deionizing column. The mild steel specimens were polished with increasing grades of emery papers (100, 400, 600, and 1500 grit size), and then degreased with acetone and washed with deionized water. The specimens were dried and kept in a desiccator. Inhibitor efficiency was determined at 60°C for 6 h by hanging the steel coupons into the acid solution (150 cm^3) containing various amounts [0 (blank), 5, 10, 25, and 400 ppm] of the polymers. After the elapsed time, the cleaning procedure consisted of wiping the coupons with a paper tissue, polishing lightly with emery paper, washing with distilled water, acetone, followed by oven drying at 110°C. Percent inhibition efficiency (%IE) was determined using the following equation:

$$\%\text{IE} = \frac{\text{Weight loss (blank)} - \text{Weight loss (inhibitor)}}{\text{Weight loss (blank)}} \times 100$$

Weight loss (blank) and weight loss (inhibitor) represent weight losses in absence and presence of inhibitor, respectively. Triplicate determinations were made with each of the polymers and with solutions containing no polymer. The average percent inhibition efficiency, reported in Table II, is found to have a standard deviation of 0.3–3.5%.

RESULTS AND DISCUSSION

Synthesis of copolymers and physical characterization

Monomers **7**(M$_1$)/**8**(M$_2$) or **7**(M$_1$)/**9**(M$_2$) were copolymerized successfully in DMSO using AIBN as initia-

TABLE II
Inhibition Efficiency for Different Concentrations of Compounds for the Inhibition of Corrosion of Mild Steel in $1M$ HCl Exposed for 6 h at 60°C

Copolymer	Inhibition efficiencies (%) at concentration (ppm) of polymers			
	5	10	25	400
M$_2$-0	70.4	82.0	82.3	83.8
10-C$_{12}$-3	76.4	86.6	91.9	94.1
10-C$_{12}$-6.1	77.5	84.4	92.2	94.3
10-C$_{12}$-9.8	80.9	89.4	94.2	94.5
11-C$_{18}$-1.6	83.8	90.9	91.6	95.2
11-C$_{18}$-3.6	82.3	87.0	93.6	94.3
11-C$_{18}$-7.6[a]	85.0	86.5	91.7	94.1
11-C$_{18}$-15.5[a]	75.9	87.2	89.3	92.1

[a] Partially soluble.

tor to give CPE **10** or **11**, respectively, in excellent yields (Scheme 2). However, we were unable to obtain the copolymers by carrying out the polymerization process in an aqueous medium as a result of the immiscibility of hydrophobic monomers **8** and **9** in the medium containing hydrophilic monomer **7**. Thus, the copolymerization of a mixture of (M$_1$+M$_2$) and water in a 65 : 35 wt ratio in the presence of 4 mol % t-butylhydroperoxide gave only a trace amount of polymer. The polymerization conditions in DMSO were kept similar as rigorously as possible to obtain polymers having similar degree of polymerization; similar polymer chain length would allow a comparative assessment of the associative behaviors of the synthesized polymers. The results of the polymerization, intrinsic viscosities, and apparent molecular weights of the resultant polymers are given in Table I. The Entry 1 in Table I describes the polymer M$_2$-0 indicating the absence of hydrophobic monomer **8** or **9** (M$_2$). The Entries 2–5 and 6–10 describe the incorporation of dodecyl-**8** and octadecyl- monomer **9**, respectively. The copolymer **11**-C$_{18}$-7.6 (Entry 8), for instance, indicates the incorporation of 7.6 mol % hydrophobic octadecyl monomer **9**. As evident from Table I, the hydrophobe incorporations did not match with the feed ratio; the mole percent hydrophobe incorporated in copolymers **10** or **11** was always found to be less than the mole percent present in the feed.

Copolymer composition

The copolymers were synthesized by varying the feed ratio of **7/8** or **7/9**. Figure 1(A,B) displays the ^{1}H-NMR spectrum of the M$_2$-0 and **10**-C$_{12}$-8. The incorporation of the hydrophobic monomers was calculated using integration of ^{1}H-NMR signals by the following two methods of calculation.
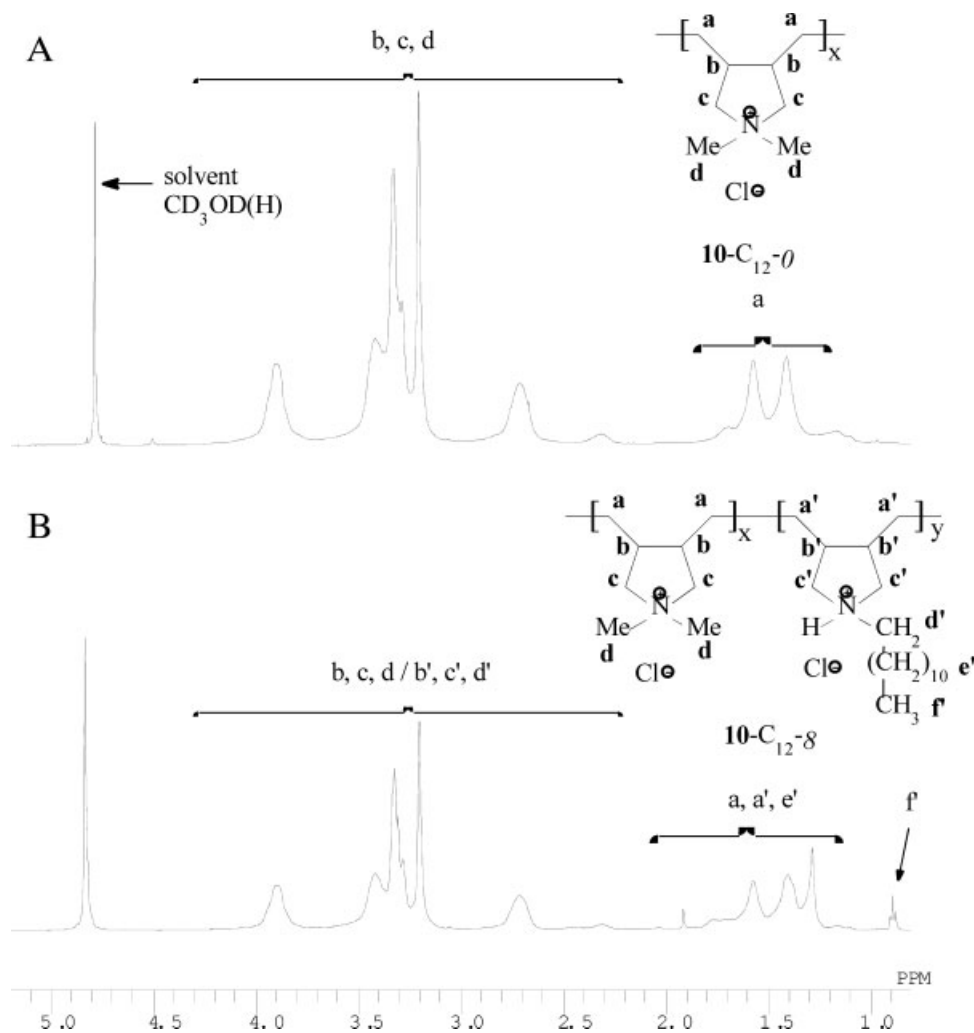
Figure 1 ^{1}H-NMR spectrum of CPE **10**-C$_{12}$-0 and **10**-C$_{12}$-8 in CD$_3$OD.

Method I

In ^{1}H-NMR spectra of polymers **10** in D$_2$O, the signals appearing at $<\delta$ 2.0 ppm are the four protons marked **a,** and 27 protons marked **a′, e′,** and **f′** (Scheme 3). So the integrated area (P) of the signals at $<\delta$ 2.0 ppm should belong to [(1-x)4 + 27x], i.e., (4 + 23x) protons. On the other hand, the signals appearing at $>\delta$ 2.0 ppm are the 12 protons marked **b, c,** and **d,** and eight protons marked **b′, c′,** and **d′.** As such the integrated area (Q) of the signals at $>\delta$ 2.0 ppm should belong to [(1-x)12 + 8x] i.e., (12 −
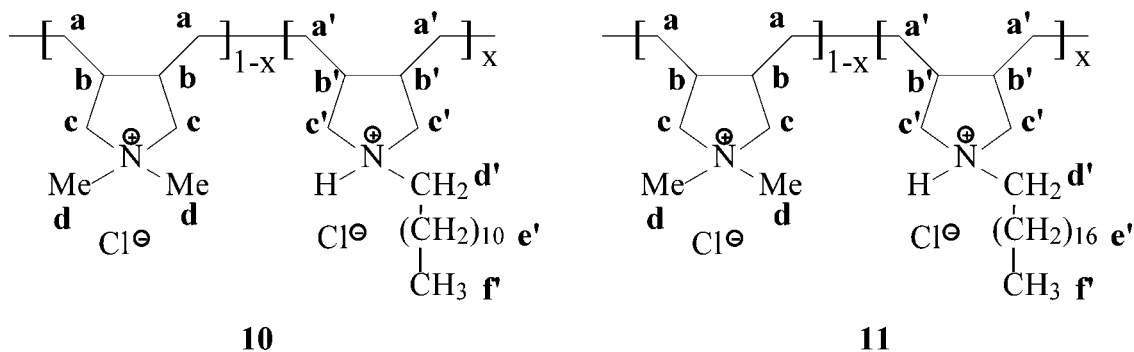
Scheme 3 Amphiphilic copolymers **10** and **11**.

4 x) protons. Equating the area for a single proton at $<\delta$ 2.0 and $>\delta$ 2.0 one would obtain

$$P/(4 + 23x) = Q/(12 - 4x),$$
$$\text{i.e.,} \quad x = (12P - 4Q)/(4P + 23Q) \tag{1}$$

Mole percent hydrophobe (i.e., $100x$) is obtained by solving eq. (1). Likewise, for the copolymer **11** having octadecyl hydrophobe, the eq. (1) is modified to eq. (2) as a result of an increase in the number of **e'** protons by 12.

$$x = (12P - 4Q)/(4P + 35Q) \tag{2}$$

Method II

In Method II, a simpler approach is taken. Even though the methyl protons of the hydrophobe chain-end appeared as an overlapping signal in D_2O, the spectrum of **10** in CD_3OD revealed the presence of CH_3 as a nonoverlapping signal at δ 0.89 (t, J 6.9 Hz) ppm. The rest of the polymer proton signals, like in D_2O, appeared at δ 1.0–4.0 ppm. The following protons, with number in parentheses, appeared at $<\delta$ 2.0 ppm: **a** (4H), **a'** (4H), **e'** (20H), and **f'** (3H) (Scheme 3).

For polymers having a C_{12} hydrophobe, the integrated area (M) at δ 0.89 belongs to 3H of methyl group (**f'**). As such the area of a single H belonging to the hydrophobe should equate to M/3. The area (T) under $>\delta$ 1.0 to $<\delta$ 2.0 ppm belongs to protons marked **a**, **a'**, and **e'**. If one subtracts the contribution of **e'** protons, which is 20M/3, then the total area for the **a** and **a'** protons [4(1-x) + 4x)], i.e., four protons becomes (T-20M/3). As such the area of a single proton belonging to the copolymer **10** becomes (T-20M/3)/4. Mole percent of the hydrophobe should then equate to 100 (M/3)/[(T-20M/3)/4]. Likewise, for the copolymer **11** containing C_{18} hydrophobe, the mole percent of the hydrophobe should be calculated as 100 (M/3)/[(T-32M/3)/4] since it has 32 protons marked as **e'**. The data from both methods agree favorably and are given in Table I along with the deviations.

Solubility and viscosity measurements

All synthesized polymers **10** and **11** were found to be soluble in salt-free water as well as methanol. All copolymers **10** containing the C_{12} hydrophobes as well as **11**-C_{18}-1.6 and **11**-C_{18}-3.6 were also soluble in 0.1N NaCl. However, copolymers **11** having higher mole percent of the C_{18} hydrophobe were found to be insoluble in 0.05 as well as 0.1N NaCl. The pK_a of an unit of tertiary amine salts **8** and **9** in the copolymers **10** and **11** is expected to be around 9.8 similar
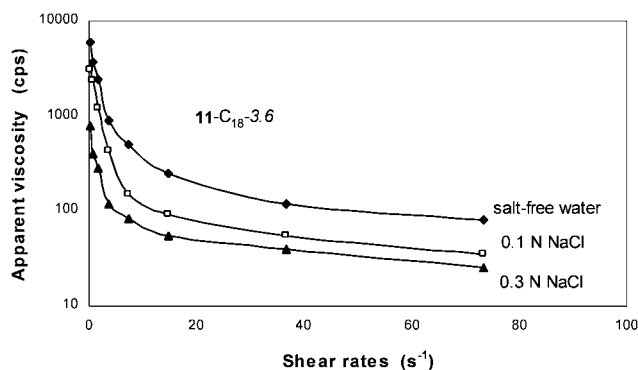
Figure 2 Variation of viscosity of a 4 g/dL solution of **11**-C_{18}-3.6 with the shear rates at various concentrations of NaCl at 30°C.

to that of trimethylamine hydrocholoride, the parent tertiary amine salt. Note that the hydrophobic units (i.e., **8** or **9**) in the copolymers are pH-responsive; as a result of being weak acids, they may dissociate to some extent to their corresponding trivalent amines. The pH of the copolymers in salt-free and salt (NaCl)-added solutions, however, was not controlled for the viscosity study. The reduced viscosity (η_{red}) of the polymer solutions at concentration $>C^*_{HA}$ increased exponentially, while at concentration $<C^*_{HA}$, η_{red} increased in a linear fashion (not shown in figure). Reduced viscosity, i.e., specific viscosity/concentration (η_{sp}/C), as a function of concentration was plotted according to the Huggins equation, and extrapolation of the linear part of the viscosity plots (η_{sp}/C vs. C) in the concentration (C) range 0.25–0.031 g/dL in 0.1N NaCl permitted us to determine the intrinsic viscosity [η] values of the polymers (Table I). The decreasing values of intrinsic viscosities with increasing hydrophobe concentration imply that these polymers form mainly intramolecular hydrophobic associations in dilute solutions as a result of random distribution of the hydrophobes (Table I).[31]

The effect of added NaCl on the viscosity of a 4 g/dL solution of **11**-C_{18}-3.6 and **10**-C_{12}-8 at various shear rates are displayed in Figures 2 and 3, respectively. The shielding of positive charges in the polymer chains by the added chloride ions leads to a decreased repulsion between the charges in the polymer chains and a compaction of the polymer coil. The presence of NaCl on the other hand makes the aqueous system more hostile to the hydrophobes and thus forces them to associate intermolecularly, and as a result the viscosity is expected to increase with increasing concentration of the added NaCl. In the case of **11**-C_{18}-3.6, the decrease of viscosity values with increasing concentration of NaCl implies the greater significance of polymer compaction by shielding than the hydrophobic associations in an
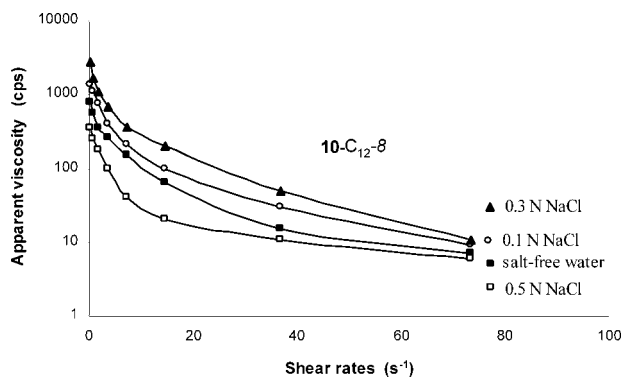
Figure 3 Variation of viscosity of a 4 g/dL solution of **10**-C_{12}-8 with the shear rates at various concentrations of NaCl at 30°C.

Figure 4 Variation of viscosity with concentration **11**-C_{18}-7.6 at various shear rates in salt-free water at 30°C (inset showing the variation in the lower concentration range).

environment increasingly hostile to the hydrophobes. The ineffective associations of hydrophobic groups in this case could be discussed in terms of critical micelle concentration similar to that for small-molecule surfactants. At low hydrophobe incorporation (3.6 mol %) and polymer concentration (4 g/dL), an insufficient number of hydrophobic groups are present on any individual polymer chain to form a stable ensemble. A contrasting salt effect was observed in the case of the polymer **10**-C_{12}-8. The viscosity values increase by changing the solvent from salt-free water to 0.1N and 0.3N NaCl, whereas it decreases and even falls below the viscosity in salt-free water upon further increasing the NaCl concentration to 0.5N. Figure 3 thus displays the role of added salt (NaCl) in an interesting demonstration of coil compaction as well as hydrophobic association. In the presence of added salt, the increase in viscosity correlates well with the known effects of NaCl on hydrophobic association.[42] The higher mole percent of hydrophobes in **10**-C_{12}-8 in comparison with **11**-C_{18}-3.6 leads to a greater significance of hydrophobic associations for the former polymer in 0.1 and 0.3N NaCl than the polymer compaction by shielding the cationic charges on the polymer chains. At the highest NaCl concentration (0.5N), further compaction of the polymer coil may encourage intramolecular micellization thereby decreasing the viscosity values.

Figures 4–6 display the variation of viscosity with concentration of **11**-C_{18}-7.6, **11**-C_{18}-15.5, and **11**-C_{18}-3.6, respectively, in salt-free water. As evident from Figure 4, the critical association concentration (C^*_{HA}) was found to be around a polymer concentration of 0.5 g/dL; changing the polymer concentration from 0.5 to 1 g/dL resulted in an increase in viscosity by a factor of 14 at a shear rate of 0.36 s^{-1}. The associative behavior of the polymers are more pronounced in the lower shear rate range as expected since higher shear rates lead to disruptions of hydrophobic associations. This observation is similar to that
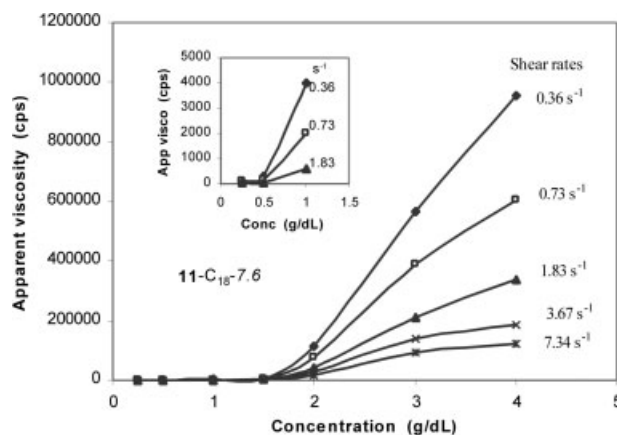
frequently observed for hydrophobically modified associative polymers.[4,43] The strong interchain associations form large aggregates (a network structure of polymer chains) as the polymer concentration passes C^*_{HA}. The network structures thus contribute significantly to the thickening. The C^*_{HA} for **11**-C_{18}-15.5 was also found to be around a polymer concentration of 0.5 g/dL (Fig. 5), however, the viscosity increase by changing the polymer concentration from 0.5 g/dL to 1 g/dL was found to be not as pronounced as in the case of **11**-C_{18}-7.6; viscosity rose by a factor of a meagre 3.3 at a shear rate of 0.36 s^{-1}. The internal micellization is more pronounced in **11**-C_{18}-15.5 because of its higher hydrophobe content than that in **11**-C_{18}-7.6. A gradual switchover from a mainly intra- to intermolecular associations in **11**-C_{18}-15.5, therefore, makes the viscosity increment less pronounced. The relatively high C^*_{HA} value of around 3 g/dL for the polymer **11**-C_{18}-3.6 (Fig. 6) is indicative of the presence of an insufficient
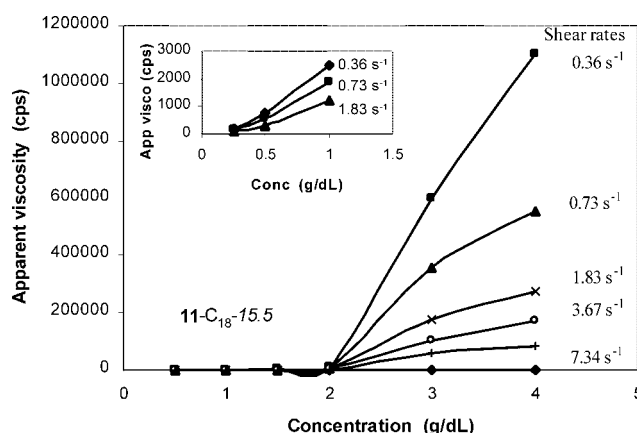
Figure 5 Variation of viscosity with concentration **11**-C_{18}-15.5 at various shear rates in salt-free water at 30°C (inset showing the variation in the lower concentration range).
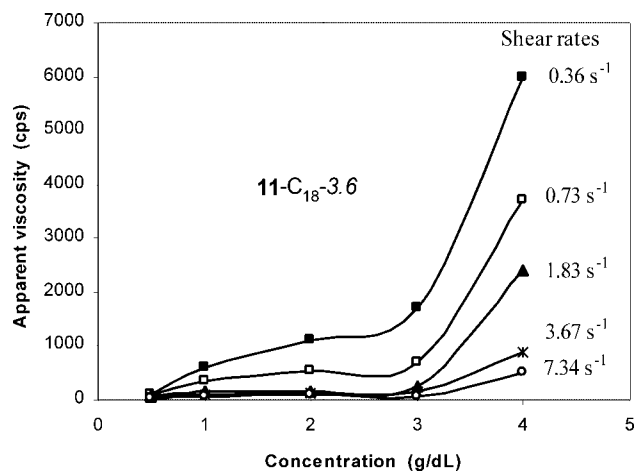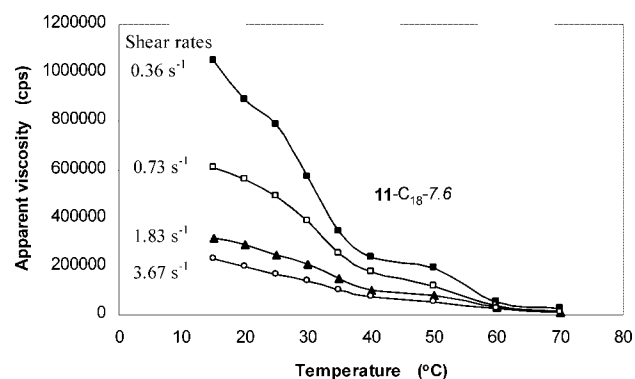
Figure 6 Variation of viscosity with concentration 11-C_{18}-3.6 at various shear rates in salt-free water at 30°C.

Figure 8 Variation of viscosity with shear rates of a 4 g/dL solution of 11-C_{18}-7.6, 11-C_{18}-15.5, 11-C_{18}-3.6, and 10-C_{12}-8 in salt-free water at 30°C.
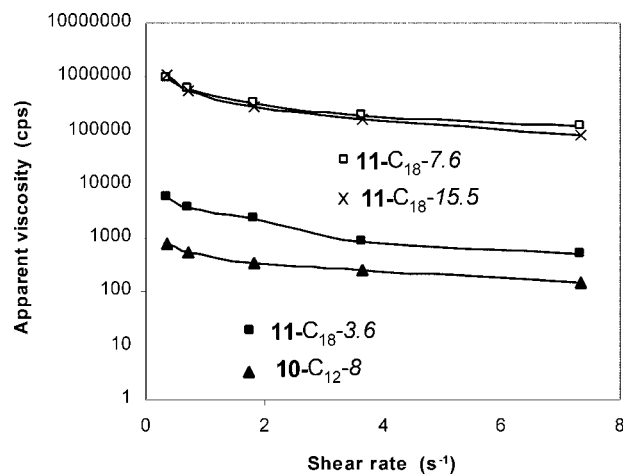
number of hydrophobic groups on any individual polymer chain to form a stable ensemble at concentrations of < 3 g/dL.

Figure 7 displays the effect of temperature on the solution viscosity of 3 g/dL solution of 11-C_{18}-7.6 in salt-free water. At higher temperatures, the viscosity decreases presumably as a result of changes in the hydration spheres of the hydrophobic groups or in the structure of water itself. The lowering of solution viscosity with increasing temperature has been reported for hydrophobically associating water-soluble polymers.[8,43,44] This effect could be attributed to the weakening of the hydrophobic effect at elevated temperatures due to the increased mobility of the polymer chains, which gives rise to loss of interchain liaisons and/or an increase in polymer solubility as the temperature increases.

Figure 8 displays the variation of viscosity of a 4 g/dL solution of 11-C_{18}-7.6, 11-C_{18}-15.5 11-C_{18}-3.6, and 10-C_{12}-8 at various shear rates in salt-free water at 30°C. The semilog plots reveal the increase in

viscosity values with the increase in the amount of hydrophobe incorporated in the polymers. The viscosity values for the 4 g/dL solutions of 10-C_{12}-8, 11-C_{18}-3.6, 11-C_{18}-7.6, and 11-C_{18}-15.5 in salt-free water at a shear rate of 0.36 s^{-1} were found to be 780, 6000, 956,000, and 1,100,000 cps, respectively. The C_{18}-7.6 polymer was thus found to have a higher viscosity than C_{18}-3.6 by a factor of 159; higher proportion of the hydrophobe thus leads to superior interchain associations. The viscosity values in a ratio of 1 : 1225 for the polymers C_{12}-8 versus C_{18}-7.6 thus demonstrate the importance of the length of the pendants in intermolecular hydrophobic associations. Both the polymers have similar mole percent of the hydrophobes ($\sim$8%), however, for the C_{18}-7.6, 18-C alkyl chain leads to an efficient and increased association from a distance far enough that minimizes interchain repulsion between the like charges. Note that the polymer 11-C_{18}-7.6 displayed slightly higher viscosity values than 11-C_{18}-15.5 at the higher shear rates, presumably as a result of an easier disruption of intramolecular micellizations for the former polymer containing the lesser amount of hydrophobe.

Polymer surfactant interactions

An interesting feature of amphiphilic polyelectrolytes with poor water solubility is that redissolution is greatly facilitated by addition of surfactants, which indicates the existence of surfactant/copolymer interactions such that surfactant micelles provide the solublization of the hydrophobic moieties of the amphiphilic polyelectrolyte. The interactions are driven by electrostatic attraction and/or association of the hydrophobic groups on the polymers and those of the surfactant molecules. The polymer

Figure 7 Variation of viscosity of a 3 g/dL solution of 11-C_{18}-7.6 with the shear rates at various temperatures in salt-free water.

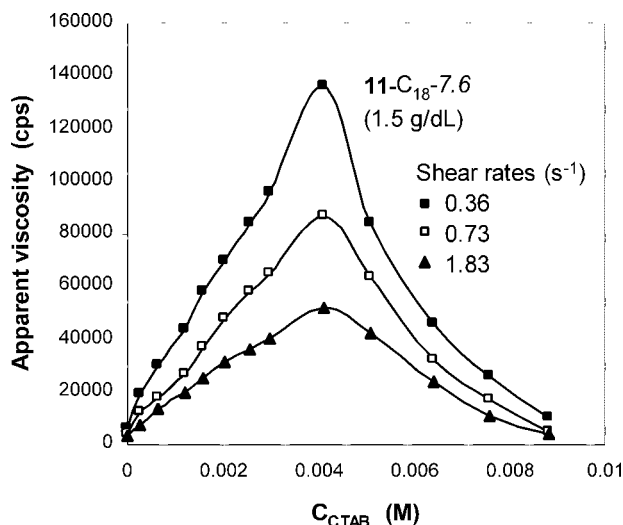**Figure 9** Variation of viscosity with CTAB concentrations of a 1.5 g/dL solution of **11**-C_{18}-7.6 at different shear rates at 30°C in salt-free water.

surfactant interaction was examined using viscometric measurements on copolymer C_{18}-7.6 (Entry 8, Table I) in the presence of cationic cetyltrimethylammonium bromide (CTAB) surfactant. Figure 9 illustrates the viscosity behavior of a 1.5 g/dL solution of C_{18}-7.6 in the presence of cationic surfactant CTAB at various shear rates. Upon the addition of CTAB above its critical micelle concentration (CMC) 9.2×10^{-4} M, the solution of **11**-C_{18}-7.6 became more viscous which indicates the existence of surfactant/polymer interactions. The copolymer is sufficiently hydrophobic to overcome competitive ionic repulsion effects, promoting the bridging micelle formation. This interaction of CPE with surfactant of like charge (CTAB) is rather unusual, but it is not unique. An interaction in aqueous solutions of hydrophobically modified polyelectrolytes with surfactants of the same charges has been recently reported.[45] Upon further increase in the CTAB concentration, the viscosity continues to increase, suggesting a gradual polymer restructuring and formation of mixed micelle domains which contain hydrophobic groups belonging to two or more distinct polymer chains. The addition of surfactants to hydrophobically modified polymers solutions can increase the viscosity of polymer solutions, provided comicellization between the polymer and surfactant provides bridging between the polymer chains.[46] Further increase in concentration of CTAB leads to the formation of more micelles and the number of micelles per polymer-bound hydrophobe increases and this eventfully disfavors comicellar bridge thus resulting in a decrease of viscosity values. In this case of the C_{18}-7.6 polymer solution (1.5 g/dL) having a hydrophobe concentration of 0.0058M, the

maximum occurs at a surfactant concentration of 0.0041M.

Corrosion inhibition study

Corrosion inhibition performance of the synthesized polymeric materials, evaluated using weight loss of mild steel in 1M HCl at 60°C for 6 h, is shown in Table II. As is evident from the table, all the copolymers **10** and **11** containing hydrophobes ($y \neq 0$) demonstrated superior inhibition effects than the homopolymer M_2-0, i.e., **10** or **11** ($y = 0$). An $\sim 10\%$ increase in the inhibition efficiencies of hydrophobically modified copolymers **10** and **11** versus M_2-0 (Table II) in the studied concentration range is indeed a reflection of the superior ability of the hydrophobically modified copolymers to cover, hence, protect the metal surface from corrosive attack.

CONCLUSIONS

The hydrophobe incorporation has considerably enhanced the viscosity values in the copolymers. In earlier works,[25–27] the electrostatic repulsive forces between the positively charged polymer chains did not permit them to move to a safer distance required for the pendents of 10, 11, and 14 CC bonds in the copolymers **4–6** (*vide supra*) to manifest interchain bridging (associations) in the semidilute regime. The shorter pendent-lengths may be the reason for the lower degree of association and very high C^*_{HA} values of 15–17 g/dL for the polymers **5** and **6**.[27] Such a very high concentration of polymers demands the presence of equivalent amount of chloride counterions, which can effectively shield the positive charges on the chains thereby allowing them to approach close enough for interchain bridging. The octadecyl pendents ($C_{18}H_{37}$) in the copolymers **11**, on the other hand, can associate intermolecularly (at a polymer concentration of ~ 0.5 g/dL) because the extended length of the pendents allows them to mingle with each other without exposing the chains to experience the adverse effects of electrostatic repulsions. The low C^*_{HA} (~ 1 g/dL) observed for the C_{18} polymer series is indeed a notable improvement over the C^*_{HA} values for the reported associating polymers.[27] The corrosion inhibition tests using gravimetric method, a simple yet reliable method, demonstrated the better inhibition efficiency of the hydrophobic copolymers. One of the important features of the copolymers **10** and **11** is the presence of amine salts **8** and **9** as the hydrophobes instead of ammonium salts in which the nitrogen valency is quenched. Upon basification, the hydrophobic units will be transformed to trivalent basic nitrogens, which may potentially be a better inhibitor in neutral

corrosive brine solutions as a result of the interaction of the nitrogen lone pair with metal *d*-orbitals. It would be interesting to investigate in a future work the effect of pH on the viscosity behavior of the copolymers.

References

1. Glass, J. E., Ed. Polymers in Aqueous Media: Performance Through Association; American Chemical Society: Washington, DC, 1989; Vol. 223: Advances in Chemistry.
2. Candau, F.; Selb, J. Adv Colloid Interface Sci 1999, 79, 149, and references cited therein.
3. Hill, A.; Candau, F.; Selb, J. Macromolecules 1993, 26, 4521.
4. Volpert, E.; Selb, J.; Candau, F. Macromolecules 1996, 29, 1452.
5. Ezzell, S. A.; McCormick, C. L. Macromolecules 1992, 25, 1881.
6. Candau, F.; Bigg, S.; Hill, A.; Selb, J. Prog Org Coat 1994, 24, 11.
7. Regalado, E. J.; Selb, J.; Candau, F. Macromolecules 1999, 32, 8580.
8. Sohel, S.; Ali, S. A.; Hamad, E. Z. J Polym Eng Sci 1999, 39, 1962.
9. Yahaya, G. O.; Ahdab, A. A.; Ali, S. A.; Hamad, E. Z.; Abu-Sharkh, B. F. Polymer 2001, 42, 3363.
10. Dowling, K. C.; Thomas, J. K. Macromolecules 1990, 23, 1059.
11. Biggs, S.; Hill, A.; Selb, J.; Candau, F. J Phys Chem 1992, 96, 1505.
12. Winnik, M. A.; Yekta, A. Curr Opin Colloid Interface Sci 1997, 2, 424.
13. Glass, J. E., Ed. Hydrophilic Polymers: Performance with Environmental Acceptability; Washington, DC: American Chemical Society, 1996; Vol. 248: Advances in Chemistry Series.
14. Glass, J. E., Ed. Associating Polymers in Aqueous Solution; Washington, DC: American Chemical Society, 2000; ACS Symposium Series 765.
15. Hester, R. D.; Squire, D. R. J. J Coat Technol 1997, 69, 109.
16. Taylor, K. C.; Nasr-El-Din, H. A. J Pet Sci Eng 1998, 19, 265.
17. Kujawa, P.; Rosiak, J. M.; Selb, J.; Candau, F. Macromol Chem Phys 2001, 202, 1384, and references cited therein.
18. McCormick, C. L.; Middleton, J. C.; Cummins, D. F. Macromolecules 1992, 25, 1201.
19. Branham, K. D.; Snowden, H. S.; McCormick, C. L. Macromolecules 1996, 29, 254.
20. Yang, Y.; Schulz, D.; Steiner, A. Langmuir 1999, 15, 4335.
21. Butler, G. B.; Ingley, F. L. J Am Chem Soc 1951, 73, 895.
22. Butler, G. B. J Polym Sci Part A: Polym Chem 1996, 34, 913.
23. Ali, S. A.; Ahmed, S. Z.; Wazeer, M. I. M.; Hamad, E. Z. Polymer 1997, 38, 3385.
24. Butler, G. B. Cyclopolymerization and Cyclocopolymerization; Marcel Dekker: New York, 1992.
25. Chang, Y.; McCormick, C. L. Polymer 1994, 35, 3503.
26. Butler, G. B.; Do, C. H. In Water-Soluble Polymers; Shalaby, W.; McCormick, C. L.; Butler, G. B., Eds.; American Chemical Society: Washington, DC, 1991; ACS Symposium Series 467, p 151.
27. Gopalkrishnan, F. S.; Butler, G. B.; Hogen-Esch, T. E.; Zhang, N. Z. In Water-Soluble Polymers; Shalaby, W.; McCormick, C. L.; Butler, G. B., Eds.; American Chemical Society: Washington, DC, 1991; ACS Symposium Series 467, p 175.
28. Umar, Y.; Al-Muallem, H. A.; Abu-Sharkh, B. F.; Ali, S. A. Polymer 2004, 45, 3651.
29. Ali, S. A.; Umar, Y.; Abu-Sharkh, B. F. J Appl Polym Sci 2005, 97, 1298.
30. Umar, Y.; Abu-Sharkh, B. F.; Ali, S. A. J Appl Polym Sci 2005, 98, 1404.
31. Umar, Y.; Abu-Sharkh, B. F.; Ali, S. A. Polymer 2005, 46, 10709.
32. Boothe, J. E.; Flock, H. G.; Hoover, M. F. J Macromol Sci Chem 1970, 4, 1419.
33. Uhlig, H. H.; Revie, R. W. Corrosion and Corrosion Control; Wiley: New York, 1985.
34. Sastri, V. S. Corrosion Inhibitors, Principles and Application; Wiley: Chichester, 1998.
35. Mernari, B.; Elattari, H.; Traisnel, M.; Bentiss, F.; Lagrenee, M. Corros Sci 1998, 40, 391.
36. El-Achouri, M.; Kertit, S.; Gouttaya, H. M.; Nciri, B.; Bensouda, Y.; Perez, L.; Infante, M. R.; El-Kacemi, K. Prog Org Coat 2001, 43, 267.
37. Frenier, W. W.; Growcock, F. B. Review on Corrosion Science and Technology; Raman, A.; Labine, P., Eds.; NACE International: Houston, TX, 1993; p 11.
38. Ulman, R. Encyclopedia of Polymer Science and Technology; Mark, H. F.; Gaylord, N. G.; Bikales, N. M., Eds., Interscience: New York, 1964; Vol. 1, p 558.
39. Annand, R. R.; Hurd, R. M.; Hackerman, N. J Electrochem Soc 1965, 112, 138.
40. Bacskai, R.; Schroeder, A. H.; Young, D. C. J Appl Polym Sci 1991, 42, 2435.
41. Ali, S. A.; El-Shareef, A. M.; Al-Ghamdi R. F.; Saeed, M. T. Corros Sci 2005, 47, 2659.
42. Saito, S. J Polym Sci Part A-1: Polym Chem 1969, 7, 1789.
43. Kopperud, H. M.; Hansen, F. K.; Nystrom, B. Macrmol Chem Phys 1998, 199, 2385.
44. Tanford, C. The Hydrophobic Effect; Wiley: New York, 1980.
45. Puspendu, D.; Steffen, J.; Francesca, M. O.; Alberto, M.; Nicholas, J. T.; Somasundaran, P. Langmuir 2003, 19, 10747.
46. Johnson, K. M.; Fevola, M. J.; McCormick, C. L. J Appl Polym Sci 2004, 92, 658.