Copolymerization of Hydrophilic and Hydrophobic 1-Alkyl-4-vinylpyridinium Monomers

Yue Xin, Ying Hu, Martel Zeldin, and Wilmer K. Fife*

Department of Chemistry, Indiana University–Purdue University at Indianapolis, 1125 East 38th Street, Indianapolis, Indiana 46205

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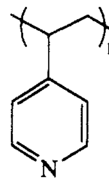
ABSTRACT: Copolymerization of a hydrophilic 1-ethyl-4-vinylpyridinium ion with a hydrophobic 1-dodecyl-4-vinylpyridinium ion was achieved for the first time in aqueous media when initiated by $S_2O_8^{2-}/S_2O_5^{2-}$ in inverse microemulsions of hexane, water, and isoamyl alcohol (26:8:1 by weight). Attempted copolymerization of the *N*-ethyl and *N*-dodecyl monomers in the absence of isoamyl alcohol produced a mixture of the related homopolymers. Similar efforts to obtain copolymers from hydrophilic and hydrophobic 1-alkyl-1-vinylpyridinium ions in aqueous suspensions or micellar media using sonication or radical initiators were also unsuccessful. The initiators included neutral, lipophilic, cationic, and anionic radicals. Only homopolymers were obtained, frequently only the one derived from the hydrophobic monomer. Significantly, copolymers were readily obtained under all conditions when mixtures of two hydrophobic monomers (e.g., *N*-octyl and *N*-dodecyl) or two hydrophilic monomers (e.g., *N*-methyl and *N*-ethyl) were used. In contrast, copolymerization of any pair of monomers was observed when polymerization was carried out thermally in melts or with radical initiation in solution.

Introduction

The research was initiated in response to our interest in water-soluble polymers whose structure in aqueous solution can be controlled by hydrophobic forces. Poly(4-vinylpyridine) (P4VP, 1) and its *N*–alkyl derivatives, 2, are well-known, versatile polymeric materials of which some family members exhibit the requisite behavior.[1] The great variety of possible structural variants of 2 and corresponding differences in their solution behavior make these substances extremely important targets for study as polyelectrolytes, surfactants, and enzyme mimics.[1–6]



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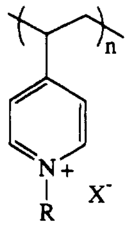

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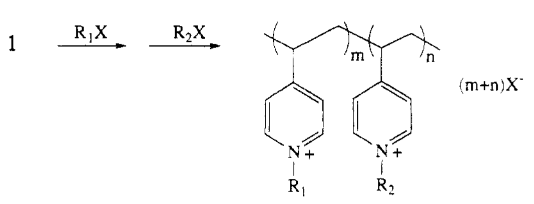
Many years ago Strauss and co-workers investigated the solution properties of copolymer 3, a polysoap which contained dodecylated and ethylated pyridine residues.[1] Polysoaps belong to a class of compounds that may express the features of both polyelectrolytes and micelles in a single macromolecule. When 3 contains 60–90% of its pyridine residues ethylated to provide polyelectrolyte properties (i.e., high charge density and water solubility) and 40–10% of its pyridine residues dodecylated, the macromolecule self-organizes in water to form intramolecular, hydrophobic domains that behave similar to micelles formed from simple surfactants.[1] The organized structure of 3 in water appears to provide an interesting mosaic of different microenvironments with regions of high charge density at the polymer–water interface and hydrocarbon domains with compact hydrophobic cores.[1,5–8] The propensity for structural organization has been utilized in several recent studies to model for enzyme-like behavior in promoting hydrolysis of *p*-nitrophenyl esters.[2,6,9]

The synthesis of 2 and 3 via alkylation of 1 (eq 1) is a well-known process. Since alkylation occurs randomly, there is limited control over polymer structure, especially the relative abundance and sequential arrangement of the different monomer components in copolymer 3. Furthermore, samples of 2 and 3 are likely to contain varying numbers of unalkylated pyridine residues[1,9] which may influence polymer properties. The potentially important alternative route to 2 and 3 via polymerization of 1-alkyl-4-vinylpyridinium salts, 4 (eq 2), assures fully alkylated homo- and copolymers. More importantly, this route offers the possibility for better control over proportions and sequential orientations of two or more monomers in copolymer 3. Control of the structure, particularly the monomer sequence and mole fractions of the different *N*-alkyl groups as well as the structure of the alkyl groups, is expected to provide an important basis for control over solution properties exhibited by 3, much like amino acid sequence controls the structure and performance of proteins.



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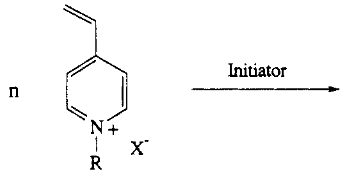

(2)

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(a) R = CH_3, X = TfO^-
(b) R = C_2H_5, X = TfO^-
(c) R = C_4H_9, X = TfO^-
(d) R = C_6H_{13}, X = TfO^-
(e) R = C_8H_{17} X = TfO^-
(f) R = $C_{12}H_{25}$ X = TfO^-

Prior to this study[10] there had been no literature precedent for copolymerization of different 1-alkyl-4-vinylpyridinium salts. However, the homopolymerization of 4-vinylpyridinium and 1-methyl-4-vinylpyridinium salts has received extensive attention in the literature.[11] Reports of the polymerization mechanism have been vague and contradictory which is undoubtedly a consequence of the complexity of the chemistry.[11,12] For example, polymerization may follow multiple paths subject to a variety of initiation mechanisms. Spontaneous polymerizations have often been observed, and they have been attributed to anionic (zwitterion) or free-radical propagation mechanisms. Polymerization is also reported to be sensitive to monomer concentration, ionic strength, elevated temperatures, and light.[11-13] This paper will focus on an investigation of the conditions required to copolymerize hydrophilic and hydrophobic 1-alkyl-4-vinylpyridinium monomers in aqueous media. Particularly noteworthy is the demonstration of copolymerization of positively charged hydrophobic and lipophilic monomers 4 in inverse microemulsions. Copolymerization of hydrophobic and lipophilic 4 in melts and solutions was also studied.

Experimental Section

All reagents and solvents used in this study were commercial materials. Samples of 4-vinylpyridine (Reilly Industries), trifluoromethanesulfonic anhydride (triflic anhydride), ethyl triflate, dimethyl sulfate, 1-butanol, 1-hexanol, 1-octanol, 1-dodecanol, pyridine, *m*-chloroperoxybenzoic acid, sodium metabisulfite, ammonium persulfate, 2,2′-azobis(isobutyronitrile), 4,4′-azobis(4-cyanovaleric acid), 2,2′-azobis(2-amidinopropane)·HCl, lauroyl peroxide, 1-dodecylpyridinium chloride, and sodium 1-dodecyl sulfate were used as received. The monomer, 1-methyl-4-vinylpyridinium methyl sulfate, was prepared by the method of Salamone.[14] Details for synthesis of the other monomers and alkyl triflates have been reported previously,[15] but the physical properties and analytical data of compounds new to this study are given below. Melting points were taken (uncorrected) on a Thomas–Hoover apparatus. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained with Varian EM 390 and GE QE 300 instruments, respectively. Dialysis was carried out by using Spectra/Por 1 porous dialysis membranes from Spectrum (6000–8000 MWCO), and samples were dialyzed against four changes of water for 4 days. Sonication of reaction mixtures was carried out with a Heat Systems W 385 sonicator equipped with $^1/_8$-in. standard tapered microtip probe. Lyophilization was done on a VIRTIS 10-324 freeze dryer. Structural characterization of copolymers was attempted by pyrolysis/tandem MS–MS using a Finnigan TSQ 700 mass spectrometer by Professor R. G. Cooks, A. Ranasinghe, and T. K. Majumdar at the Aston Laboratory, Purdue University.

Octyl Triflate. A literature procedure[15] was used to obtain octyl triflate as a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 0.9 (m, 3H, CH_3), 1.33 (m, 10H, CH_2), 1.8 (m, 2H, OCH_2CH_2), 4.53 (t, 2H, OCH_2). Anal. Calcd for $C_9H_{17}F_3O_3S$: C, 41.21; H, 6.53. Found: C, 40.90; H, 6.23.

***N*-Octyl-4-vinylpyridinium Triflate (4e).** A previously reported procedure[15] was used to obtain **4e**. The crude residue isolated from the reaction mixture was repeatedly washed with dry ether to give the product as a colorless liquid. Yield: 85%. IR (neat, cm^{-1}, assign): 1263 (C–N str), 1646 (C=N str, C=C str), 2835, 2910 (aliphatic CH str), 3055, 3120 (aromatic C–H str). ^{1}H NMR ($CDCl_3$): δ 0.9 (t, 3H, CH_3), 1.3 (br s, 10H, $(CH_2)_5CH_3$), 1.9 (m, 2H, NCH_2CH_2), 4.6 (t, 2H, NCH_2), 6.0 (d, 1H, J_{cis} = 9 Hz), 6.45 (d, 1H, J_{trans} = 17 Hz), 6.9 (dd, 1H, $CH{=}CH_2$), 8.0–8.9 (AB q, 4H, Py^{2,3,5,6}). Anal. Calcd for $C_{16}H_{24}F_3NO_3S$: C, 52.30; H, 6.58; N, 3.81. Found: C, 51.92; H, 6.17; N, 3.39.

Copolymerization of 1-Alkyl-4-vinylpyridinium Ions 4. A variety of initiators, reaction media, and conditions were investigated for copolymerization of two different ions 4. Details for these methods are described below. The results are summarized in Tables I and II.

Table I. Polymerization of Monomer Mixtures in Aqueous Suspensions, Micelles, and Inverse Microemulsions[a]

monomer mixture	surfactant[b] or medium	radical initiator[c]	polymeric product(s)[d]
	Suspensions in Water		
4b/**4f** (4:1)		none[e]	**2f**
4b/**4f** (4:1)		$S_2O_8^{2-}/S_2O_5^{2-}$	**2f**
4b/**4f** (4:1)		$S_2O_8^{2-}/S_2O_5^{2-}$	**2b**, **2f**
4b/**4f** (10:1)		$S_2O_8^{2-}/S_2O_5^{2-}$	**2b**, **2f**
4e/**4f** (1:1)		$S_2O_8^{2-}/S_2O_5^{2-}$	**3** ($R_1 = C_8H_{17}$, $R_2 = C_{12}H_{25}$)[f]
	Micellar Systems		
4b/**4f** (10:1)	DPC	$S_2O_8^{2-}/S_2O_5^{2-}$	**2b**, **2f**
4b/**4f** (10:1)	DPC	ACVA	**2b**, **2f**
4b/**4f** (10:1)	DPC	AAP	**2b**, **2f**
4b/**4f** (10:1)	SDS	$S_2O_8^{2-}/S_2O_5^{2-}$	**2b**, **2f**
4b/**4f** (10:1)	SDS	ACVA	**2b**, **2f**
4b/**4f** (10:1)	SDS	AAP	**2b**, **2f**
4b/**4f** (10:1)	SDS	LP	**2f**
	Inverse Microemulsion[g]		
4b/**4f** (5.8:1)	hexane/water/isoamyl alcohol	$S_2O_8^{2-}/S_2O_5^{2-}$	**3** ($R_1 = C_2H_5$, $R_2 = C_{12}H_{25}$)[h]
4b/**4f** (5.8:1)	control[i]:hexane/water	$S_2O_8^{2-}/S_2O_5^{2-}$	**2b**, **2f**

[a] Reaction conditions: 45–50 °C, 10 h, total monomer concn 0.10 M. [b] DPC ≡ 1-dodecylpyridinium chloride, 0.08 M; SDS ≡ sodium dodecyl sulfate, 0.4 M. [c] Initiator concn 0.5 mol %. ACVA ≡ 4,4′-azobis(4-cyanovaleric acid), AAP ≡ 2,2′-azobis(2-amidinopropane)-HCl, LP ≡ lauroyl peroxide. [d] Structrual confirmation and mole fractions of monomer in copolymers were determined by ^{1}H NMR analysis. [e] Reaction mixture was sonicated for 10 min at 80–100 °C. [f] Isolated yield = 76%. [g] Hexane:water:isoamyl alcohol = 26:8:1 by wt. [h] Isolated yield = 60%. Monomer ratio of **4b**:**4f** = 65:35. [i] Stirred suspension of hexane:water = 13:4 by wt.

Attempted Copolymerization of 4b and 4f by Sonication in Water. The polymerization was carried out in a 50-mL flask. To 10 mL of water were added 0.082 g (0.2 mmol) of **4f** and 0.23 g (0.8 mmol) of **4b**. The reaction mixture was sonicated (45 W) at 80–100 °C for 10 min. The mixture became turbid immediately after initiation of sonication. An insoluble material developed during the reaction period. This crude mixture was dissolved in 10 mL of CH_2Cl_2 and combined with CH_2Cl_2 layers from extraction (2×) of the water layer with 10 mL of CH_2Cl_2. Rotary evaporation furnished 0.06–0.07 g of **2f**. ^{1}H NMR (1:1 CD_3OD/DMSO-d_6): δ 0.9 (s, 3H, CH_3), 1.3 (br s, 20 H, $(CH_2)_9CH_3$ and backbone CH_2), 2.0 (br s, 2H, NCH_2CH_2), 2.3 (s, 1H, backbone CH), 4.6 (br s, 2H, NCH_2), 8.0 and 8.7 (br s, 4H, Py^{2,3,5,6}).

A similar control experiment was carried out in D_2O to establish the presence of unreacted **4b** or of water-soluble **2b** in the aqueous layer. The ^{1}H NMR spectrum of this portion of the reaction mixture confirmed the presence of **4b**. ^{1}H NMR (D_2O): δ 1.5 (t, 3H, CH_3), 4.6 (q, 2H, CH_2), 6.0 (dd, 1H, J_{cis} = 11 Hz, J_{gem} = 1 Hz), 6.55 (dd, 1H, J_{trans} = 18 Hz, J_{gem} = 1 Hz), 7.10 (dd, 1H, $CH{=}CH_2$), 8.1–9.1 (AB q, 4H, Py^{2,3,5,6}).

Attempted Copolymerization of Monomer Mixtures by Radical Initiation in Water. The procedure above was repeated with aqueous suspensions containing 0.8 or 2.0 mmol of **4b** or 0.2 mmol of **4e** and 0.2 mmol of **4f** in 10 mL of water. Following sonication (45 W) at room temperature for 10 s to form an emulsion, the reaction mixture was stirred and flushed with a stream of nitrogen for 30 min. Finally, 0.5 mol % each of ammonium persulfate and sodium metabisulfite was added, and the reaction mixture was stirred and heated at 45–50 °C for 10 h. The reaction mixtures of **4b** and **4f** gave the water-soluble homopolymer **2b** [^{1}H NMR (D_2O): δ 1.5 (br s), 2.3 (br s), 4.5 (br s), 8.0 and 8.7 (br s)] and the water-insoluble homopolymer **2f** as described above. Mixtures of **4e** and **4f** gave a water-insoluble material which contained 76% of the total monomer mass and gave an ^{1}H NMR spectrum in CD_3OD/DMSO-d_6 similar to that of **2f**.

Attempted Copolymerization of 4b and 4f by Radical Initiation in Micellar Aqueous Media. Reaction mixtures that contained 0.8 or 2.0 mmol of **4b**, 0.2 mmol of **4f**, 0.08 M 1-dodecylpyridinium chloride (DPC), or 0.4 M sodium dodecyl sulfate (SDS) and 0.5 mol % radical initiator in 10 mL of water

Table II. Copolymer 3 from Monomer Mixtures in Melts and Solution

monomer mixture[a] (ratio)	medium[b]	initiator[c]	%	evidence[d]	monomer ratio
4b/**4a** (3:2)	melt	thermal	85	^{1}H NMR, H_2O sol	~3:2
(2:3)	melt	thermal		^{1}H NMR, H_2O sol	~2:3
4b/**4f** (5:1)	melt	thermal		^{1}H NMR, H_2O sol	~5:1
(7:3)	melt	thermal	86	^{1}H NMR, H_2O sol	~7:3
(1:1)	melt	thermal		^{1}H NMR, H_2O insol	~1:1
4a/**4b** (1:1)	solution/H_2O	$S_2O_8^{2-}/S_2O_5^{2-}$	88	^{1}H NMR	~1:1
4a/**4b** (1:1)	solution/*n*-BuOH	AIBN	90	^{1}H NMR	~1:1
4b/**4c** (1:1)	solution/H_2O	$S_2O_8^{2-}/S_2O_5^{2-}$		^{1}H NMR, H_2O sol	~3:2
4b/**4f** (4:1)	solution/*n*-BuOH	AIBN		^{1}H NMR, H_2O sol	~4:1
4b/**4f** (7:3)	solution/*n*-CH_3OH	AIBN	84	^{1}H NMR, H_2O sol	~7:3
4e/**4f** (1:1)	solution/*n*-BuOH	AIBN	82	^{1}H NMR, H_2O insol	~1:1

[a] Total amount of monomers = 1.0 mmol. [b] Solvent volume = 10 mL. [c] 0.5 mol %. [d] Mole fractions of monomers in copolymers were determined by ^{1}H NMR analysis.

were sonicated, degassed, and polymerized as described above. The homopolymer **2f** was isolated by decantation of the other components of the reaction mixture. Then, **2f** was purified by dissolution in methanol and precipitation by dilution with 10 volumes of cold acetone. Finally, the insoluble material was redissolved in a methanol/water solution, transferred to dialysis tubing (6000–8000 MWCO), and dialyzed against four changes of water over 4 days. A waxy solid which separated inside the tubing was identified as **2f** by its ^{1}H NMR spectrum as given above. The mass of **2f** corresponded to at least 80% of the **4f** originally added to the reaction mixture.

Homopolymer **2b** was isolated by dialysis of the aqueous phase of the reaction mixture in 6000–8000 MWCO tubing against four changes of water over 4 days. The aqueous solution in the tubing was lyophized to obtain a pale-green solid which was identified as **2b** by its ^{1}H NMR spectrum as above.

Experiments that utilized lauroyl peroxide as initiator produced homopolymer **2f** only. Dialysates obtained as described above were concentrated by lyophilization, and unreacted **4b** was identified in the residues (≤80% recovery) by ^{1}H NMR analysis.

Copolymerization of 4b and 4f in an Inverse Microemulsion. A mixture of 0.05 g (0.12 mmol) of **4f** and 1.3 g of hexane was treated with 0.05 g of isoamyl alcohol and with an aqueous solution that contained 0.40 g of water, 0.20 g (0.7 mmol) of **4b**, 0.001 g of ammonium persulfate, and 0.001 g of sodium metabisulfite. A transparent microemulsion formed immediately with stirring and was heated at 45–50 °C for 10 h. The viscous reaction mixture was diluted with methanol, transferred to dialysis tubing (6000–8000 MWCO), and dialyzed against four changes of water over 4 days. The copolymer was obtained in 60% yield as a pale-green solid after water was removed by lyophilization. ^{1}H NMR spectral analysis of the material in D_2O or 1:1 CD_3OD/DMSO-d_6 gave the following: δ 0.9 (s, dodecyl), 1.3–2.2 (br s, backbone CH_2, NCH_2CH_3, $NCH_2(CH_2)_{10}$), 2.3 (br s, backbone CH), 4.6 (br s, NCH_2), 8.0 and 8.7 (br s, $Py^{2,3,5,6}$). The presence of **4b** and **4f** in the copolymer was further confirmed by pyrolysis/tandem mass spectrometry which identified diads, triads, and tetrads with masses consistent with the presence of both **4b** and **4f** in the fragments.[19]

Control Experiment for Copolymerization in an Inverse Microemulsion. A two-phase reaction mixture identical in content to that immediately above *except for the omission of the cosurfactant isoamyl alcohol* was stirred and heated at 45–50 °C for 10 h. A mass of insoluble material separated during the reaction period. It was isolated by decantation of the liquid phases and purified by repeated (3×) dissolution in methanol followed by dilution with cold acetone. This material was identified as **2f** by its ^{1}H NMR spectrum.

The two liquid phases were concentrated by rotary evaporation, and the residue was purified by dissolution in methanol followed by precipitation with cold acetone. ^{1}H NMR analysis confirmed this substance to be the homopolymer **2b**.

Copolymerization of 4b and 4d or 4f by a Thermal-Melt Method. To a 50-mL round-bottomed flask was added 0.2 g (0.7 mmol) of **4b**, 0.32 g (0.3 mmol) of **4f**, and 5 mL of anhydrous acetonitrile. The monomers were dissolved by swirling the flask; then the solvent was removed by rotary evaporation. The residue, a liquid film, was heated under vacuum (<1 Torr), and the temperature was held at 125–130 °C for 15 min. The contents of the reaction flask were dissolved in 5 mL of methanol, diluted with several drops of water, transferred to dialysis tubing (6000–8000 MWCO), and dialyzed against four changes of water over 4 days. The copolymer **3** was obtained in 86% yield by lyophilization of the aqueous solution left in the tubing, and it contained approximately 70% of **4b** and 30% of **4f** based on integration of its ^{1}H NMR spectrum.

The results of this experiment and related ones are summarized in Table II.

Copolymerization of Monomer Mixtures by a Radical-Solution Method. To 10 mL of acetonitrile in an 50-mL round-bottomed flask were added 0.2 g (0.7 mmol) of **4b**, 0.32 g (0.3 mmol) of **4f**, and 0.5 mol % of 2,2′-azobis(isobutyronitrile) (AIBN). The reaction mixture was stirred and heated at 55 °C for 10 h. The copolymer **3** was isolated by diluting the reaction mixture was 8 volumes of methanol followed by precipitation in cold acetone. The precipitate was redissolved in a methanol/water solution, transferred to dialysis tubing (6000–8000 MWCO), and dialyzed against four changes of water over 4 days.

Copolymer **3** was obtained as a pale-green solid in 84% yield after lyophilization. Integration of its ^{1}H NMR spectrum indicated a **4b**/**4f** monomer ratio of ~7:3 in the copolymer.

Estimation of Monomer Ratios in the Copolymer from ^{1}H NMR Spectra. The mole fractions of monomers in copolymers were determined from integration of signals in the ^{1}H NMR spectra from the aromatic and *N*-alkyl regions. For copolymers of **4b** and **4f**, the signals used were at δ 8.7 (br s, 2H, $Py^{2,6}$), 8.0 (br s, 2H, $Py^{3,5}$), 4.6 (br s, 2H, NCH_2), and 0.9 (s, 3H, $N(CH_2)_{11}CH_3$). The relative integrated areas are given by 2:2:2:3N_x, where N_x is the mole fraction of **4f** in the copolymer. For copolymers of **4a** and **4b**, the signals used appeared at δ 8.7 (br s, 2H, $Py^{2,6}$), 8.0 (br s, 2H, $Py^{3,5}$), 4.4–4.6 (br s, NCH_2, NCH_3), and 1.3–1.5 (br s, backbone CH_2, NCH_2CH_3). The relative integrated areas are given by 2:2:[2N_x + 3(1-N_x)]:(2 + 3N_x) where N_x is the mole fraction of **4b** in the copolymer.

Results and Discussion

Copolymerization of mixtures of different variants of **4** was accomplished for the first time by a variety of methods. Thermal polymerization of mixtures of **4b** and **4d**, as well as mixtures of **4b** and **4f**, occurs readily in vacuum at 120–125 °C. Radical-initiated copolymerization of two hydrophilic, two lipophilic, or mixtures of hydrophilic and lipophilic **4** in solution was also accomplished with different initiators and solvents. The results are listed in Table II.

Copolymerization of hydrophilic and hydrophobic **4** in multiple-phase media such as aqueous suspensions, micellar systems, and inverse microemulsions presented unexpected problems. The results from this series of experiments are summarized in Table I. Most investigations utilized **4b** as the hydrophilic monomer and **4f** as the hydrophobic monomer. The resultant copolymer obtained previously from a two-step alkylation procedure by Strauss and co-workers[1] was well characterized and was known to exhibit the self-organizing capability required to pursue our primary interest, i.e., the design, synthesis, and evaluation of synthetic polymers as enzyme mimics. We found that the polymerization of **4b** can be completely separated from the polymerization of **4f** in aqueous suspensions under sonication. Furthermore, **4f** is more easily polymerized than **4b** under mild conditions.[16,17] For example, in polymerization initiated by sonication of reaction mixtures containing **4b** and **4f** at 80–100 °C for 10 min, **2f** was the only polymer obtained. Monomer **4b** remained unchanged in the aqueous layer. This suggests that the hydrophobic forces that lead to aggregation of **4f** in water can effectively compensate for the electrostatic repulsive forces between the cationic monomers. In the presence of radical initiators and/or at higher concentrations (>1.0 M), **4b** will also homopolymerize.

Addition of a surfactant at concentrations above its cmc provides another interesting perspective on radical-initiated copolymerization of **4b** and **4f**. In the micellar system formed from either 1-dodecylpyridinium chloride, a cationic surfactant, or sodium dodecyl sulfate, an anionic surfactant, only the two homopolymers are formed when $S_2O_8^{2-}/S_2O_5^{2-}$, 4,4′-azobis(4-cyanovaleric acid), or 2,2′-azobis(2-amidinopropane)·HCl are used as initiators. Interestingly, **4f** can be selectively homopolymerized in the presence of **4b** in sodium dodecyl sulfate micelles when lipophilic lauroyl peroxide is used as the initiator. It is important to note that up to 80% of unreacted monomer **4b** can be recovered in this experiment. Apparently, the lauroyl radicals and **4f** monomers are effectively compartmentalized within the anionic micelles, and **4b** monomers are restricted to the aqueous phase (Table II).

Hamid and Sherrington recently commented on the conditions required for polymerization within a micelle.[18] For topochemical polymerization of vinyl monomers solubilized by surfactants, they point out that the rate of monomer addition to a propagating radical must be greater than the rate of exchange of micellar monomer with the corresponding species in solution. If the rate of propagation is slow, a polymer of high molecular weight is obtained. This appears to be the case for homopolymerization of **4** in this study. Significantly, no evidence for copolymerization of cationic hydrophilic monomer with cationic hydrophobic monomer was observed in our experiments conducted in micellar media! Thus, the rate of equilibration of micellar **4f** with solution **4b** and rate of copolymerization of **4b** and **4f** must be slow relative to the rate of polymerization of micellar **4f**.

Finally, we investigated the possibility of copolymerization of **4b** and **4f** in an inverse microemulsion that contained hexane, water, and isoamyl alcohol in the proportions 26:8:1 by weight. In this case, the less reactive **4b** is present at high concentration in a relatively small amount of water and the concentration of the more reactive **4f** is diluted by the large amount of hexane. In addition, the large interfacial area of the microemulsion is expected to enhance access of **4b** and **4f** to one another at the phase boundary. Copolymer **3** ($R_1 = C_2H_5$, $R_2 = C_{12}H_{25}$) was in fact produced in this manner for the first time under conditions that compartmentalize **4b** and **4f** in different phases. The importance of the microemulsion medium was demonstrated by a control experiment in which the cosurfactant, isoamyl alcohol, required for formation of a microemulsion was omitted. In the control experiment only the two homopolymers were obtained.

Characterization of Copolymers

The issue of characterization of copolymer **3** is vitally important to this investigation. Characterization of **3** is particularly problematic for several reasons. For example, reliable chromatographic separation methods have not been established for these materials. Separation and purification of crude products have utilized fractionation by solubility differences. Repeated dissolution of the impure polymer in methanol or methanol/water followed by precipitation with ether, acetone, or ethyl acetate has frequently provided samples of reasonable purity. This approach was used in our past work with homopolymers **2**. For those compounds, ^1H and ^{13}C NMR spectral analysis provided unambiguous structural characterization of the materials derived from different variants **4**. However, characterization of **3** is complicated by the possibility that the material in question may also be a mixture of the two homopolymers **2**. In that event, NMR spectral analysis, as well as IR and UV–vis spectral analyses, and elemental analysis do not provide definitive evidence for copolymer structure. Two simple, yet reliable, sources of data for distinguishing between a copolymer and a mixture of its related homopolymers derived from hydrophilic and hydrophobic monomers are mass balance and solubility. For example, when a high percentage of monomer is converted to polymer, the appropriate spectral changes (^1H and ^{13}C NMR, IR, UV–vis) may be noted. Then, the solubility of the polymer may be determined in water and an organic solvent such as CH_2Cl_2. For polymerization of **4b** and **4f**, homopolymer **2b** is highly soluble in water and relatively insoluble in CH_2Cl_2. The solubility behavior of **2f** is reversed in the same solvents. A copolymer of **4b** and **4f** will exhibit the NMR spectral bands of both homopolymers and *will also exhibit appreciable solubility in water* when the mole fraction of **4b** in **3** is greater than 0.60. Thus materials are identified as copolymers in this study only after satisfying the following criteria:

(1) The weight of the isolated polymeric product must represent >60% of the combined weights of the starting monomers.

(2) The isolated product must be retained by 6000–8000 MWCO dialysis membranes.

(3) ^1H and ^{13}C NMR and IR spectra of the isolated product must be consistent with the structures of homo- and copolymers **2** and **3**, respectively.

(4) The solubility of copolymers in water confirms the presence of a hydrophilic component such as **4b**.

Attempted Structural Characterization of Copolymers 3 by Pyrolysis/Tandem MS

A unique feature of the copolymer structure, potentially analytically accessible, is the mass of diads, triads, etc., that contain different monomeric units. Homopolymers, of course, would contain only one kind of constituent structural unit. Mass spectral analysis of the presumed copolymers was carried out by R. G. Cooks and co-workers on a Finnigan TSQ 700 mass spectrometer.[19] Pyrolysis/tandem mass spectrometry has been shown to be uniquely capable of determining structural details, including monomer sequence information, in biological and synthetic polymers.[19–22] Unfortunately, detailed analysis of data obtained from presumed copolymers **3** indicates that dealkylation and realkylation processes proceed quickly by both intra- and intermolecular pathways/processes during the analysis.[19,23] Therefore, this powerful method for structural analysis is compromised to the extent that it cannot distinguish between copolymers and mixtures of homopolymers derived from 1-alkyl-4-vinylpyridinium ions.

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