Direct Determination of the Residual Acrylamide Concentration in Inverse (Water-in-Oil) Polyacrylamide Emulsions Following Phase Inversion: Size Exclusion Chromatography Using a Micellar Mobile Phase

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SYNOPSIS

A rapid and low cost method has been developed for the direct analysis of the residual monomer concentration of acrylamide from inverse-emulsion reactions. Inverse-emulsion polymerizations involve the dispersion of a water soluble monomer in aqueous solution in a continuous organic phase. The addition of a low-medium hydrophilic–lypophilic balance (HLB) steric stabilizer and continuous agitation is required to maintain emulsification. This method consists in inverting the "inverse" (water-in-oil) emulsion by utilizing a high HLB surfactant, large amounts of water and rapid stirring to produce a "direct" (oil-in-water) emulsion. Once the residual acrylamide is in the continuous aqueous phase, aliquots of this inverted mixture are then injected into a liquid chromatograph where the polymer and the residual acrylamide are separated by size exclusion chromatography using an aqueous micellar mobile phase. The micellar mobile phase is used to solubilize the organic phase and emulsifier present in the original inverse-emulsion recipe. The organic phase present in the original water-in-oil emulsion is trapped inside the micelles of the mobile phase and these elute with a retention volume comparable to that of the polymer. The large pore volume of the column separates the polymer from the residual monomer and provides sharp and symmetric acrylamide peaks with a good plate count. This method results in linear calibration curves for the acrylamide monomer up to 100 ppm. Further, the elimination of an organic mobile phase reduces the analysis cost considerably. In addition, the sample preparation time is reduced from between 30 minutes to several days for the traditional methods to 15 minutes for the newly proposed method. Therefore, this inversion procedure is suitable for rapid data analysis from reaction mixtures obtained from inverse-emulsion polymerizations. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyacrylamide is applied as a coagulant and flocculant in the multibillion dollar waste water treatment industry. It is also used as a pushing fluid in enhanced oil recovery, as a drag reduction agent and drilling fluid, as well as in other industries such as mining and paper making. Acrylamide-based polymers are produced commercially in the form of water-in-oil (inverse) emulsions. These products consist of heterophase water-swollen polymer droplets of 0.1–10 microns in diameter and organic continuous phase stabilized with nonionic steric surfactants. Due to environmental concerns, the level of residual acrylamide in inverse-emulsions is mandated to be reduced to less than 500 ppm.[1] The literature cites several techniques to analyze free acrylamide in the above products including gas chromatography[2-4] and high-performance liquid chromatography.[5-10] For example, one HPLC procedure for the determination of residual acrylamide monomer involves breaking the emulsion through

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centrifugation, decanting the organic phase, and the subsequent redissolution of the monomer–polymer mixture in a purified aqueous solvent. This last step can require several days for the high molecular weight polyacrylamides (over 10 million Daltons) to redissolve.[7] Other HPLC methods are based on the precipitation of the polymer in a nonsolvent, the separation of the polymer by centrifugation, and the injection of aliquots of the supernatant liquid into a liquid chromatograph using cyano-bonded silica columns[7,8] and reversed-phase columns.[8–10] The disadvantage of these methods is the use of expensive mobile phases. In an attempt to overcome these limitations, a novel, rapid, and low-cost procedure to analyze the level of residual acrylamide in inverse-emulsions of polyacrylamide is described.

This method is based on the idea that water-in-oil emulsions can be transformed into oil-in-water emulsions using a high hydrophilic lypophilic balance (HLB) inverting surfactant and massive amounts of water.[11,12] This concept is applied routinely in the water-soluble polymer industry to invert inverse water-soluble polymer emulsions prior to application.[13–18] This method can be used for quality control or research purposes to follow the kinetics of inverse-macroemulsion polymerization processes of acrylamide.

EXPERIMENTAL

HPLC System

The HPLC system consisted of a Hitachi L6000 isocratic pump (Hitachi Instruments, Tokyo, Japan), a Hitachi L4000H variable wavelength UV detector operating at 214 nm, and a Rheodyne 7725i injector (Cotati, CA). Chromatograms were collected on a 486 computer running Viscotek GPC PRO Version 4.01 software (Houston, TX). A short Shodex OHPAK SB-800P column (50 × 6 mm i.d., JM Science, Inc., Buffalo, NY) was used as the stationary phase. The mobile phase consisted of highly deionized water with 25 mmol/L of electrophoresis-grade sodium dodecyl sulfate (SDS) (Fisher Scientific, Norcross, GA). This concentration of SDS (greater than the CMC) was added to solubilize the organic phase present in the original inverse-emulsion that may otherwise deposit at the surface of the sorbent, causing permanent damage to the column. The mobile phase flow rate was kept at 0.5 mL/min. A 100 μL glass syringe (Hamilton Co., Reno, NV) was used for injections.

Materials

Reagent-grade water (deionized Type I water, Continental Water, San Antonio, TX) with a resistivity ≥ 16.7 μΩ-cm was filtered through a 0.2 μm nylon membrane filter (Scientific Resources, Inc., North Brunswick, NJ) and used immediately for analysis. The acrylamide monomer was purchased from Cytec (Charlotte, NC) and was purified by recrystallization in chloroform (ACS reagent grade, 99.9% pure, Fisher, Norcross, GA), dried in vacuum at room temperature, and stored in desiccators until use.

Tergitol TMN-10 (2,6,8-trimethyl-4-nonyloxypolyethylenoxyethanol, CAS number: 60828-78-6), Tergitol 15-S-9 (a mixture of linear secondary alcohols reacted with ethylene oxide, CAS number: 84133-50-6), and Triton N-101 and Triton N-60 [poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omega-hydroxy-, branched, CAS number 127087-87-0] were used as received as inverting surfactants (Union Carbide Chemicals and Plastics Co., Inc., Danbury, CT).

Polymer Synthesis

In this work, the polyacrylamides were synthesized by inverse-emulsion polymerization. This involved the dispersion of the aqueous monomer mixture (50% weight aqueous phase) in an isoparaffinic continuous phase (Isopar-M, Exxon; supplied by ChemCentral, Nashville, TN). The mixture was stabilized with HB239, a nonionic block copolymeric steric stabilizer, provided by ICI Americas (Wilmington, DE), and agitated at 440 rpm throughout the reaction. Prior to the synthesis, the aqueous and organic phases were individually sparged with nitrogen (99.9% pure, AL Compressed Gas, Nashville, TN) for 30 min. This lowered the dissolved oxygen concentration to below 1.5 ppm as measured with an Ingold dissolved oxygen probe (Ingold, Wilmington, MA). Azobisisobutyronitrile (Wako, Richmond, VA), purified by recrystallization with methanol (Certified ACS Grade), was used as the chemical initiator. Syntheses were performed isothermally at temperatures between 42 and 47°C. This resulted in a dispersion containing small particles ($dp \approx 180$–250 nm).[19]

Syntheses were performed in a 5 L stainless-steel reactor equipped with an external heating/cooling jacket. The reactor was computer-controlled using an error-squared proportional-integral-derivative controller to within ±0.3°C throughout the reaction by varying the chilled water-to-steam ratio entering the cooling jacket. The reactor was sparged contin-

Table I Effect of the Inverting Surfactant Concentration (TMN-10) on the Peak Area of Residual Acrylamide After 10 Min of Fast Agitation

Inverse Emulsion Sample	Weight (g)	TMN-10 Concn (mmol/L)	Peak Area[a]
A	0.0073	5.52	0.211
B	0.0073	4.31	0.212
C	0.0072	2.87	0.210
D	0.0073	1.43	0.212

[a] The peak area represents an average of three separate injections.

ually with purified nitrogen to remove any residual oxygen which could consume radicals and interfere with the polymerization.[19]

Twenty milliliter aliquots were withdrawn from the reactor at 5–10 min intervals in glass scintillation vials (Fisher Scientific, Norcross, GA) containing 200 ppm of hydroquinone. The hydroquinone terminated the reaction. These samples were then stored in ice water for the remainder of the reaction and then transferred to a refrigerator where they were maintained at a temperature below 10°C until they were analyzed, usually the next day.

RESULTS AND DISCUSSION

Selection of the Inverting Surfactant

A series of inverting surfactants were evaluated to identify a system where stable inverted (oil-in-water) emulsions could be produced following phase inversion. In addition, it was required that the inverting surfactants should not interfere with the determination of residual acrylamide. Specifically, they should not show any significant ultraviolet absorption at 214 nm, where the acrylamide shows a maximum absorption. Dilute solutions of several inverting surfactants in highly deionized water ($\approx$ 1 g/L) were prepared. The surfactants evaluated included Tergitol TMN-10, Tergitol 15-S-9, Triton N-101, and Triton N-60. Aliquots of 100 μL of these solutions were injected into the HPLC and the UV absorbancy was monitored at 214 nm. Triton N-101 and Triton N-60 present a very strong UV absorption as evidenced by a large and broad peak. Tergitol TMN-10 was found to be the best inverting surfactant of those tested since it provided negligible UV absorbancy at the mentioned wavelength. It is possible, however, that other inverting surfactants not used in the present study may work with the same efficiency as that of Tergitol TMN-10.

Phase Inversion

The optimum amount of inverting surfactant used to invert a water-in-oil emulsion was determined by trial and error. A small drop of a water-in-oil emulsion (nominally 0.0050–0.01 g) was weighed in an analytical balance to four decimal places in a clean 20 mL glass scintillation vial. Twenty milliliters of a solution containing a known concentration of Tergitol TMN-10 in highly deionized water was then added to the vial and the contents were agitated vigorously for 10 min with a magnetic stirrer. Concentrations of Tergitol TMN-10 from 1.43–5.52 mmol/L were tested. Aliquots of 100 μL of these solutions were then injected into the liquid chromatograph. The peak area corresponding to the residual acrylamide was essentially independent of the concentration of the inverting surfactant employed, as is indicated in Table I. The effect of the agitation time on the peak area of acrylamide is shown in Table II. It is clear that the time of agitation of the water-in-oil samples does not play any role in the analysis revealing the equilibrium thermodynamic nature of the inversion and extraction steps. A concentration of 5.52 mmol/L of Tergitol TMN-10 and 10 min of stirring time were used for the phase inversion throughout the remainder of this study.

Size Exclusion Chromatography

To quantify residual acrylamide levels, size exclusion chromatography (SEC) must initially be applied to separate the polyacrylamide from the residual acrylamide monomer since both absorb UV light at 214 nm. Figure 1 shows a typical chromatogram of an inverted inverse acrylamide/polyacrylamide emulsion sample. The sharp peak at a retention volume of $\approx$ 1 mL corresponds to residual acrylamide while the broad peak at lower retention volumes corresponds to the polyacrylamide as well as to the micelles which have solubilized the residual organic

Table II Effect of the Agitation Time on the Peak Area of Residual Acrylamide at a Constant Inverting Surfactant Concentration (TMN-10) of 5.52 mmol/L

Inverse Emulsion Sample	Weight (g)	Agitation Time (min)	Peak Area[a]
1	0.0068	5	0.192
2	0.0067	10	0.191
3	0.0067	15	0.191
4	0.0067	20	0.191
5	0.0067	25	0.192
6	0.0067	30	0.192

[a] The peak area represents an average of three separate injections.

phase from the reaction mixture. The organic phase present in the initial water-in-oil emulsion is trapped inside the micelles and elutes at very low retention volumes due to exclusion from the sorbent pores. Good peak separation is observed between the acrylamide and the high molecular weight interferents at any acrylamide/polyacrylamide ratio. Figure 2 shows a chromatogram of a mixture of pure acrylamide dissolved in the inverting surfactant in highly deionized water with small amounts of the organic phase. The small peaks at low retention volumes are further indications that the organic phase present in the original water-in-oil emulsion is trapped in the micelles of SDS of the mobile phase and that they elute with a retention volume comparable to that of the polymer. The signal peak area corresponding to the residual monomer could be quantitatively measured within a 1% error limit as shown in Table III for a typical inverse-emulsion sample. In all cases, the inverted reaction mixtures were limited to concentrations below 100 ppm of acrylamide since this was the corresponding limit for Beer's law.[7] Residual monomer concentrations were determined from a calibration curve between 0 and 100 ppm for the acrylamide as shown in Figure 3.

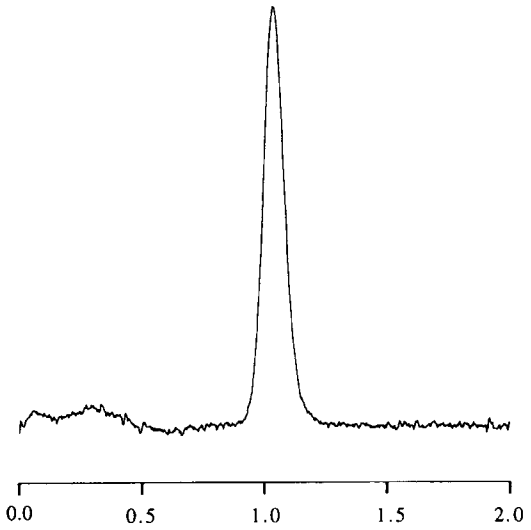

Figure 1 Chromatogram of an inverted water-in-oil acrylamide/polyacrylamide sample. The broad peak at low retention volumes is the polyacrylamide along with solubilized organic phase. The peak at high retention volumes is acrylamide. Stationary phase: Shodex OHPAK SB-800P column (50 × 6 mm i.d.). Mobile phase: highly deionized water with 25 mmol/L of electrophoresis SDS at 0.5 mL/min and 214 nm.

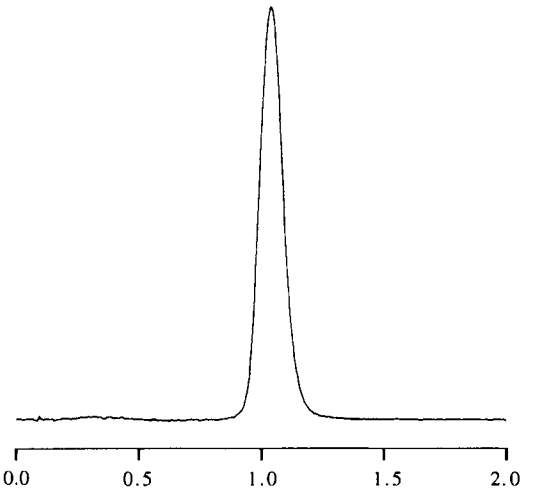

Figure 2 Chromatogram of a standard containing 103 ppm of acrylamide/deionized water/organic phase/inverting surfactant. Stationary phase: Shodex OHPAK SB-800P column (50 × 6 mm i.d.). Mobile phase: highly deionized water with 25 mmol/L of electrophoresis SDS at 0.5 mL/min and 214 nm.

Table III Repeatability of the Phase-inversion Micellar Mobile Phase Method Using the Same Inverted Sample

Replicate	Peak Area
1	0.309
2	0.308
3	0.309
4	0.308
5	0.307
6	0.308
7	0.308
8	0.306
9	0.308
10	0.308
Mean value, $\bar{x}$	0.3079
Standard deviation, σ_{n-1}	0.0087

This was prepared each day prior to analysis and duplicated at the end of the analyses. Samples from a given experiment were always analyzed together within an 8 h period.

Effectiveness of the Method

Figure 4 compares the analysis time of this method and that of a widely used liquid chromatographic technique employing a cyano-bonded silica sorbent

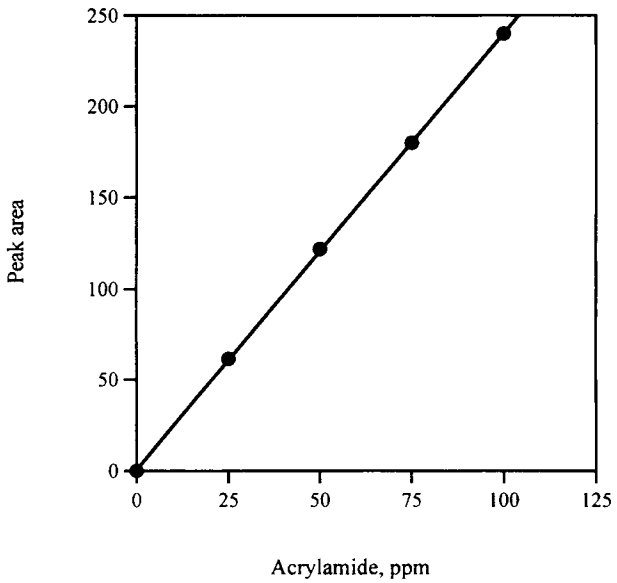

Figure 3 Calibration curve for acrylamide using the phase-inversion micellar mobile-phase method. Stationary phase: Shodex OHPAK SB-800P column (50 × 6 mm i.d.). Mobile phase: highly deionized water with 25 mmol/L of electrophoresis SDS at 0.5 mL/min and 214 nm.

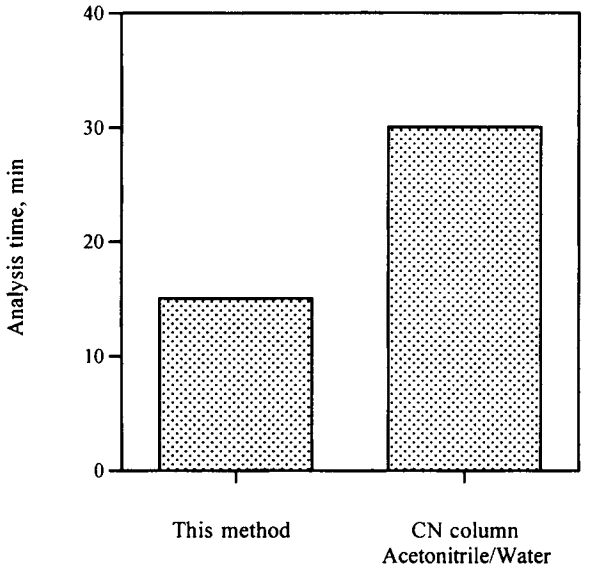

Figure 4 Comparison of the analysis time for the phase-inversion micellar mobile-phase method and a chromatographic method using a cyano-bonded silica sorbent and 50 : 50 vol/vol acetonitrile/water as the mobile phase.

with acetonitrile–water (50 : 50 vol/vol) as the mobile phase.[7,8] Preparation of the inverse-emulsion samples by this method included the precipitation of the polymer, centrifugation, or filtration of the polymer and chromatographic analysis of the residual monomer. Reductions of at least to 100% in analysis time are obtained with the proposed method since precipitation of the polymer and centrifugation steps are unnecessary. Figure 5 shows the costs of the mobile phase (based on 100 injections) of the new method in comparison with the cyano-bonded silica sorbent/acetonitrile–water procedure. The mobile phase cost of the present method is greatly reduced since the solvent is essentially highly deionized water. In addition to reducing both the analysis time and the mobile phase costs, the initial costs of the proposed method are lower than those of the traditional methods since the column used is short and relatively inexpensive. It also requires less maintenance than do the radial compression systems which are often used to improve the efficiency of the cyano-bonded silica sorbent-based columns.

Applications of the Method to the Characterization of Reaction Mixtures

Figure 6 shows a plot of the conversion vs. time for an inverse emulsion polymerization of acrylamide at 47°C as determined using the present method. The results of two independent measurements are

overlaid to demonstrate both the repeatability of the polymer synthesis and also the phase-inversion micellar mobile phase method. Clearly, a smooth trend in the conversion vs. time plot is observed, demonstrating that this method can be applied to commercially relevant inverse-emulsion syntheses. Further, with a retention time of less than 2.5 min, it is a technique easily adapted and automated for rapid data acquisition.

CONCLUSIONS

A novel method has been developed to directly analyze the level of residual acrylamide in inverse (water-in-oil) emulsions of polyacrylamide based on the concept of the phase inversion of emulsions. A suitably high HLB inverting surfactant, Tergitol TMN-10, was selected. The concentration of this inverting surfactant in highly deionized water and time of agitation were evaluated. The chromatographic conditions for the separation of the residual acrylamide from the polymer and the other components of the reaction mixture were also reported. It was found that a short hydrophilic column for aqueous SEC, Shodex OHPAK SB-800P, provides for rapid analysis and good separation of small molecules of the residual acrylamide monomer from all the high molecular interferents. Sharp and symmetric acrylamide peaks are also observed. The mobile phase consists of highly deionized water with electrophoresis-grade SDS at a concentration higher than the CMC in order to solubilize the organic phase present in the original inverse (water-in-oil) emulsion that may otherwise deposit at the surface of the sorbent, causing permanent damage to the column. All of the organic phase trapped inside the micelles elutes at very low retention volumes, providing a good SEC separation from residual acrylamide. This method is very reliable, accurate, economical, and expedient, requiring a maximum of 15 min for sample preparation and analysis. Therefore, this inversion procedure is suitable for rapid data analysis from reaction mixtures obtained from inverse-emulsion polymerizations for quality control or R&D.

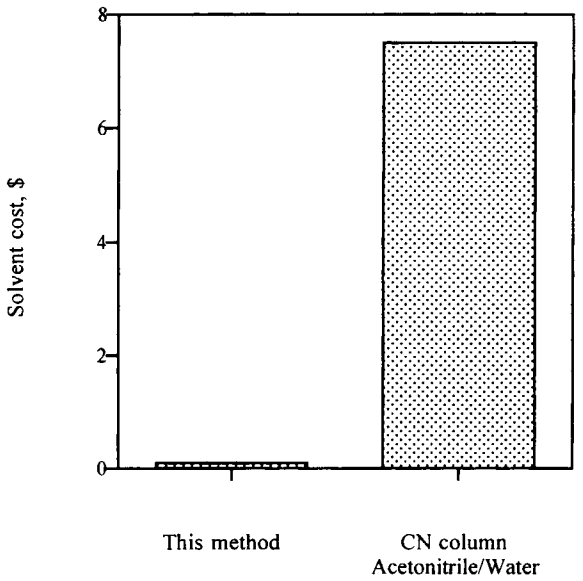

Figure 5 Comparison of the mobile phase cost for the phase-inversion micellar mobile-phase method and a chromatographic method using a cyano-bonded silica sorbent and 50 : 50 vol/vol acetonitrile/water as the mobile phase (based on 100 injections).

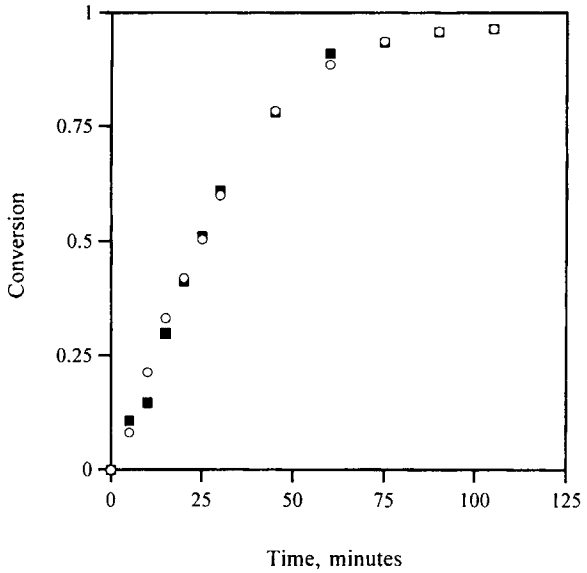

Figure 6 Repeatability studies for the determination of the conversion from the residual monomer concentration for an inverse emulsion polymerization of acrylamide using a copolymeric surfactant (HB239). Experimental conditions: $T = 47°C$, [AIBN] = 4.52×10^{-3} mol/L_o, [M] = 3.87 mol/L_w, [E] = 0.015 mol/L_o, aqueous-phase/oil-phase ratio (vol/vol) = 0.78 and 440 rpm.

REFERENCES

1. B. T. Croll, G. M. Arkell, and R. P. J. Hodge, *Water Res.*, **8**, 989 (1974).
2. B. T. Croll, *Analyst*, **97**, 67 (1971).
3. B. T. Croll and G. M. Simkins, *Analyst*, **97**, 281 (1972).
4. A. Hashimoto, *Analyst*, **101**, 932 (1971).

5. E. R. Husser, R. H. Stehl, D. H. Prince, and R. A. DeLap, *Anal. Chem.*, **49,** 155 (1977).
6. F. J. Ludwig and M. F. Besand, *Anal. Chem.*, **50,** 185 (1978).
7. D. J. Hunkeler, PhD Thesis, McMaster University, Hamilton, Ontario, 1990.
8. D. J. Hunkeler, H. Ni, J. Hernández-Barajas, and M. Petro, to appear.
9. *Hamilton HPLC Application Catalog,* Hamilton Co., Reno, NV, 1992.
10. L. Brown and M. Rhead, *Analyst,* **104,** 391 (1979).
11. S. Berkman and G. Egloff, *Emulsions and Foams,* Reinhold, New York, 1941.
12. M. Rosen, *Surfactants and Interfacial Phenomena,* Wiley, New York, 1978.
13. D. R. Anderson and A. J. Frisque, U.S. Pat. 3,624,019 (1971).
14. D. R. Anderson and A. J. Frisque, U.S. Pat. 3,734,873 (1973).
15. G. J. Venema, U.S. Pat. 3,852,234 (1974).
16. L. R. Mura, U.S. Pat. 4,230,608 (1980).
17. J. C. Chuang, U.S. Pat. 5,206,316 (1993).
18. D. Moench, H. Hartmann, and H.-U. Wekel, U.S. Pat. 5,292,800 (1994).
19. J. Hernández-Barajas and D. J. Hunkeler, *Polym. Adv. Technol.*, **6,** 509 (1995).

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