

Phase Inversion of Polyacrylamide Based Inverse-Emulsions: Effect of the Surfactant and Monomer on Postinversion Equilibrium Properties

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Received 7 July 2006; accepted 18 August 2006

DOI 10.1002/app.25309

Published online 26 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The influence of the interfacial chemistry on the phase inversion of polymerized water-in-oil emulsions has been investigated. For copolymerizations of acrylamide with cationic monomers, the effect of substituting of fatty acid esters and ethoxylated fatty acid esters with ABA block type stabilizers, on the kinetics and extent of phase inversion, were examined. It was determined that the solution viscosity was a valid metric to identify the mechanism by which inversion occurs, while conductivity provided a means to quantify inversion efficiency. Therefore, the interfacial chemistry was found to influence not only the plateau value of the viscosity of the polymer solution but also its kinetics. The most suitable inversion was observed with a polymer emulsion stabilized with low block copolymer stabilizer levels in the blend (8 wt %), relative to traditional fatty acid esters and ethoxylated fatty acid esters. This provided an ultimate solution viscosity 30% higher than for a polymer synthesized under identical conditions though with higher levels of the ABA block stabilizer. Overall, the

optimal formulation (8% ABA) was found to liberate 88% of the latent viscosity. Given that the options in regards to inverting surfactants can be, legislatively, limited, the present work makes a case for the selection of the interfacial composition not only for its stability during reaction, and the molecular weight of the synthesized polymer, but also for the extent and rapidity of inversion. The formulation-composition map approach provided an understanding of phase inversion applied to polymer emulsion and was a useful fingerprint to qualitatively describe the catastrophic mechanism of inversion. The surfactant affinity difference applied to a blend of surfactant was found to be a convenient formulation parameter which allowed us to locate the representative point on the map of the polymer emulsion stabilized with different surfactant blend composition. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2328–2341, 2007

Key words: acrylamide; alcohol ethoxylates; HLB; inverting surfactant; suspension polymerization

INTRODUCTION

Inverse-emulsion polymerization is a widely applied technology for the preparation of high molecular weight water-soluble macromolecules,^{1,2} owing to the fact that high concentrations of monomers can be contained within the aqueous droplets, while maintaining an inviscid latex. These polymers, which are generally based on acrylamide copolymerized with anionic or cationic monomers, are applied as flocculants, as retention aids in papermaking, in the treatment of potable water and mining wastes, as rheology modifiers in oil recovery and cosmetics, and for aqueous solid-liquid separations in general.³ When considering applications in wastewater treatment, the overall performance of the flocculant is a function of the polymer chemistry, structure, as well as concentration. Furthermore, a polymer's efficiency is related to the ability to invert the water-in-oil system

completely, and rapidly, into an excess of water, or brine, depending on the application. Therefore, the complete liberation of the polymer, encapsulated in the water droplets, is essential. Indeed, the thermodynamics and kinetic factors influencing the phase inversion of water-in-oil emulsions are critical complements to the polymer physical chemistry in the optimization of the dilute solution properties of charged polymers.

Phase inversion involves passing from one simple form of emulsion morphology, such as a water-in-oil system, to another where the continuous and dispersed phases are reversed.⁴ There exists a separation frontier referred to as the standard inversion line which delineates the W/O region from the O/W region on an appropriate map.^{5–7} The influence of the water-oil interface on the inversion process has not, however, been reported to date, although it is suspected to affect the overall invertability. Indeed, the stability of this interfacial film is strongly dependent upon the surfactant adsorption-desorption kinetics, solubility, interfacial rheological properties,^{8–10} as well as the HLB of the surfactants.¹¹ In practice, nonionic surfactant blends provide more efficient

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Journal of Applied Polymer Science, Vol. 106, 2328–2341 (2007)
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TABLE I
Experimental Conditions

Run	Block copolymeric surfactant content (%)	Sorb. sesquioleate/POE sorbitol hexaoleate (g)	ABA block copolymeric surfactant (g)	Total surfactant (g)
110100	8.0	27.71	2.41	30.20
101200	30.0	21.10	9.10	30.20
103000	30.0	21.20	9.01	30.21
102700	58.0	12.61	17.44	30.05
102500	82.0	5.40	24.68	30.08
102300	95.0	1.53	28.47	30.00

emulsification than single species since the entropy of mixing is maximized and the molecules of the blend associate at the W/O interface and form a complex, which renders the interfacial film more condensed.¹²

The thermodynamically based surfactant affinity difference (SAD) has been used as an alternative formulation variable to differentiate properties of the various surfactant blend composition. The SAD, expressed as the difference of standard chemical potential of surfactant in the oil phase and the corresponding term in the water phase,⁶ is a generalized parameter that relates variables such as partitioning of the surfactant and salinity.¹³ To investigate the influence of surfactant blend composition on the phase inversion of polymer emulsion, the properties and kinetics of the inversion of the final polymer emulsion must be monitored.

The aim of the present study was to investigate the influence of the interface constituting the water-in-oil emulsion on the inversion process. The composition of the surfactant blends prepared at various ratios of polyoxyethylene sorbitol hexaoleate, sorbitan sesquioleate, and a triblock copolymeric surfactant were the primary variables evaluated. There are very few basic investigations which examine the phase inversion of water-in-oil polymerized systems¹⁴ and none, to which the authors are aware, which examine the influence of interfacial chemistry on the

extent, and kinetics, of the inversion. The present study targets such an investigation.

EXPERIMENTAL

Polymer synthesis

Copolymerizations of acrylamide with dimethylaminoethyl acrylate (methyl chloride quaternized) were carried out in a temperature-controlled 1.5-L stainless steel reactor. The organic phase was a paraffinic mixture (Isopar-M from Exxon, supplied by Shell, Switzerland), with the water-to-organic phase ratio 2 : 1 on a weight basis. The monomer concentration was 25 wt % of the total mass of emulsion. The experimental conditions are summarized in Table I.

To permit the investigation of the effect of the surfactant blend composition on the phase inversion of the final polymer emulsion, the overall HLB, temperature, monomer composition, and aqueous-to-organic phase ratio were maintained constant throughout all experiments. This approximate constancy of molecular weight is observed in Table II, where all polymers prepared, with the exception of that with 82% of the ABA stabilizer, have an intrinsic viscosity of 19.8 ± 2 dL/g. Furthermore, in all cases, again with the exception of the reaction with 82% of the ABA block stabilizer, the Huggins coefficient were suitably low to indicate very good solubility of

TABLE II
Intrinsic Viscosity and Huggins Coefficient Data Evaluated from Huggins Equation at Different Surfactant Blend Composition

Run ^a	S ₁ : S ₂ : S ₃ composition (wt %)	Intrinsic viscosity (dL/g)	Huggins coefficient	Regression coefficient
102300	95 : 3.2 : 1.8	20.53	0.132	0.996
102500	82 : 1.5 : 6.5	11.85	0.439	0.991
102700	58 : 26.9 : 15.1	21.77	0.111	0.990
103000	30 : 44.8 : 25.2	17.86	0.166	0.999
110100	8 : 58.9 : 33.1	18.64	0.134	0.996

S₁, ABA type block copolymeric surfactant; S₂, sorbitan sesquioleate (Arlacel 83); S₃, polyoxyethylene sorbitol hexaoleate (Atlas G-1086).

The surfactants were blended to obtain a constant HLB value of ~ 6.0 .

^a Surfactant composition based on the total mass of the blend.

the resulting polymer chains. The polymerizations were further carried out at an overall surfactant concentration of 3 wt % of the total reaction mass and the block copolymeric stabilizer composition was varied from 8 to 95 wt %, of the total surfactant mass, in the stabilizer blend at a constant HLB value of ~ 6.0 .

Materials

Hypemer HB239 (a linear ABA-type block copolymer of polyester-polyethylene oxide-polyester prepared by reacting condensed 12-hydroxystearic acid with polyoxyethylene), sorbitan sesquioleate (Arlacel 83), polyoxyethylene sorbitol hexaoleate (Atlas G-1086), gifts from Uniquema (Brussels, Belgium) and used as nonionic stabilizers without any purification. Nonylphenol with 10-ethoxylated units (NP-10) was employed as an inverting surfactant. As the nonylphenol's role is in the phase inversion of the inverse-emulsions, it will be referred to as an emulsion breaker (EB). A previous study examined the influence of EB types¹⁴ wherein the advantages of the aforementioned nonylphenol were noted.

The chemical initiator 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65, Wako Chemicals, Neuss, Germany) dissolved into xylene was added into the reactor at 40°C. The reaction time was 360 min and the temperature of reaction was further increased stepwise up to 52°C. The conversion was measured by HPLC following the method described in Armanet.¹⁴ Particle diameters were estimated by quasielastic light scattering at 514 nm and an angle of 90° as is also described in the preceding reference as is a complete list of the chemicals used with their origin.

Viscosity of polymer solutions

An automated dilution viscometer equipped with an Ubbelohde capillary tube (inner diameter 0.58 mm) was used (Viscologic TI-I, SEMATech, Nice, France) to determine polymer intrinsic viscosities. Dry polymer powder was dissolved, at room temperature, in 0.5M NaCl at a concentration of 0.7 g/L. The apparatus automatically measures the efflux times at six polymer concentrations by dilution of the initial solution with 0.5M NaCl solution. For each concentration, the averaged value of seven measurements was taken to evaluate the specific viscosities. Extrapolation to zero concentration leads to the intrinsic viscosity and Huggins coefficient according to the Huggins equation.

Polymer precipitation

Polymer powder was obtained from precipitation of the polymerized inverse-emulsion into acetone

(Fluka, Buchs, Switzerland). A solution of ~ 14 g/L was prepared by dropping the final inverse-latex into acetone under vigorous agitation. The solution was further stirred (40–50 min) to break down remaining chunks, such that particles were finely divided and dispersed. Subsequently, the polymer solution was filtered and washed, and the polymer was dried into a vacuum oven (37°C, 30 m bar) until constant mass was obtained, for a period of up to 24 h.

Rheological characterization of polymer emulsions

A controlled stress rheometer (CS-10, Bohlin Instruments, Germany) was used for rheological characterization. Measurements of polymer-based water-in-oil emulsions were carried out at $(25 \pm 0.2)^\circ\text{C}$ and were allowed to rest 5 min after loading to permit induced stress to relax and temperature equilibration.

Inverse viscosity test: procedure and viscosity measurements

To study the influence of the surfactants stabilizing layer surrounding the polymer droplets, the surfactant composition was varied and inversion achieved with (10)-polyethoxylated nonylphenol (NP-10, Uniquema, Belgium) as the EB. To investigate the effect of stabilizing interface separating the two immiscible phases, two types of experiments were performed. In the standard procedure, polymer emulsions were stabilized with various surfactant blend compositions. The polymer emulsion containing the EB was subsequently agitated in excess water for 5 min at a fixed stirring speed. The duration of the process was determined to be acceptable based on preliminary experiments which indicated a plateau viscosity after this time. The second type of experiment estimated the polymer solution viscosity change during the initial 2 min of inversion.

The inversion properties of a polymerized emulsion were determined by preparing a dilute solution at 0.1 wt % of the polymer in deionized water and measuring the viscosity with a model L VDVII+ viscometer (Brookfield, Stoughton, MA). Measurements were carried out at 50 rpm and a temperature of $(20 \pm 0.2)^\circ\text{C}$. The precision in the measurement of the inverse viscosity was $\pm 2\%$ with an accuracy, compared to calibrations using rheometers of $\pm 4\%$ for the ranges of solution viscosities evaluated herein.

Conductivity measurements

Phase inversion and, more particularly, polymer release in excess water were carried out in a stirred vessel, in which the dissolved polyelectrolyte was

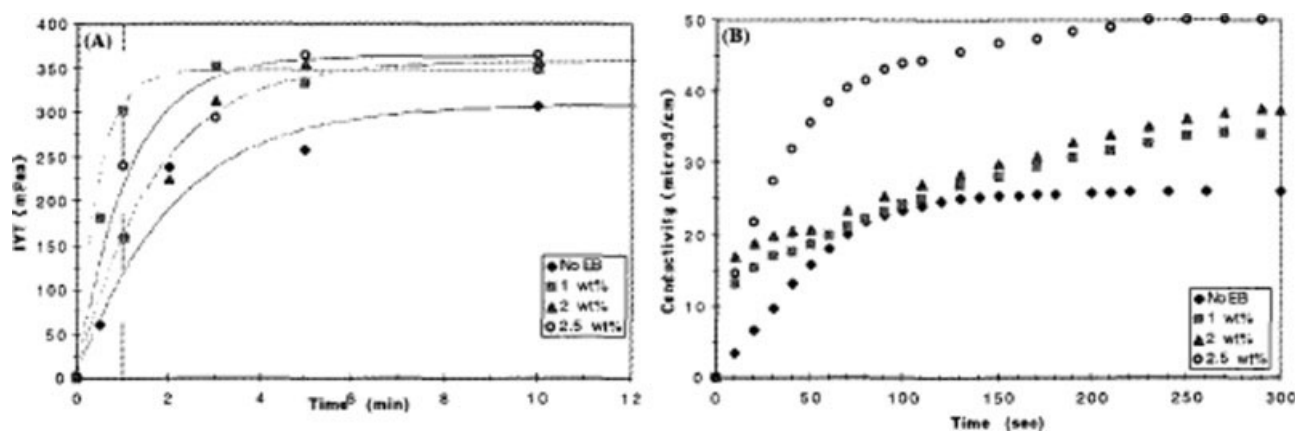


Figure 1 Viscosity (A) and conductivity (B) changes during the phase inversion of polymer emulsion stabilized with a surfactant blend composition of 95:3.2:1.8. The effect of inverting-surfactant (NP-10) on the inversion process is shown. The vertical dashed line separates the initial inversion region from the rest of the process (A). Experimental conditions: The emulsifier system was an ABA triblock copolymeric surfactant (HB-239), with sorbitan sesquioleate (Arlacel 83) and polyoxyethylene sorbitol hexaoleate (G-1086). The agitation speed was 600 rpm with an inversion temperature of $(25 \pm 0.5)^\circ\text{C}$.

measured by means of conductivity (712 Conductometer, Metrohm AG, Herisau, Switzerland). The conductivity measuring cell, with a cell constant of 0.82 cm^{-1} (Pt platinized electrode, Metrohm AG, Herisau, Switzerland), was immersed in the agitated water phase and measurements started as soon as the EB-based polymer emulsion was injected to the continuous phase for the duration of the process.

RESULTS AND DISCUSSION

Effect of the interfacial chemistry on the inversion rate and extent

Figures 1 and 2 follow the inversion process for an inverse-emulsion stabilized with various levels of

ABA type triblock copolymeric stabilizers in relation to the lower molar mass fatty acid esters and ethoxylated fatty acid esters. With 95% of the interface comprised of the block copolymeric stabilizer, the solution viscosity increased, from its plateau value, with higher concentrations of the EB (NP-10) [Fig. 1(A)]. These inversion profiles were characterized by a rapid viscosity rise during the first 60–80 s, followed by a reduction in the rate of inversion until a saturation value was reached at $\sim 300 \text{ s}$. The conductivity behavior was similar to the viscosity, revealing a sharp initial increase during the first 60 s of the inversion, followed by a reduction in the rate of inversion until a plateau value was obtained. The lowest inversion efficiency was determined for EB-free polymer emulsion as would be expected.

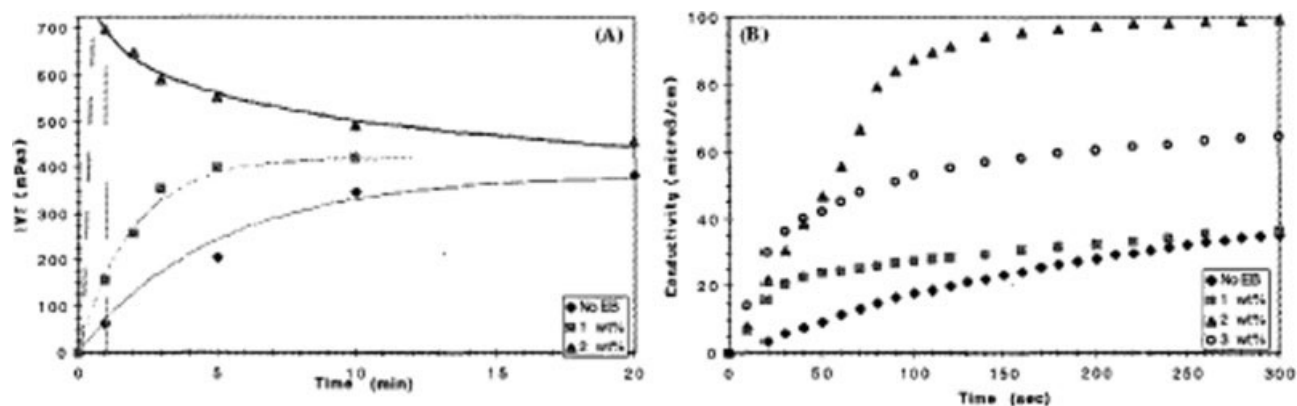


Figure 2 Viscosity (A) and conductivity (B) changes during the phase inversion of polymer emulsion stabilized with a surfactant blend composition of 8:58.9:33.1. The effect of inverting-surfactant (NP-10) on the inversion process is shown. The vertical dashed line separates the initial inversion region from the rest of the process (A). The slanted dashed line corresponds to a dramatic viscosity increase during the initial inversion. Experimental conditions: the emulsifier system consisted of an ABA triblock copolymeric surfactant (HB-239), with sorbitan sesquioleate (Arlacel 83) and polyoxyethylene sorbitol hexaoleate (G-1086). The agitation speed was 600 rpm with an inversion temperature of $(25 \pm 0.5)^\circ\text{C}$.

The copolymer contained within the W/O emulsion had 87.5 mol % of nonionic groups. Therefore, the cationic monomers are roughly separated by nine nonionic acrylamide units, such that the charge distance likely exceeds the Bjerrum length implying that counterion condensation can be excluded.^{15,16} Furthermore, as the conductivity of a solution depends on the ionic mobility,¹⁷ the low solution viscosity at the outset of inversion permits a more rapid conductivity increase.

For polymer emulsions stabilized with a low level of the block copolymeric stabilizer (8 wt %), inversion efficiency increased with the EB level [Fig. 2(A)]. The magnitude of inversion efficiency was also larger compared to the case with higher concentrations of ABA block copolymer stabilizers. Specifically, with 2 wt % of EB and a stirring time of 5 min, the inverse viscosity maximum was 550 m Pa s when 8% ABA stabilized was employed, compared to 350 m Pa s in the case where emulsions were stabilized with 95% ABA block copolymer. At low EB concentration (ranging up to 1–1.5 wt %), the viscosity profiles showed a rapid viscosity increase during the initial inversion step, followed by a slowing of the inversion process until a plateau was reached. As the EB concentration was further increased, a quite different viscosity profile was observed [Fig. 2(A)]. In these cases, the solution viscosity increased rapidly to a maximum, which was then accompanied by an asymptotic decrease. Interestingly, such nonconventional behavior was systematically observed as soon as the optimum EB concentration was reached and exceeded (for clarity, 3 wt % NP-10 was not shown in Fig. 2(A), although it showed the same characteristics with a lower magnitude).

When reporting conductivity versus stirring time [Fig. 2(B)], one observes that the curves maintained the typical characteristics already seen in Figure 1(B): a rapid conductivity increase during the first 60 s of inversion, followed by a reduction of inversion rate until a plateau value was reached. By comparing phase inversion carried out on two polymer emulsions with different surfactant blend compositions, the initial rate of inversion, defined as the viscosity change during the first 60 s, was thought to be the critical step affecting the inversion process [Figs. 1(A) and 2(A)].

Overall, Figures 1 and 2 indicate that the chemistry of the interface used during the synthesis has a quite significant influence on the ultimate ability to liberate polymer from the water-in-oil droplets during inversion. The interfacial chemistry influences not only the plateau value of the viscosity of the polymer solution, when contacted with an excess of water, but also the kinetics of such a release, which are thought to be influenced also by the size of the stabilizer at the interface. These effects will be inves-

tigated in the following subsections. It is important to note that, in all syntheses, the key variables that can influence the molecular weight of the resulting polymer were held constant. This includes the monomer concentration, aqueous-to-organic phase ratio, surfactant type and concentration as well as temperature. In this way, the discussion on the influence of inversion can be related to rheological parameters of a colloidal nature and not due to the viscosity of the polymer solution itself.

The inversion is clearly more effective (Table I) when higher levels of traditional sorbitan fatty acid esters are employed in the surfactant blend. Since it has been demonstrated in the past that relatively small levels of higher molar mass triblock stabilizers improve the ultimate stability of inverse-emulsions, there would be no technical reason to add the poly-12-hydroxyteric acid based materials to the formulation at high levels. The fatty acid esters have higher equilibrium inverse viscosities quite likely due to their propensity, via their five hydroxy groups, to hydrogen bond to polyacrylamide. This association was demonstrated approximately two decades ago.¹⁸ Therefore, the interfacial chemistry most appropriate for inversion is one that is mobile and also can form intermolecular complexes that can be subsequently liberated. In this sense, the hydrogen bonding serves as a vehicle to extend further the polymer in solution much as a temperature treatment does, rearranging intramolecular hydrogen bonds in favor of intermolecular ones.

Characterization of diluted polymer solution following inversion

Evaluation of polymer solution homogeneity

Table III summarizes the various solution characteristics of polymer emulsions inverted with a single inverting-surfactant of the polyethoxylated nonylphenol type. The EB concentration was chosen to be expressed in units of the total water content, including the excess water, to emphasize the effect of surfactant aggregation (CMC) on the properties of the final diluted polymer solutions. Following inversion, the diluted polymer solutions were perfectly homogeneous and free of any agglomerates, irregardless of the concentration of inverting-surfactant. This observation was valid for all surfactant blend compositions with the exception of those with the highest levels of block copolymeric stabilizers (82 and 95 wt % in the blend).

The presence of large amounts of ABA triblock copolymeric surfactant render the inversion of emulsions less effective with inversion efficiency not exceeding 48%, as will be detailed subsequently. The ABA triblock copolymeric stabilizer contains a long

TABLE III
Characteristics of the Final Diluted Polymer Solution Following Inversion. The Metrics Used to Describe the Polymer Solution are the Appearance, the Presence of Clumps and the Consistency (Viscous Solution or Viscoelastic)

Composition of interface (wt %) ^a $S_1 : S_2 : S_3$	C_{NP-10} (g/mL) ^b	C_{NP-10} (wt %) ^c	Appearance	Presence of clumps ^d	Gel consistency ^e	IVT (m Pa s) ^f
95 : 3.2 : 1.8	0	0	Very turbid	+–	—	257
	4.02×10^{-5}	1	White opaque	+–	—	307
	8.03×10^{-5}	2	White opaque	+–	—	340
	1.00×10^{-4}	2.5	White opaque	+–	—	371
82 : 11.5 : 6.5	0	0	White opaque	+–	—	297
	4.02×10^{-5}	1	White opaque	+–	—	334
	8.03×10^{-5}	2	White opaque	–	—	333
	1.20×10^{-4}	3	No data	No data	No data	No data
58 : 26.9 : 15.1	0	0	Turbid-opaque	–	—	261
	4.02×10^{-5}	1	White opaque	–	–	386
	8.03×10^{-5}	2	White opaque	–	+	383
	1.20×10^{-4}	3	White opaque	–	+	335
30 : 44.8 : 25.2	0	0	White opaque	–	–+	238
	4.02×10^{-5}	1	White opaque	No data	No data	453
	8.03×10^{-5}	2	White opaque	–	–+	498
	1.00×10^{-4}	2.5	White opaque	–	–+	480
	1.20×10^{-4}	3	White opaque	–	–	317
8 : 58.9 : 33.1	0	0	White opaque	–	No data	206
	4.02×10^{-5}	1	White opaque	–	–+	413
	8.03×10^{-5}	2	White opaque	–	+	525
	1.20×10^{-4}	3	White opaque	–	—	437

^a Surfactant composition based on the total mass of the blend. S_1 = ABA type block copolymeric surfactant; S_2 = sorbitan sesquioleate (Arlacel 83); S_3 = polyoxyethylene sorbitol hexaoleate (Atlas G-1086). S_1 - S_2 - S_3 were blended to obtain a constant HLB value of ~ 6.0 .

^b EB concentration in units of the total water phase content, which is g/mL of excess water.

^c EB concentration based on the total mass of the overall mixture.

^d The symbols (–) to (+) indicate the existence of clumps, where (–) indicates an absence of it and (+) its presence within the mixture after inversion. (+–) denotes an intermediate level of clumps.

^e The symbols (–), (–) up to (++) indicate the consistency of the final diluted polymer solution (after inversion). (–) denotes a viscous behavior, while (++) indicates a highly viscoelastic mixture. (–+) denotes an intermediate state.

^f NT denotes the viscosity of the diluted polymer solution after inversion. All measurements were carried out at 50 rpm and room temperature ($20 \pm 2^\circ\text{C}$).

hydrophilic chain (B = polyoxyethylene chain) that may anchor at the W/O interface rendering its mobility restricted. Indeed, the many hydroxy groups of the hydrophilic moiety might be viewed as adsorption sites reducing, thus, the surfactant mobility.¹⁹ With high ABA triblock levels at the interface, only part of the polymer is released rapidly while the remaining agglomerated and more slowly dissolving and, hence, liberating less rapidly the polymer viscosity. This description follows the hypotheses of Dickinson²⁰ who proposed that the stirring of an emulsion might provide sufficient energy to the system such that it jumped over an energy threshold. This implies that inversion is mechanico-chemical with the agitation forces preventing a diffusional limitation of excess water to the destabilized aqueous droplet and reducing the formation of agglomerates and liberating the latent viscosity. The larger ABA triblocks at the interface dampen the mechanical energy input, permitting only a partial ingress of the excess water.

Morphology of the final polymer solution: influence of inverting-surfactant concentration

A transition from a viscous- to viscoelastic-like structure, or *vice versa*, was observed with increasing EB concentration. Such change occurred at the optimum EB concentration, as is shown in Figure 3. As reported elsewhere,¹⁴ the diluted polymer solution that results from phase inversion is a complex mixture where three phases coexist: an oil phase, an aqueous phase containing the polymer and water as well as a mixture. This leads to a variety of noncovalent interactions including hydrogen bonding, hydrophobic interactions, and electrostatic forces that affect the rheology of these mixed solutions.

Similar to mixed polymer–surfactant solutions, where the nature of the association (cooperative versus noncooperative) depends on the surfactant concentration, as well as the polymer type,^{18,21,22} diluted polymer solutions are thought to be governed by similar mechanisms of association. This viscosity enhancement may be due to some interactions

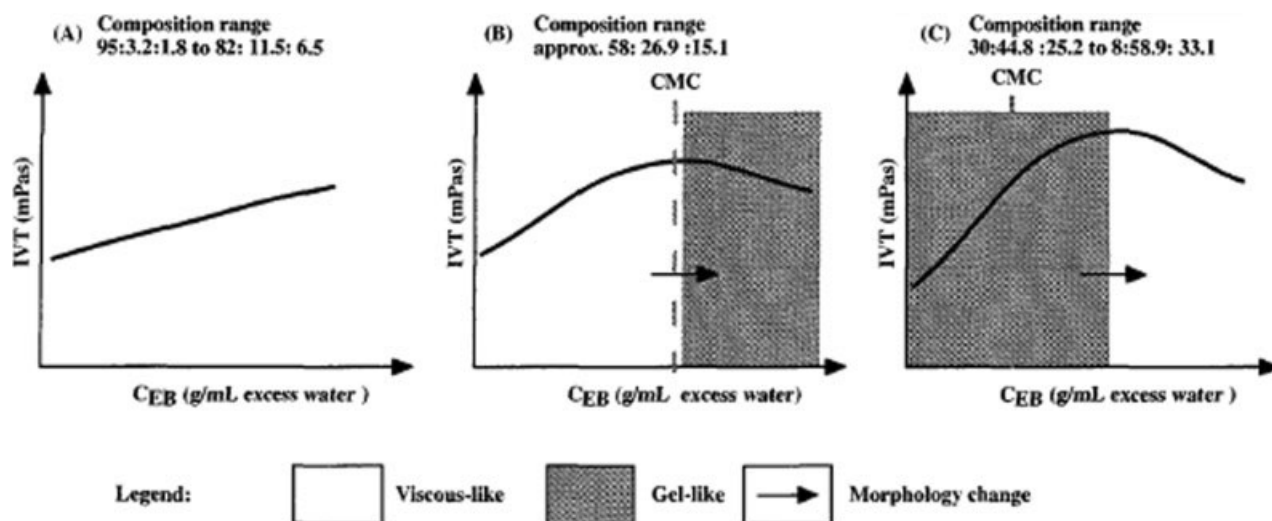


Figure 3 Morphology of the final diluted polymer solution, after inversion, as a function of the surfactant blend composition and the inverting surfactant concentration. To emphasize the influence of the surfactant aggregation, the EB concentration is expressed in units of the total water phase content. These dashed lines indicate the critical micellar concentration for pure EB solution and equals 5×10^{-5} g/mL.

between the polymer, the newly formed oil droplets (resulting from inversion W/O to O/W), and the water-soluble surfactants in the form of particulate aggregates. In this work, the authors assumed that the oil soluble emulsifiers were entrapped inside the resulting oil droplets, following inversion, such that their contribution might be negligible.

Overall, Case (B) (Fig. 3), might be best described by a cooperative association since the viscosity increase occurred below the CMC of the pure water-soluble surfactant (the CMC of NP-10 is 5×10^{-5} g/mL). As the optimum EB concentration is passed, which is approximately equal to the CMC of pure inverting-surfactant, and further EB is added, the solution viscosity decreased and the solution morphology changed to viscoelastic-like. The viscosity decrease can be attributed to the disruption of aggregates caused by the excess micelles, in analogy to the interaction of polymer-surfactants mixture characterized by a cooperative association.²¹ Another observation concerns the viscoelastic-like consistency observed above the CMC. Zhang et al.,²³ who studied polyacrylamide-surfactant interactions, proposed that the polyacrylamide might form a complex with the nonionic-surfactants at the water/oil interface.

An additional explanation is possible if one considered the inversion process as an emulsification of oil droplets. In such cases, the addition of EB to the system is thought to cause inversion from W/O to O/W system, such that oil droplets are formed. As EB is further added, the oil particle size might be reduced and droplet aggregation with polymer enhanced, as a result of improved colloidal forces.²⁴ At the CMC, and beyond, oil droplets attained their minimum size and the strong colloidal forces coupled

with the presence of polymer, as well as micelles in the continuous water phase could have promoted a viscoelastic-like effect. As the CMC is exceeded, micelles may disrupt aggregates, which results in a viscosity decrease since the continuous phase is liberated from the interstices.

In the opposite situation, where a viscosity increase occurred approximately beyond the CMC (Case (C), Fig. 3), noncooperative associations were thought to describe the situation, although the system did not correspond to a pure polymer-surfactant mixed solution. The viscosity increase, in this case, would indicate unfavorable hydrophobic interactions with the micelles. Therefore, one would not expect cooperativity in the interaction to cause the hydrophobes to nucleate the EB at concentrations lower than the CMC.²¹

Overall, higher levels of the EB provide of a more efficient phase inversion. Given that polymer-surfactant interactions are well known for acrylamide copolymers¹⁸ and that such copolymers, in the presence of fatty acid esters, tend to terminate with the interface and incorporate surfactant into the macromolecule,¹ it seems reasonable that association and a change to viscoelastic behavior accompanies effective inversion.

Influence of surfactant blend composition on the inversion efficiency

The experimental phase inversions of polymer-based W/O emulsion, as a function the EB concentration, for various surfactant blend compositions, are presented in Table III. As expected, the efficiency of inversion increases with increasing levels of fatty

TABLE IV
Maximum Polymer Solution Viscosity at the Optimum Concentration for the Different Surfactant Blend Composition Stabilizing Initial Polymer Emulsions

$S_1 : S_2 : S_3^a$	Particle size (nm)	$C_{\text{optimum, NP-10}}$ (wt %) ^b	IVTmax (m Pa s)
95 : 3.2 : 1.8	359	No optimum	No maximum
82 : 11.5 : 6.5	–	1.5 ± 0.2	334
58 : 26.9 : 15.1	316	1.2 ± 0.2	386
30 : 44.8 : 25.2	–	2.0 ± 0.2	498
8 : 58.9 : 33.1	346	2.0 ± 0.2	525

^a Surfactant composition based on the total mass of the blend. S_1 = ABA block copolymeric surfactant; S_2 = sorbitan sesquioleate (Arlacel 83), S_3 = polyoxyethylene sorbitol hexaoleate (Atlas G-1086). S_1 - S_2 - S_3 were blended to obtain a constant HLB value of ~ 6.0 .

^b The range indicated for the NP-10 level indicates that the efficiency of inversion had an optimal range. Therefore, 2.0 ± 0.2 indicates that for NP-10 levels between 1.8% and 2.2% the performance was similar within the precision of the measurements.

acid esters in the surfactant blend (less triblock copolymeric stabilizer). Furthermore, the inversion efficiency rose as the concentration of the inverting-surfactant increased up to a maximum value, above which the inverse viscosity (IVT) of the diluted polymer solution decreased. The optimum concentration was attributed to a complete, or at least optimized, coverage of the water/oil interface, such that phase inversion process was promoted and followed by the polymer “release” into the excess water phase. As EB was further added to the polymer emulsion, the viscosity decrease was attributed to a subsequent dissolution of the inverting-surfactant in either oil or water depending on its relative solubility, partitioning, and HLB. As a result, enhanced emulsion stability was observed, due to the repulsion forces generated by the layers of surfactant molecules surrounding the droplet surface. This explanation has been proposed by Zaki et al.^{21,25} and Goldzal et al.,²⁶ when studying de-emulsification of water-in-oil emulsions.

It should be pointed out that the inverted polymer emulsion containing the stabilizing blend with the highest amount of the ABA block stabilizer showed no maximum, over the EB concentration range tested (Table III). Furthermore, a coagulum build up was observed if more than 3 wt % EB was added. This might be due to steric hindrance caused by the presence of block copolymeric surfactant and the excess of inverting-surfactant molecules that tend to reach the vicinity of the W/O interface. As a result, the flow of the continuous phase separating droplets is drastically reduced up to the point of being stopped, which resulted in the formation of a block.

Surfactant blend composition and its influence to optimum EB-concentration

The optimum EB concentration necessary to obtain a maximized solution viscosity was observed to

depend on surfactant blend composition. Furthermore, the optimum EB concentration exhibited a shallow minimum at ~ 58 -wt % of the triblock stabilizer in the stabilizing surfactant blend, as depicted in Table IV. To explain the optimum concentration dependency, one could consider particle size and interfacial tension properties of the stable polymer droplets. The blend of emulsifiers contains the ABA triblock copolymeric agent (HB-239) providing enhanced steric hindrance and very low interfacial tension (approaching zero), with fatty acid ester type agents (Arlacel 83 and G-1086) of lower steric hindrance and moderate interfacial tension. Therefore, at high ABA triblock levels, the W/O interface consisted mainly of large surfactant molecules, whose surface coverage is important (300 \AA^{227}), and which generate very low interfacial tensions. As has been recently observed,¹⁴ the very low interfacial tension conferred by HB-239 could not explain the low curvature. Other contributions, such as the bending rigidity and the saddle splay modulus of the surfactant film, according to the Helfrich curvature energy,²⁸ were thought to impart the low curvature of the droplets, due to the large size of the copolymeric surfactant. In other words, the small amount of molecules and its probable rigidity might result in low free energy of the film.

In the opposite situation, that is a dominant presence of fatty acid ester-based surfactants, a similar particle size and, thus a low curvature, was measured. In this case, the low free energy of the film might be attributed to a moderate interfacial tension and a moderate to low bending rigidity and saddle splay modulus. Despite the presence of these two agents at the W/O interface, it is likely that the bending rigidity is small, due to low interactions. Although the interface seems to be more “condensed” due to the variety of molecules at the W/O interface (such as they ensure steric hindrance), the low bending rigidity might be attributed to limited/

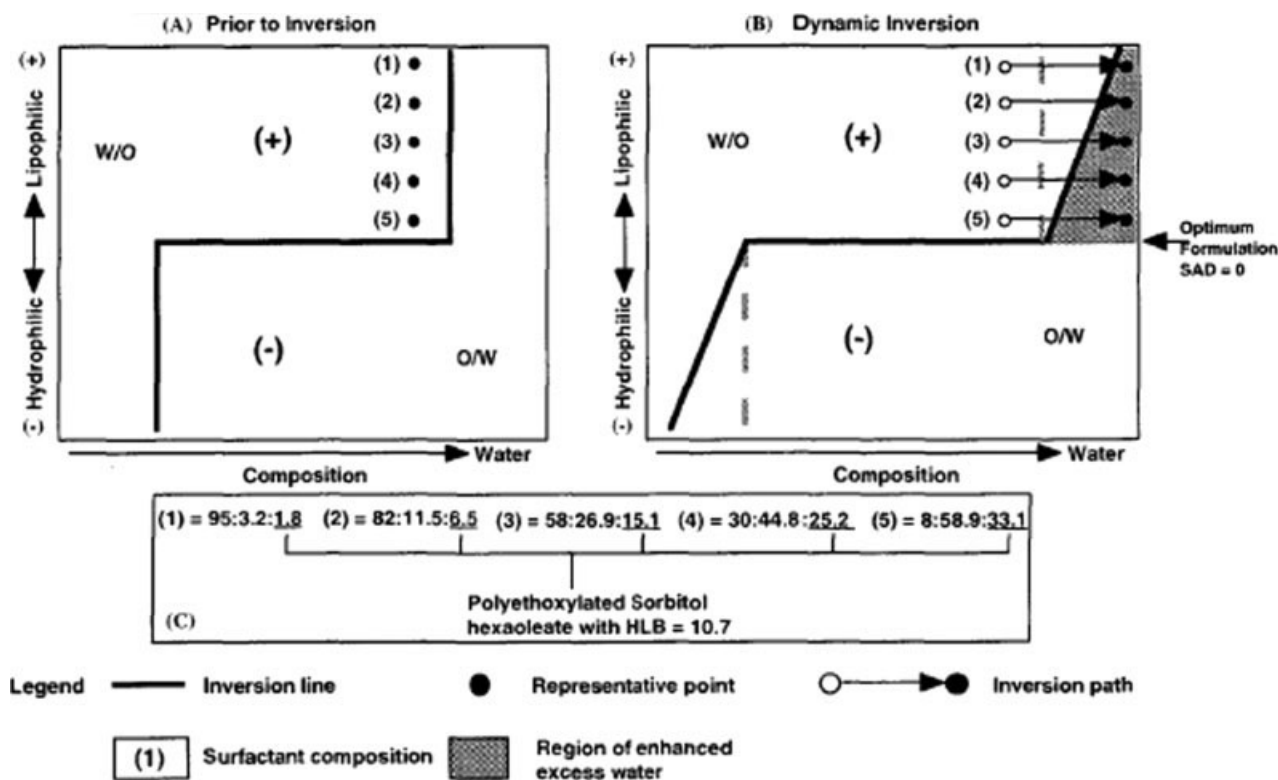


Figure 4 Dynamic inversion patterns of polymer emulsion containing (10)-polyethoxylated nonylphenol (NP-10) as inverting-surfactant, adapted from ref. 5. The effect of surfactant blend composition (described by the affinity) on the inversion process at a fixed EB concentration (2 wt %, for example) is shown. The region labeled (+) denotes the surfactant affinity greater for oil, while the region labeled (−) indicates a greater surfactant affinity for water. Before inversion (solid points in A), the polymer emulsion is located in the upper part since stabilizing surfactants are oil soluble. The high HLB surfactant, contained in the blend, affects the overall affinity, as is indicated in B. As is shown in C, the total amount of this high HLB surfactant increases in the blend such that the overall affinity to oil might be reduced and, thus approaching the optimum formulation. Therefore, EB is thought to facilitate the inversion as shown in B. It should be pointed out that the formulation–composition map concerns only a single concentration of inverting-surfactant.

reduced interactions between the surfactants molecules. Therefore, the ethoxylated fatty ester evaluated (HLB = 10.2) and sorbitan fatty acid ester employed (HLB = 3.7) have rather opposite affinity to the liquid phases in play, such that it results in low stiffness and a low free energy of the film. At intermediate concentrations of ABA triblock copolymeric stabilizers and fatty acid esters (roughly 50 : 50 as was achieved by Armanet¹⁴ and Renken²⁹), the particle size was minimized. It is likely the surfactants have reached the most condensed state, such that the stiffness of the film is greater and the free energy of the film is maximized. As an illustration, Table IV reports the particle size, the optimum EB concentration, and the maximum solution viscosity as a function of surfactant blend composition.

To best describe the path of inversion, a formulation–composition map is ordinarily applied.^{6,14,30} Figure 4 shows formulation–composition maps before and during inversion of polymer emulsions stabilized with different surfactant blend compositions (this follows strictly our experimental conditions).

The formulation variable chosen for the discussion is the surfactant affinity difference (SAD), since a single HLB of ~ 6.0 was used to formulate all emulsions and thus cannot be used as a formulation variable. The SAD is defined as the difference between the standard chemical potentials of the surfactant in the oil and water phases and may be related to the partition coefficient (K_p) of the surfactant between water and oil:¹³

$$\text{SAD} = -RT \ln(K_p) \quad (1)$$

If one considers the HLBs and solubility of each emulsifier as detailed in Table V, SAD might be qualitatively approached. Indeed, one may reasonably think that is likely greater than unity, due to its water affinity, while $K_{p,S_3} > K_{p,S_2}$ and may range below unity since they are essentially oil soluble ($K_{p,S_3} > K_{p,S_2} > K_{p,S_1}$). Consequently, would be negative while and would be positive at the corresponding temperature. Since all emulsifiers are blended and assuming that the SAD of a surfactant mixture

TABLE V
Physicochemical Properties of the Emulsifiers
Comprising the Blend

Emulsifier ^a	HLB ^b	Solubility ^b
S ₁ : HB-239	5-6	Oil
S ₂ : Arlancel-83	3.7	Oil
S ₃ : Atlas G-1086	10.2	Water

^a Surfactants are described by their commercial name. Details of the chemical description are provided in the Experimental Section.

^b Provided by the Material Safety Data Sheet of each component.

could be calculated from a linear averaged mixing rule based on weight composition, intermediate SAD could be attained by using the following relationship:

$$SAD_{\text{Mixture}} = \sum_{i=1}^n x_i \cdot SAD_i \quad (2)$$

where X_i denotes the surfactant mass fraction within the blend and SAD_i characterizes the emulsifier. It has to be pointed out that this relationship was inspired by the HLB scale used for surfactant mixtures.³¹ Furthermore, there is no evidence that this relationship is true as applied to surfactant blends, since the various interactions in play are not considered. However, this oversimplified view may be sufficient to justify the different locations (representative point) of the stable polymer emulsion within the formulation-composition map. For small quantities

of G-1086 (S_3) in the surfactant blend SAD_{mixture} would be positive (the dominant affinity of the surfactant blend is for the oil, since we promoted W/O emulsions and, thus, should be located in the positive region) and elevated [Fig. 4(C), while enhancing its concentration in the blend would lower the SAD_{mixture} value (still positive) such that $SAD_{\text{mixture}(1)} > SAD_{\text{mixture}(2)} > SAD_{\text{mixture}(3)} > SAD_{\text{mixture}(4)} > SAD_{\text{mixture}(5)}$, as depicted in Figure 4(A). Furthermore, the enhancement of inversion efficiency requires the use of an inverting-surfactant, which promotes the inversion process. Therefore, as EB is added to the stable polymer emulsion, it might affect the overall affinity or at least perturb their interfacial properties of the surfactant layer in a way that promotes inversion. Salager et al.⁷ and Brooks et al.^{32,33} observed that the inversion did not proceed immediately after crossing the vertical inversion line. Instead, it was displaced with respect to the standard inversion line, in the sense that the emulsion could take up an amount of dispersed phase beyond that expected, before inversion happened.³⁴ As a result, a highly lipophilic system required a greater amount of dispersed phase to achieve inversion while a less lipophilic system required a smaller amount of water for inversion. As an illustration, Figure 4(B) shows a slanting of the inversion line, described as dynamic inversion,⁷ which has been previously demonstrated for the system under study herein.¹⁴

By assuming that a water phase excess of $\sim 99.6\%$ (by volume) brought the composition over the

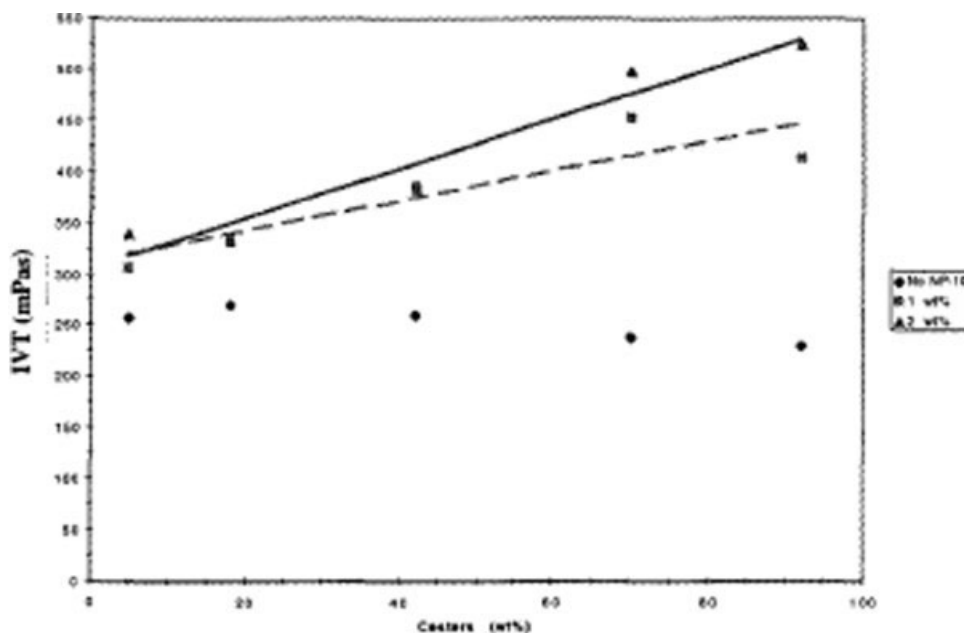


Figure 5 Viscosity of diluted polymer solution as function of surfactant blend composition. The effect of inverting-surfactant concentration on the efficiency of inversion is shown. The full line refers to inversion carried out with 2 wt % EB while the dashed line corresponds to emulsion inversion with 1 wt % EB.

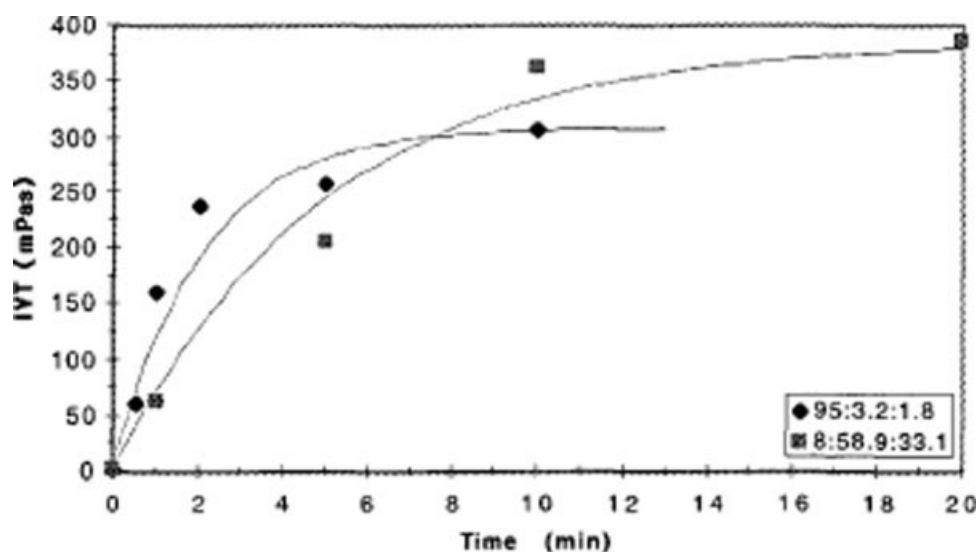


Figure 6 Phase inversion of an EB-free polymer emulsion as a function of stirring time. The effect of surfactant blend composition is shown. Experimental conditions: an agitation speed of 600 rpm was employed with a temperature of $(22 \pm 2)^\circ\text{C}$. Emulsifier system: S_1 = ABA triblock copolymeric stabilizer (HB-239); S_2 = sorbitan sesquioleate (Arlacel 83); S_3 = polyoxyethylene sorbitol hexaoleate (G-1086).

slanted inversion line, one might expect that phase inversion would have been complete, irregardless the surfactant blend composition of the polymer emulsion used. However, as shown in Figure 5, the viscosity of diluted polymer solution after inversion depends on surfactant blend composition and inverting-surfactant concentration. The authors propose the following hypothesis to explain this dependency:

1. As inversion proceeds, the viscosity of the continuous aqueous phase increases due to the *polymer release*. This increase could slow down the inversion process, such that further rises in viscosity are retarded. Brooks observed³⁵ that phase inversion occurs locally in the medium leaving other regions unchanged. The presence of polymer might enhance this effect. Furthermore, if one compares the excess water required to invert a polymer emulsion at the two opposite sides of the surfactant blend composition range [Fig. 4(B)], it is evident that one case requires less excess water to cross the inversion line. The excess water may dilute the polymer solution to reduce the retardation effect caused by the rapid viscosity increase. Therefore, polymer emulsion stabilized with a large amount of fatty acid esters provides an enhanced solution viscosity.
2. The surfactant blend composition may affect the efficiency of inversion such that it hinders the *inverting-surfactant that promotes destabilization of the interface*. The presence of the ABA triblock copolymeric stabilizer in the surfactant blend is thought to inhibit the interfacial activity of the EB, by maintaining the Marangoni-Gibbs effect

and a low surface mobility. The triblock polymeric stabilizer, which contains a water soluble polyethylene oxide (B), may be anchored to the interface and the poly (12-hydroxystearic acid) end (A) is free to move in the continuous phase,³⁶ such that surface mobility is reduced and steric hindrance is enhanced. This may result in enhanced emulsion stability. Therefore, at high block copolymer levels, phase inversion is limited and solution viscosity is lower.

3. Depending on the exact location of the inversion line, there may be the situation where inversion is partial and coexists with other emulsion morphologies. This case might be particularly true at high ABA stabilizer fractions in the surfactant blend.

TABLE VI
Effectiveness of Phase Inversion of two Polymer Emulsions Stabilized at Two Different Surfactant Blend Compositions

Surfactant blend composition ^a	$C_{\text{NP-10}}$ (wt %)	Effectiveness
8 : 58.9 : 33.1	0.0	0.32
8 : 58.9 : 33.1	1.0	0.32
8 : 58.9 : 33.1	2.0	0.88
8 : 58.9 : 33.1	3.0	0.57
95 : 3.2 : 1.8	0.0	0.25
95 : 3.2 : 1.8	1.0	0.33
95 : 3.2 : 1.8	2.0	0.36
95 : 3.2 : 1.8	3.0	0.48

^a Surfactant composition based on the total mass of the blend. S_1 = ABA type block copolymeric surfactant, S_2 = sorbitan sesquioleate (Arlacel 83), S_3 = polyoxyethylene sorbitol hexaoleate (Atlas G.1086). S_1 - S_2 - S_3 were blended to obtain a constant HLB value of ~ 6.0 .

TABLE VII
Comparison of the Polymer Solution Viscosities Obtained from the Inversion and the Dissolution of the Polymer in Water, in the Absence of Inverting-Surfactant

Composition of interface (wt %) ^a $S_1 : S_2 : S_3$	Preparation path	Appearance	IVT (m Pa s) ^b
95 : 3.2 : 1.8	Inversion of polymer emulsion	Very turbid	257
95 : 3.2 : 1.8	Polymer precipitation followed by polymer dissolution in water	Transparent	136
8 : 58.9 : 33.1	Inversion of polymer emulsion	White-opaque	206
8 : 58.9 : 33.1	Polymer precipitation followed by polymer dissolution in water	Transparent	138

^a Surfactant composition based on the total mass of the blend. S_1 = ABA type block copolymeric surfactant, S_2 = sorbitan sesquioleate (Arlacel 83), S_3 = polyoxyethylene sorbitol hexaoleate (Atlas G.1086). S_1 - S_2 - S_3 were blended to obtain a constant HLB value of ~ 6.0 .

^b IVT denotes the viscosity of the diluted polymer solution. All measurements were carried out at 50 rpm and at room temperature ($20 \pm 2^\circ\text{C}$).

For the phase inversion of EB free polymer emulsion, as depicted in Figure 5, the solution viscosity was nearly independent of surfactant blend composition. Figure 6 illustrates the effect of stirring time on the inverse viscosity (IVT).

Quantification of inversion efficiency

The evaluation of the inversion efficiency was carried out from an analysis of the conductivity data [Figs. 1(B) and 2(B)]. Contrary to the viscosity data, which take into account the different interactions conductivity is essentially a function of the polyions and its counterions. We have defined the effectiveness of inversion as the ratio of the conductivity of pure polymer solution at the corresponding solid

concentration (0.1 wt %). Conductivity data were based on a stirring time of 5 min. As an illustration, Table VI presents inversion effectiveness of two polymer emulsions as a function of the EB concentration. As expected, the effectiveness of inversion was dependent on the inverting-surfactant concentration and the maximum efficiency of 0.88 was obtained at ~ 2 wt % EB, which destabilized a polymer emulsion containing a low amount of the block copolymer stabilizer in the blend. As the optimum EB concentration was exceeded, the effectiveness was observed to decrease, due to possible subsequent dissolution of EB in either phase (water and oil). This may result in an enhanced emulsion stability owing to the repulsive forces generated by the layers of inverting-surfactants molecules adsorbed on the

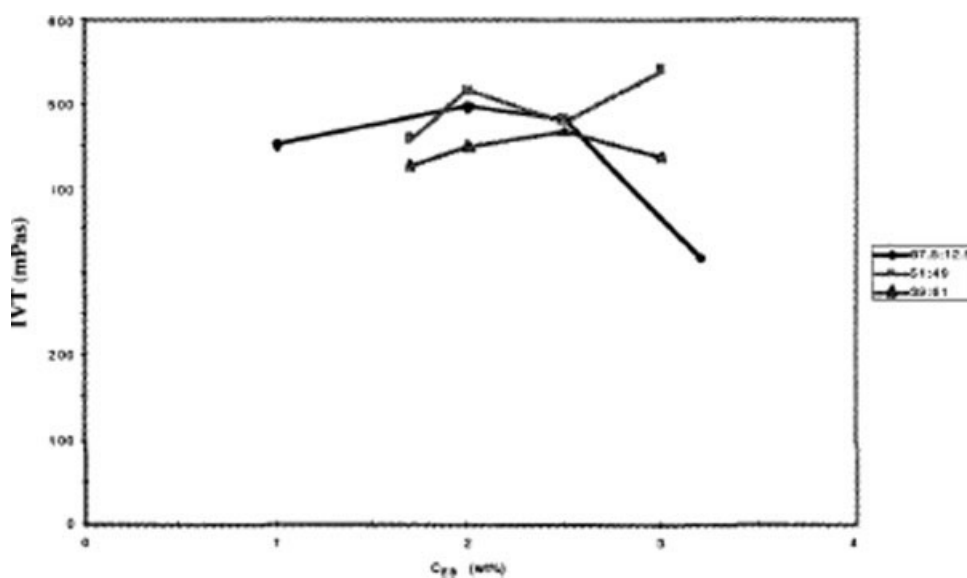


Figure 7 The viscosity of diluted polymer solution, following inversion, is shown as a function of inverting-surfactant concentration. The molar ratio of acrylamide to quaternary ammonium monomer is varied from 87.5 : 12.5 (acrylamide/cationic monomer) to 39 : 61. A mixture of three nonionic surfactants was used to stabilize the polymer emulsion at the following composition: $S_1 : S_2 : S_3 = 30 : 44.8 : 25.2$. The emulsifier mixture was ABA triblock copolymeric surfactant (HB-239) with sorbitan sesquioleate (Arlacel 83) and POE sorbitol hexaoleate (G-1086).

TABLE VIII
Intrinsic Viscosity and Huggins Coefficient Data Evaluated from Huggins Equation at Different Acrylamide to Quaternary Ammonium Monomer Ratios

Run ^a	AAM/DMAEA (mol %)	Total monomer ^b (mol)	Intrinsic viscosity (dL/g)	Huggins coefficient	Regression coefficient
103000	87.5 : 12.5	2.89	17.86	0.166	0.999
101700	51.0 : 49.0	1.91	21.58	0.045	0.999
101900	39.0 : 61.0	1.72	16.75	0.098	0.995

^a Experimental conditions: Initiator = 2,2'-azobis(2,4-dimethylvaleronitrile); a blend of 30 wt % ABA triblock copolymeric surfactant (HB-239) associated with 44.8 wt % sorbitan sesquioleate (Arlacel 83) and 25.2 wt % polyoxyethylene sorbitol hexaoleate (Atlas G-I086) was used. The total solid content represents 25 wt % of the total emulsion mass; $T = 40^{\circ}\text{C}$.

^b Molecular weight of AAM = 71.08 g/mol and DMAEA = 193.68 g/mol.

droplets' surfaces.²⁵ In the opposite situation, where polymer emulsion was stabilized with a greater amount of block copolymer in the blend, the maximum effectiveness did not exceed 0.48 at 2.5 wt % NP-10. Additionally, no optimum EB concentration was found over the concentration range tested, which seemed to indicate a poor inversion performance resulting from this formulation. Overall, conductivity measurements substantiated the conclusions of the viscosity measurements.

Table VII shows the viscosities data of the diluted polymer solutions obtained by the inversion process and the dissolution of the polymer powder in water. To reduce the number of interconnected parameters, the polymer solutions were prepared without inverting-surfactants. Interestingly, the dissolution of the polymer in water resulted in a smaller viscosity (136 m Pa s) than for polymer solution obtained by inversion (206–257 m Pa s), indicating, as is known from the patent literature, that the process of drying and subsequent redissolution results in a loss of viscosity.

Phase inversion of polymer emulsions: influence of monomer composition

The phase inversion of polymer emulsions was carried out at EB concentrations ranging from 1 to 3 wt %. Figure 7 shows the polymer solution viscosities, after inversion, as a function of EB concentration for various polymer compositions. Table VIII lists the corresponding Huggins coefficients, all of which are suitably low to imply very good solubility of the polymers prepared. The intrinsic viscosities in Table VIII indicate that the various polymers were of approximately equal chain length. Specifically, intrinsic viscosities were, for the three syntheses, 19 ± 2.5 dL/g. This represents slightly more variation in intrinsic viscosity than the polymers noted in Table II, though still well controlled given the variation in the experimental conditions. The solution viscosities revealed a rather minimal dependence on the comonomer composition, over the concentration range tested. The optimal inversion efficiency of the polymer emulsion

was observed at concentrations of $\sim 2 \pm 0.2$ wt % inverting-surfactant. The investigation of comonomer composition seems to indicate its relative lack of effect on the inversion efficiency.

CONCLUSIONS

The addition of a water-soluble inverting-surfactant to the polymer emulsion did not significantly influence the shape of the viscosity profile, although its viscosity varied with concentration. The flow curves followed what was generally observed for emulsion, that being a low shear viscosity, followed by a shear thinning region and the onset of a high shear viscosity. The viscosity curves were successfully described by the Cross model equation, when applied up to 2 wt % NP-10, as the EB, in the mixture.

The catastrophic phase inversion process was strongly influenced by its initial rate. The comparison of inversion efficiency evaluated by viscosity measurements and conductivity measurements were in close accordance. The optimal inversion was observed with a polymer emulsion stabilized with a low block copolymer stabilizer levels in the blend (8 wt %) and reached an effectiveness of 0.88 (level of polymer release in water relative to one). On the contrary, polymer emulsion containing a higher level of block copolymeric stabilizers resulted in a less effective inversion. Phase inversion of polymer emulsion was further studied through variation of comonomer composition. The results showed a rather minimal dependence on the composition.

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