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Ethel Zaiser Casassa[a]
[a] Chemical Engineering Department, Carnegie-Mellon University, Pittsburgh, PA

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Colloid and Interface Effects of Additives in Interfacial Polycondensation

Ethel Zaiser Casassa

Chemical Engineering Department
Carnegie-Mellon University
Pittsburgh, PA. 15113

ABSTRACT

Interfacial polycondensation reactions are routinely conducted with empirically developed methodology which might be improved if some well-known principles of colloid and surface chemistry were invoked. An example in the interfacial synthesis of polymers is the use of additives such as catalysts and emulsifiers to enhance the degree of polymerization. In this paper possible modes of action of surfactants and quaternary ammonium catalysts in stirred interfacial polycondensation are examined. The agents are considered variously as ions, molecules, and micellar aggregates, acting upon each component of the system, i.e. monomers, oligomers, polymers, and solvents. The functions delineated include emulsification of the solvent phases, solubilization of monomers in regular or inverse micelles, solubilization of oligomers and polymers, phase transfer catalysis, and micellar catalysis.

INTRODUCTION

In colloidal dispersions, since the ratio of surface to volume of the dispersed particles is very high, the contribution of surface energy to the total free energy is large. Most so-called colloid phenomena are merely the consequence of ordinary processes of diffusion, adsorption, and electrostatic and van der Waals interactions, which take on special aspects because of the extra free energy and the small particle size (0.01 to 10 μ) of colloids. Heterogeneous reaction systems, which are of obvious interest to surface scientists, become all the more fascinating when the different phases are highly dispersed into units of colloidal size. Nowhere is this interest more evident than in free-radical emulsion polymerization where both the formation of a latex and the colloidal properties of latex particles have been widely studied [1]. One aspect of emulsion polymerization which has been clarified by thorough investigation is the role of the surfactant or emulsifier which is nearly always employed. A surfactant, as an amphiphile, tends to be distributed at a polar/nonpolar interface in a concentration in excess of the bulk value in solution, and has in addition a tendency to aggregate at a characteristic concentration, the critical micelle concentration (CMC). These properties, which are of course related, are put to excellent use in emulsion polymerization.

Current understanding of the functioning of surfactant in emulsion polymerization is in part the outcome of intensive research into the colloid and surface science of such systems. Interfacial polymerization, which has received far too little attention from colloid chemists, differs from free-radical emulsion polymerization in important ways. This paper offers an overview of the range of phenomena that principles of colloid and surface chemistry suggest are likely to be found in interfacial reaction systems, with special emphasis on the behavior of surfactants and other additives.

COLLOID AND SURFACE ASPECTS OF INTERFACIAL POLYCONDENSATION

Interfacial synthetic methods are particularly suited to polycondensation, as in the production of polyamides and polyesters where they are valued for speed, low energy requirements, and the high degree of polymerization they afford. The reactions, which are generally nucleophilic substitutions involving pairs of reactants of dissimilar chemical nature and solubility, require careful selection of system variables to ensure the growth of long chains and to minimize side reactions. Interfacial reaction systems have the following elements in common:

(1) Two immiscible solvent phases, usually water and a nonpolar liquid.

(2) Two monomers, each insoluble in the phase that dissolves the other.

(3) Monomers that are bifunctional, reacting to form regular chains of alternating monomer residues.

In a polyester synthesis, for example, one monomer is the enolate anion of a bisphenol in strongly alkaline water solution, the other a diacid chloride in a chlorinated hydrocarbon. The condensation reaction occurs either at the phase boundary, or within either liquid phase near that surface, hence stirring facilitates reaction by creating a dispersion of high interfacial area. Virtually complete reaction is so much the rule that efforts to improve interfacial preparative methods have dwelt upon achievement of a high degree of polymerization rather than upon improvement of the yield. Early work in the field offers many good examples of organic industrial chemical research directed toward the empirical achievement of a desired product. System variables that have been explored in depth are the concentrations and relative amounts of reactants, the selection of the nonpolar solvent, the chemical structure of the monomers, rate of stirring, sequence of addition of reactants, and the use of additives such as catalysts or emulsifiers [2,3,4]. More recently, reviews have dealt with the transport of reactants across phase boundaries [5], interface effects on reaction rates [6], and the fluid mechanics and transfer aspects of stirring [7]. Mechanistic studies have not been concerned with the functioning of the additives which are generally used. Although the heterogeneity and complexity of interfacial polycondensation systems is daunting, insofar as they are colloidal dispersions, it may be profitable to consider the colloid phenomena which can occur when additives are used to enhance the molecular weight of the product. These effects can be classified as emulsification, solubilization, and catalysis. Wherever specific examples of systems are mentioned, the reference will be to polyesterification as a typical polycondensation reaction. With minor modifications this approach may of course also be applied to other polycondensation reactions.

EMULSIFICATION IN INTERFACIAL POLYCONDENSATION

An emulsion, i.e. a liquid-liquid colloidal dispersion, is the most intimate mixture possible for the two mutually insoluble solutions which comprise an interfacial reaction system. Because of surface-tension lowering by organic solutes, even in the absence of additives, surface tensions of both solvents in interfacial polymerization systems can be expected to be less than those of pure solvents by reason of the dissolved monomer in each phase. This reduction, which varies with different solute-solvent pairs, and is larger for the aqueous phase than for the organic one, undoubtedly aids in the dispersion of one phase in the other when the system is stirred. As the surface-tension lowering is the result of a surface excess of solute, droplets of either phase dispersed in the other will have a slight surface excess of whichever monomer is dissolved in the liquid of the droplet. This surface excess should favorably affect the availability of that monomer for reaction with the second monomer in the other liquid phase. Emulsions formed in the absence of surfactant additives, however, are unlikely to persist if stirring is discontinued as most monomers are not markedly amphiphilic. Also for lack of amphiphilic character symmetrical quaternary ammonium salts (tetramethyl- or tetraethylammonium bromide, for example) which are often added as catalysts should not materially enhance emulsification.

Surfactant "emulsifiers," often added to polycondensation systems are effective stabilizers of emulsion droplets regardless of the charge type of the surfactant. If we restrict discussion here to surfactant concentrations below the CMC, we need not be concerned with the action of micellar aggregates of surfactants but only with stabilization conferred by adsorption of individual amphiphilic molecules or ions at the polar/nonpolar liquid interfaces of emulsion droplets. Since the polar portions of amphiphiles thus adsorbed are attracted to the aqueous phase and the nonpolar portions to the organic liquid, the posture of an adsorbed amphiphile will depend on which liquid makes up the droplets and which the continuous phase of the emulsion. In any case, cationic, anionic, and nonionic surfactants will confer not only stability but positive, negative or zero charges, respectively, upon droplets on which they are adsorbed. If such charges attract or repel charged reactive monomer species (e.g. enolate ions in polyesterification), they will aid or hinder the mutual approach of reactive species residing in the different phases. Just such a charge effect may account for the superiority we have found for cationic over anionic and nonionic surfactants at low concentrations in a linear aromatic polycondensation [8]. Thus while emulsification in itself may be an aid in interfacial polycondensation, the charge type of the dispersal agent can be an important consideration. We cannot neglect to mention that the emulsifying action of surfactants at concentrations in excess of the CMC is, if anything, stronger than at lower concentrations, but it is difficult to separate this from other phenomena which fall in the category of solubilization.

SOLUBILIZATION BY SURFACTANTS IN INTERFACIAL SYSTEMS

Solubilization, the enhancement of the solubility of a substance in a liquid by action of a third substance, may figure in two ways in interfacial polymerization. The most often cited role of this phenomenon in stirred interfacial polymerization is the conferral of solubility, or partial solubility, on oligomers as well as growing polymer chains by the action of surfactant. The prevention of premature precipitation of polymer must of course aid in attainment of high molecular weight, although there is evidence that polymerization continues after precipitation of the polymer [9]. The most likely cause of such solubilization is adsorption by the polymer of surfactant ions or molecules, or perhaps even micellar aggregates. Another form of partial solubilization is the swelling of the polymer by the nonpolar solvent of the reaction system. It is well known that such solvent interaction aids in attaining a high degree of polymerization, possibly because swollen polymer remains permeable to monomers.

The form of solubilization most familiar to the colloid chemist, however, is micellar solubilization, which becomes manifest only at concentrations in excess of the CMC in surfactants [10,11]. Micellar aggregates which appear at and above the CMC contain typically 50 to 100 surfactant ions or molecules, and exhibit a solubilizing effect on species ordinarily sparingly soluble in the medium. Note that micelles formed in water have polar groups on the outside, and hydrocarbon-type groups on the interior, while inverse micelles, which may form in nonpolar media, have polar groups and a small amount of water on the inside. The interior environment of a micelle, which thus is very different from the medium in which it is formed, is the most likely location for solubilized material that is not ordinarily dispersible in the liquid medium. Micelles of surfactant in the aqueous phase of interfacial polycondensation systems are capable of solubilizing any nonpolar component of the system, e.g. monomer from the organic phase, the organic solvent itself, or even oligomers. Note that such solubilizates are molecularly dispersed, a condition not to be confused with an emulsion type of dispersion where the droplets are made up of solvent containing dissolved monomer. In polyesterification, diacid chloride monomer solubilized in micelles in the aqueous phase might be available for reaction with the enolate monomer of the aqueous phase; but as a given micelle can accommodate very few solubilizate molecules, it is not certain that such dispersal would be helpful beyond the early stages of polymerization. Furthermore, diacid chloride monomer in the aqueous phase is vulnerable to base-catalyzed hydrolysis, a side reaction which may be important if the rate is comparable to that of the condensation reaction. Inverse micelles, if formed in the organic phase, would carry with them a little solubilized water and water-soluble monomer species, but this is a less likely occurrence than formation of micelles in the aqueous phase.

As with surfactant-stabilized emulsion droplets, the charge type of the surfactant is important to its effect as a micellar solubilizing agent. Micelles of cationic surfactants which may carry solubilized diacid chloride into the aqueous phase are positively charged and thus attract oppositely charged enolate ions. Micelles of anionic and nonionic surfactants would not be helpful in this respect, and whatever advantages they may furnish in polyesterification must arise solely from their action as dispersal agents in increasing the interfacial surface area of the emulsion and in solubilizing oligomer and polymer chains.

It is generally found that there is an optimal concentration of surfactant, different for each polymerizing system, above which the degree of polymerization of the product decreases [2,3]. This may be the consequence of extreme dispersal of diacid chloride monomer either in ultra-fine emulsion droplets of the organic solution phase, or, more likely, in surfactant micelles. With extreme dispersal, polymerization may begin at so many sites at once that the consequent severe depletion of monomers slows chain growth and permits side reactions to become important.

CATALYSIS IN INTERFACIAL POLYCONDENSATION

Catalytic effects of micelles of surfactants on organic reactions have been intensively studied [12]. The mechanism of a reaction and the charge type of the reacting species in the rate-limiting step are important determining factors in the effect of micelles upon reaction rates. There are many examples of nucleophilic substitution in which the two reacting species are respectively an uncharged molecule and a negatively charged ion, and in which catalysis by micelles has been demonstrated. Micelles of cationic surfactants are good catalysts in such reactions, while those of anionic and nonionic ones are not. Similar effects might be predicted for polyesterification reactions where enolate anions react with uncharged diacid chloride molecules. Other types of reactions may be found to be accelerated by anionic or nonionic micelles. Micellar catalysis takes place only at concentrations above the CMC in solutions containing amphiphiles which exhibit hydrophobic bonding to the point of aggregation. Many of the additives or "accelerators" used in polycondensation are quaternary ammonium compounds which are not micelle-formers, however, and a different explanation must be advanced for catalytic effects which they produce.

A second form of catalysis which may play a role in interfacial polycondensation is phase-transfer catalysis [13]. The usual phase-transfer catalysts are quaternary ammonium cations which form ion pairs with negatively-charged reacting species in nucleophilic substitutions. In a two-phase system these ion pairs are better able than the anion alone to penetrate the nonpolar environment where the uncharged reacting species is found. Thus the reaction is accelerated, while the catalyst emerges unchanged. This kind of catalytic effect in polyesterification could facilitate passage of enolate ion into the organic phase. Note that it is the quaternary ammonium ion which performs this function, not micelles of quaternary ammonium surfactant. Indeed micellization, by limiting the concentration of free cation to the value of the CMC, may be a detriment, even though the amphiphilic character of cationic surfactants might favor ion-pair formation. Phase-transfer catalysts generally used in organic synthesis, such as tetramethyl- or tetraethyl- or benzyltrimethyl-ammonium bases or salts, do not form micelles.

CONCLUSIONS

The action of additives such as surfactants and catalysts may give rise to numerous phenomena of emulsification, solubilization and catalysis in the complex heterogeneous reaction systems that are common to stirred interfacial polycondensations. The agents that must be considered responsible are the ions, molecules, and, where applicable, the aggregates of the additives. All components of the systems must be considered as acted upon, not merely the monomers but oligomers, polymers, and the solvent components as well.

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