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Cationic Surfactants in Interfacial Synthesis of Linear Aromatic Polyester

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ABSTRACT

The polycondensation of terephthaloyl chloride and bisphenol A was used as a model reaction for the production of linear aromatic polyesters in stirred interfacial polymerization. The evaluation of several catalytic and surfactant additives to this system was based upon yields and intrinsic viscosities of the products obtained with both low and high concentrations of cationic surfactants of the quaternary ammonium type, of an anionic surfactant, and of a non-micelle forming quaternary ammonium salt. Although yields were similar in most cases, viscosity differences were marked. The highest intrinsic viscosities, hence highest degrees of polymerization, were found for preparations where cationic surfactant in excess of the critical micelle concentration was employed. Modes of action for such surfactants are suggested. The possibilities include, but are not limited to, solubilization of the product, solubilization of either or both monomers, emulsification of the liquid phases, catalytic phase transfer of one monomer, and micellar catalysis.

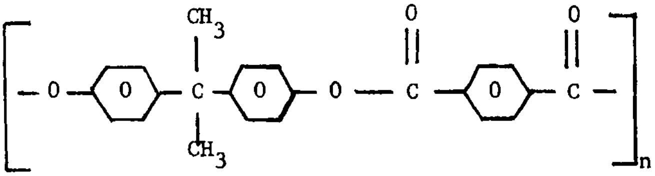
INTRODUCTION

Stirred interfacial reaction as a rapid, low-energy synthetic method has been extremely useful in applications-oriented explorations for novel polymers. Both polyamidization and polyesterification have been subjected to extensive attempts to optimize the yield and, more importantly, the degree of polymerization [1,2,3]. As a result the literature is full of empirical data on effects upon the polycondensation product of such variables as the chemical structure of the monomers, the concentrations and relative amounts of the reactants, the identity of the nonpolar solvent, the rate of stirring, and the presence of additives. The heterogeneity of the systems, the complexity of the reaction mixtures, and the extreme rapidity of the reactions have not encouraged conventional thermodynamic and kinetic analyses. Nevertheless by isolating elements of the problem a closer understanding may be possible, as at least one study of polyamidization has shown [4].

One factor which has been insufficiently explored is the effect of additives upon interfacial polymerization. A surface-active agent, sodium dodecylsulfate (SDS), is known to enhance the degree of polymerization in the interfacial production of polymers and indeed the use of SDS or other emulsifiers has been the subject of optimization studies [2,5]. Sometimes interfacial polycondensations, as types of nucleophilic displacement, are carried out with phase-transfer catalysts [6,7,8], generally small symmetric quaternary ammonium cations [9,10]. It has been suggested [11] that both surfactant and catalytic functions could be combined through the use of cationic surfactants which, as quaternary ammonium compounds, could also aid in transport of monomer between phases. Indeed the use of cationic surfactants has been the subject of patents for polycarbonate and other syntheses [12], but few details have been published. The choice of an aromatic polyesterification reaction for the present study was influenced by current interest in polyarylesters for the desirable thermal and mechanical properties which they display at high degrees of polymerization. The selection of a model polymerization system for the preparation of a linear aromatic polyester, and the differences in the reaction products obtained with the use of additives are described in this paper. The performances of different cationic surfactants, of the anionic SDS, and of a quaternary ammonium nonsurfactant compound are evaluated in terms of yield and intrinsic viscosity of the product, and the results are discussed in the light of some aspects of the colloid chemistry of the reaction systems.

MODEL POLYMERIZATION SYSTEM

The model system adopted for this study of stirred interfacial polycondensation is the two-phase one of bisphenol A (BPA) dissolved in aqueous sodium hydroxide, and terephthaloyl chloride (TPC) dissolved in chloroform. These monomers were selected for chemical stability and ease of purification, and, with a view to future phase-partitioning studies, for their suitability for spectroscopic analysis. The polar aqueous phase must contain enough NaOH to dissolve BPA completely as the reactive phenolate ion, leaving as little as possible undissociated BPA which could be extracted by the organic phase. The nonpolar chloroform phase is an excellent solvent for terephthaloyl chloride and oligomers formed in the reaction, although not for polyesters of higher molecular weight. The reactive monomer in each phase is quite insoluble in the other phase. The choice of chloroform was dictated by the need to avoid solvents having double bonds which would interfere with projected spectroscopic studies. Because the use of the para isomer of phthalic acid dichloride renders unlikely the formation of cyclic oligomers the polymer is completely regular in structure:



Two possible side reactions are the alkaline hydrolysis of TPC and dichlorocarbene formation by the action of aqueous NaOH on chloroform. The low solubility of TPC in water serves to protect it from hydrolysis by the alkali. Moreover, the very slow rates of the side reactions, as compared to the polycondensation, insure that neither the course of polymerization nor the yield are adversely affected.

All conditions of the system and procedure, including the amount of each reactant, the phase volumes, stirring rate and time, polymer isolation and purification procedures, were maintained as nearly the same as possible for different preparations, so that the only variable was the kind and amount of additive used. The conditions used were similar to those employed in other polymerizations of this type [5,13,14,15). Exploratory work with a similar system [16] indicated a higher molecular weight of the product when cationic surfactants were used, and on the basis of that work decyl-, dodecyl-, and hexadecyl-trimethylammonium bromides were tested at concentrations both above and below the critical micelle concentration (CMC). For comparison the anionic SDS was also tested, above and below the CMC, and tetramethylammonium bromide as typical of the non-aggregating quaternary ammonium salts often employed as catalysts. Non-ionic surfactants were not used because of the poor results noted with them in the past [1,2,5,16].

EXPERIMENTAL

Materials

Bisphenol A (Pfaltz and Bauer) was recrystallized from toluene, and terephthaloyl chloride (Eastman) from *n*-hexane. The aqueous phase was composed of boiled distilled water and sodium hydroxide (Baker). Chloroform (Baker Analyzed) was washed repeatedly with water to remove the alcohol stabilizer and dried over calcium sulfate. Hexadecyltrimethylammonium bromide (B.D.H.) as received was free of surface-active impurity (by the surface tension versus concentration criterion), and it, as well as sodium dodecyl sulfate (B.D.H.) and tetramethylammonium bromide (Eastman), were used without further purification. Decyltrimethylammonium bromide and dodecyltrimethylammonium bromide (both Eastman) as received showed depressions in surface-tension versus concentration plots, and were recrystallized from acetone/ether to remove the surface-active impurities. The solvent for intrinsic viscosity measurements was *o*-chlorophenol, 98+% (Aldrich). Other solvents used for recrystallization of reagents and washing of polymer were reagent grade (Baker).

Polymerization Procedure

The reaction was carried out in an electric blender with a rheostat to control the speed. An initial charge of 0.025 mole of NaOH dissolved in a total of 72.5 ml of water was stirred at a moderate speed with 0.0125 mole of BPA until solution was complete, when an appropriate amount of additive (surfactant or other) dissolved in 10 ml of water was added. The organic phase was prepared by dissolving 0.0125 mole terephthaloyl chloride in 35 ml of chloroform. The stirring speed of the blender was raised to the maximum value, and the organic phase was introduced rapidly. Mixing was continued thereafter for 5 minutes in cases where the reaction system remained emulsified. In other instances the reaction mass turned to a semisolid paste which adhered to the blender jar walls and stirring was discontinued as ineffective. Nevertheless, a total of 5 minutes was allowed to elapse so that the reaction presumably could continue for the full time, as is known to occur in precipitates in similar systems [17]. At the end of the 5-minute period, stirring (if still in progress) was interrupted and 500 ml of acetone was added to the blender jar. After one minute of gentle stirring the polymer was filtered off and washed with acetone to remove unreacted monomers and chloroform. The moist product was returned to the blender jar, stirred with distilled water to wash out excess alkali and salts, then filtered. This water wash was repeated twice more. The polymerized product was dried to constant weight in a vacuum oven at 40°C.

Examination of Products

The polymeric products produced in 85 to 95% yield were white, granular, and high-melting (> 300°C). Although insoluble in common organic solvents they were completely soluble at room temperature in *m*-cresol/*sym*tetrachloroethane mixtures (50:50 by volume) and in *o*-chlorophenol as well as in more highly acidic solvents. Flow times were measured at 30°C in Ubbelohde viscometers for *o*-chlorophenol solutions containing from 0.1 to 0.5% polyester. Extrapolation to zero concentration to obtain the intrinsic viscosity was carried out from combined Huggins and Kraemer plots of the reduced and inherent viscosities. In the concentration range studied these plots show no signs of polymer aggregation in o-chlorophenol, nor in the m-cresol/symtetrachloroethane medium. Although the intrinsic viscosity is the best viscosity function for evaluating the degree of polymerization, at least on a comparative basis, many investigators have used other viscosity functions measured for the single polymer concentration of 0.5%. The best of these alternatives is the inherent viscosity, much better than the relative viscosity which is regrettably sometimes still used.

RESULTS AND DISCUSSION

The concentration-dependent aggregation of surfactants was taken into consideration in planning polymerization experiments to test the effects of additives. The substances tested were mainly employed at two different concentrations. The first was the constant low molality of 5×10^{-4} in the aqueous phase, a figure chosen so as to permit comparison of effects of ions only, as this concentration is below the critical micelle concentration of all the surfactants used in this study. A second series of preparations employed much higher concentrations where most of the surfactant is in micelles (except of course in the one non-micelle-forming quaternary ammonium salt). These higher concentrations were chosen so that there would be in each case an excess molality of 0.024 over the critical micelle concentration, i.e. 0.024 M surfactant in the micellar form. The total concentrations were different, of course, as were the concentrations of surfactant ions, because of the differences in the CMC's of the various additives. The concentrations of additives, both absolute and relative to the CMC, the polymer yields and intrinsic viscosities are given in Table I.

It is immediately apparent, as others have noted [1,2] that the yield varies very little with the additive chosen. As a

TABLE I

Additive effects in interfacial polymerization of bisphenol A and terephthaloyl chloride

Additive in alkaline aqueous phase						Polymer product	
Identity	CMC 10^4 M	Total 10^4 M	Multiple of CMC	Micellar 10^4 M	Ionized 10^4 M	Percent Yield	$[\eta]$
None	n.a.	0	n.a.	0	0	93.4 ± 2.0	0.50 ± 0.03
TMAB	n.a.	5	n.a.	0	5	90.5	0.48
SDS	82	5	< 1	0	5	89.3	0.48
DTMAB	630	5	< 1	0	5	90.5	1.24
DDTMAB	142	5	< 1	0	5	90.1	0.58
HDTMAB	9.2	5	< 1	0	5	89.6	0.48
DTMAB	630	100	< 1	0	100	93.7	1.50
DDTMAB	142	100	< 1	0	100	92.6	1.05
TMAB	n.a.	240	n.a.	0	240	90.6	0.62
SDS	82	320	4	240	82	85.3	1.00
DTMAB	630	870	1.2	240	630	88.6	1.60
DDTMAB	142	382	2.7	240	142	89.6	1.27
HDTMAB	9.2	248	27.	240	9.2	94.4	0.79

Key:

CMC — critical micelle concentration
M — moles/liter
$[\eta]$ — intrinsic viscosity, dl/g
TMAB — tetramethylammonium bromide
SDS — sodium dodecylsulfate
DTMAB — decyltrimethylammonium bromide
DDTMAB — dodecyltrimethylammonium bromide
HDTMAB — hexadecyltrimethylammonium bromide

5% difference in the yield represents only 220 mg of polymer, variations of less than 5% are not significant in light of the difficulty of quantitative recovery of polymer in the several steps involved in isolating and washing it. The *intrinsic viscosity*, however, as a criterion of polymer molecular weight, shows important differences under the influence of additives. These differences can be believed if the polymerization procedure outlined above is rigorously followed. For example, the preparation without additive was repeated by two different operators, months apart, with different batches of purified reagents, to give the same value of the intrinsic viscosity $[\eta]$ with an uncertainty of ± 0.03. Thus we can say that the extremely low level of 5×10^{-4} M in tetramethylammonium bromide (TMAB), sodium dodecyl sulfate (SDS), or hexadecyltrimethylammonium bromide (HDTMAB) has, within experimental error, no demonstrable effect on the intrinsic viscosity. Both decyltrimethylammonium bromide (DTMAB) and dodecyltrimethylammonium bromide (DDTMAB), however, give increased intrinsic viscosities, the decyl compound affording a more than two-fold increase. This must be ascribed to specific effects of the cations of these surfactants, as the additives at 5×10^{-4} M have no effect as emulsifiers when the reaction systems are stirred -- in fact, such reaction mixtures turn into semisolid polymer pastes after only 20 seconds of mixing. It was in just such preparations that stirring was discontinued after 20 seconds as ineffectual, and the 5-minute time of contact of the reagents was permitted to elapse without further attempt at mixing.

The two most interesting additives, DTMAB and DDTMAB, were tested at a still higher concentration of 100×10^{-4} M in the aqueous phase. The homologous HDTMAB was not tested at this concentration because we wished first to isolate effects of the cations, and HDTMAB (with a CMC of only 9.2×10^{-4} M) would be present largely in the micellar form at 100×10^{-4} M. The twenty-fold increase in $DTMA^+$ and $DDTMA^+$ from 5×10^{-4} to 100×10^{-4} M gave further increases in intrinsic viscosity of 3-fold and 2-fold times the respective values in the absence of additive. Although $[\eta]$ was still in the order DTMAB > DDTMAB at the higher of the two concentrations, the proportional increase in $[\eta]$ in going from 5×10^{-4} to 100×10^{-4} M additive was greater for DDTMAB. It is moreover of some interest that 100×10^{-4} M of either of these surfactants, though well below the CMC's, proves an effective emulsifier, the reaction mixtures remaining stirrable throughout the 5-minute reaction time. This emulsification may influence the course of polymerization in ways to be discussed later.

The series of polyesters prepared with additive concentrations of CMC + 0.024 M show enhanced intrinsic viscosity in every case, compared with the results for lower additive concentrations. This is true even of the non-aggregating quaternary salt TMAB, although the effect even at 0.024 M is still not as large as that given by 5×10^{-4} M DTMAB and DDTMAB. Thus quaternary cations in sufficient dosage do result in higher molecular weight of the product, but the <u>specific effects</u> of the long decyl and dodecyl substituents are more important, and apparently not wholly dependent on emulsifying properties. In the preparations made with CMC + 0.024 M additives, only TMAB gave a pasty, unstirrable reaction mixture -- all the others were stirrable emulsions. It is noteworthy that the emulsifying effect of the anionic SDS did enhance the degree of polymerization of the product, even though the dodecylsulfate anion at 5×10^{-4} M had no effect whatever. Finally, the intrinsic viscosities of products with all three surfactant quaternary salts at

CMC + 0.024 M exceeded those found with lower concentrations of the same additives. The effects here are undoubtedly complex, as these higher concentrations represent not only equal molalities of micellar material but unequal (and in varying degrees larger) concentrations of surfactant cations than in the experiments at 5 x 10^{-4} and 100 x 10^{-4} M surfactant. Considering first the HDTMAB case, little or no effect would be expected for 9.2 x 10^{-4} M cation, since 5 x 10^{-4} M cation has no effect. Thus the entire effect of HDTMAB at CMC + 0.024 M must be ascribed to the micelles. The increased intrinsic viscosity of the polymer when DDTMAB is increased from 100 x 10^{-4} M to CMC + 0.024 M may be due in part to the concomitant increase of the cation concentration to 142 x 10^{-4} M and in part to a micellar effect. It is surprising, however, that the highly specific DTMAB shows relatively small improvement of the product when the concentration is increased from 100 x 10^{-4} M to CMC + 0.024 M, as this represents a 6-fold increase in cation concentration as well as providing 0.024 M in the micellar form. It appears that opposing effects are in operation, and that perhaps a maximum intrinsic viscosity would be achieved with some intermediate DTMAB molality.

CONCLUSIONS

In the study of a model interfacial polyesterification reaction, consideration of the contributions of additives in the aqueous phase both as ions and aggregates offers at least a partial understanding of the complex effects upon the degree of polymerization as measured by the criterion of intrinsic viscosity. At very low additive concentrations, highly specific enhancement of the viscosity by asymmetric quaternary ammonium cations is noted, with maximal effect for decyl and dodecyl homologs of $R(CH_3)_3N^+$. The anion of the surfactant SDS, on the other hand, has no such effect even though it bears a dodecyl chain. Because of their amphilic character, surfactant ions are present at polar/nonpolar interfaces at higher concentration than in the bulk phase. Electrostatic forces from ions adsorbed at such interfaces in stirred polymerization systems have of course no effect on the uncharged monomer TPC in the organic phase. Adsorbed cations, however, will attract (and anions repel) the negatively charged monomer BPA^- in the aqueous phase. Whether the diffusion of BPA^- into the nonpolar phase to react with TPC is aided merely by this attraction and the consequently increased concentration of BPA^- at the phase boundary, or whether the surfactant cations also act as phase-transfer catalysts which actually penetrate the nonpolar phase, has yet to be demonstrated.

When surfactants are present at higher concentrations where they act as "emulsifers" (but still not so high as to form micelles) they may be expected to exert two effects. One is merely to adsorb upon and solubilize the growing polymer chains, keeping them in suspension and accessible to further addition of monomers from the liquid phases. The other is to aid dispersal of one liquid phase in the other as emulsion droplets, thus increasing the surface area available for diffusion of monomer from one phase into the other phase where reaction can occur. (Note that we deliberately refrain from specifying which is the continuous and which the dispersed phase.) Both effects can be ascribed to all surfactants, whether cationic, anionic, or non-ionic. However, cationic surfactants are likely to have the same enabling effects at the surfaces of emulsion droplets as they display at the lesser expanses of surface generated merely by stirring, and may thus manage still to outstrip mere emulsion-formers.

The fact that emulsification can go too far is well known, as there is generally an emulsifier concentration beyond which the degree of polymerization of the product falls off [1,2]. This is possibly due to extreme dispersion of the nonpolar phase in drops so small that the diacid chloride is insufficiently protected from hydrolysis, or that too many different polymer chains are started and the reactants are depleted before a satisfactory degree of polymerization is reached. The latter possibility may account for the success enjoyed by some workers with stepwise addition of monomers to build up high molecular weights [16,17,18].

Another category of surfactant effects is the dispersal of monomers as solubilized molecules within micelles of surfactant. The latter might be ordinary hydrophobic micelles in which TPC could be solubilized in the aqueous phase, or even inverted micelles in which bisphenolate could be solubilized in the chloroform phase. In both cases, one monomer would be placed within easy reach of the other, but perhaps not in sufficient concentration to encourage long-chain growth. Such solubilization might give rise to micellar catalysis, particularly if micelles of cationic surfactant were to catalyze the nucleophilic displacement that is central to the polymerization mechanism. The results presented here, however, give no indication that a micellar catalytic effect is present, and indeed if it did occur it might well have a negative effect on the degree of polymerization analogous to the case of "over-dispersal" by emulsification.

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