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Synthesis of poly(vinyl alcohol-g-4-vinylpyridine hydrochloride) for application as a surfactant in emulsion polymerization of methyl methacrylate

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Summary

A redox initiation system composed of ceric ion and poly(vinyl alcohol) was used to successfully synthesize poly(vinyl alcohol-g-4-vinylpyridine hydrochloride). The aqueous solutions of this polycationic surfactant exhibited no sharp CMC value and tended to become turbid upon standing. This turbidity was related to the formation of crystalline-like aggregates in solution, and was thermally reversible. PMMA latices were unstable when formulated with turbid surfactant solutions, but when surfactant solutions were thermally equilibrated, the final PMMA latices were stable.

Introduction

Several non-ionic as well as polyelectrolyte homopolymers have been used as surfactants in emulsion polymerizations, including poly(vinyl alcohol), and poly(4-vinylpyridine hydrochloride). Both of these homopolymers have been used independently to stabilize emulsions of acrylate polymers, but no attempt has been made to combine the stabilizing properties of these two polymeric surfactants. One way to accomplish the combination of properties is to synthesize an isostructural graft copolymer with poly(vinyl alcohol) as the backbone. This synthesis is easily carried out by a redox system published by Mino and Kaizermann[1] where tetravalent cerium is the oxidizing agent and poly(vinyl alcohol) is the organic reducing agent. According to the mechanism of this reaction, verified by Kimura and Inaki[2], only carbon centered radicals vicinal to the PVA hydroxyl groups are formed. The amount of 4-vinylpyridine grafted onto PVA can be varied for the purpose of optimizing the surfactant's ability to stabilize the emulsion polymerization system under study.

Experimental

The commercial poly(vinyl alcohol) (mol. wt. 25,000) was dissolved at 90°C in distilled water in bottles equipped with magnetic stirring bars. Aliquots of 12M HCl and 4-vinylpyridine (4-Vpy) were followed by 0.2M ceric ion solution and water. The reactions were allowed to proceed for 24 hours at room temperature. The polymer was precipitated with acetone, washed with acetone and water to remove any contaminants of 4-vinylpyridine homopolymer. The air dried polymer was dissolved at 60°C in concentrations of 10% by weight in aqueous 0.1M HCl solution. The weight ratio of the PVA to 4-Vpy for the synthesis of the copolymer was varied from 1:0.25, 1:0.50, 1.1, to 1:2.

The emulsion polymerizations of methyl methacrylate to produce stable emulsions, needed from 20 to 60g of the surfactant per 100g monomer and 800g water. The polymerizations were carried out in 4 oz bottles rotated end-over-end in a thermostated water bath. The conversions were obtained gravimetrically, and the latex particle sizes and size distributions were determined by electron microscopy. Most of the study reported in this paper was carried out with the 1:1 ratio PVA to 4Vpy graft copolymer surfactant.

Results and Discussion

Polymeric surface active materials have been used in conjunction with short chain ionic surfactants to enhance latex stability. These polymeric surfactants have been primarily nonionic in character, as for example, poly(vinyl alcohol) or poly(ethylene-propylene) copolymers. Since polymeric surfactants are receiving increasingly more attention and usage in both industrial and academic arena, the synthesis of custom designed polymeric surface active materials has gained importance.

The study reported here deals with the synthesis of a graft copolymer and its subsequent use in emulsion polymerization. The importance of the research was to gain insight into the mechanism of polymerization and particle stabilization with a polymeric amphiphile as the sole stabilizer.

The synthesis of the cationic graft copolymer, poly(vinyl alcohol-g-4-vinylpyridine hydrochloride) (PVA-g-4Vpy HCl) was carried out having in mind its application as a surfactant in methyl methacrylate polymerization. Although PMMA emulsions have been stabilized, with some success, by the isostructural homopolymer components of this graft copolymer, attempts have not been made to combine the stabilizing properties of the two into one compound.

PVA-g-4VpyHCl copolymers were synthesized by means of ceric ion/PVA redox initiation system. Under acidic conditions, ceric ions oxidize the tertiary carbon hydrogen bonds that are vicinal to the PVA hydroxyl groups[1-3]. The resulting carbon-centered radicals can initiate vinyl polymerization, and in the presence of 4-vinylpyridine, in acidic medius, a polycationic graft copolymer is formed. The structure of the purified copolymer was verified by both infrared and ultraviolet spectra. The graft copolymers were stored in 10% aqueous solutions for the following two reasons: i) less time is required to formulate emulsion polymerizations with pre-prepared surfactant solutions; and ii) if the graft copolymers were not redissolved within 20 hours from the time they were precipitated, they became virtually water insoluble. The PVA-g-4VpyHCl copolymers were redissolved under acidic conditions to facilitate the dissolution process, and to ensure that all of the pyridine moieties remained protonated.

The surface tension measurements of acidic aqueous solutions of PVA-g-4VpyHCl showed no dramatic change in surface activity over a wide range of concentrations. This type of behavior is typical of polycationic surfactants[4]. Polycationics tend to form intra- and intermolecular aggregates at all concentrations in aqueous solutions.

Of the four PVA-g-4VpyHCl graft copolymers synthesized, the one prepared with the weight ratio of 4Vpy to PVA of 1:1 was capable of stabilizing MMA emulsion polymerization at the lowest concentration, 30% by weight monomer. Consequently, this surfactant was used to conduct a more detailed study of the characteristics of MMA polymerization. A comparison with 98% hydrolyzed PVA showed that the minimum concentration of this surfactant required to stabilize PMMA emulsion was 60% PVA by weight monomer.

A study of the effect of PVA-g-4VpyHCl concentration showed that an increase in surfactant concentration increases the overall rate of polymerization as well as the number of particles. Table I shows the results.

TABLE I

Effect of PVA-g-4VpyHCl Concentration on Rate of Polymerization and Number of Particles

Surfactant Concentration (per 100g monomer)	Rate R_px10^{-4} (mol/ℓ sec)	Number of Particles		D_w/D_n
		Conv. (%)	N/cm^3 (x10^{-13})	
30	1.71	27	7.1	1.04
		68	7.3	1.04
40	1.74	30	7.7	1.04
50	2.06	29	8.1	1.03

It is obvious from the results that this cationic polymeric surfactant functions as expected, an increase in the surfactant concentration increases the number of particles formed, and thus the rate of reaction. The narrow particle size distribution indicates a short particle formation period, which is also supported by the very small change in particle number from low to high conversion.

Polymerizations of MMA at three different temperatures 40°, 50°, and 60° were carried out to obtain an overall activation energy. The polymerization rates were calculated from the initial linear regions of each rate curve only since above ca. 50% conversion acceleration of rate occurred due to the Trommsdorff effect. The overall activation energy, E_a was found to be 70 kJ/mol which agrees very well with documented values obtained for both emulsion and homogeneous solution polymerization of this monomer.

An interesting feature of the PVA-g-4VpyHCl is the change of appearance of stored aqueous solutions. The solutions that are prepared from freshly synthesized surfactants are clear and translucent. However, during aging process, the solutions gradually become turbid and opaque. The turbid solutions are noticeably more viscous than fresh solutions, but when equilibrated at 90°C for several hours, they regain their translucency. Solutions of highly hydrolyzed PVA are known to behave in a similar way[5] [6]. They have been found to form crystalline like aggregates upon standing in solution, which cause an increase in turbidity and viscosity. PVA crystallization process can be partially reversed by equilibrating the turbid solution at higher temperature[7]. These findings suggest that PVA-g-4VpyHCl may have some of the same physical characteristics of its homopolymer counterpart. Turbid surfactant solutions that were aged for more than one month produced unstable latices of MMA. Coagulation began at about 50% conversion. Thermally regenerated solutions gave normal polymerizations.

The MMA latices prepared with the PVA-g-4VpyHCl as the sole stabilizer exhibited excellent freeze-thaw stability, and were stable to mechanical agitation.

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