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NOTES

POLYMER-WATER INTERACTION IN EMULSION COPOLYMERIZATION OF VINYL ACETATE

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ABSTRACT

In the case of copolymer latexes of vinyl acetate with maleic diesters, the amount of water bound to particles decreases with the increase of comonomer hydrophobicity. Increasing the concentration of bound water for more polar polymers determines a decrease of free water concentration. Therefore, the concentration of free surfactant and initiator in free water is higher and results in an increase of decomposition rate of potassium persulfate initiator. The increase of more polar copolymers hydration results in the increase of latex particle size.

INTRODUCTION

It is well known that polar polymers, e.g. acrylic derivatives [1] or poly(vinyl acetate) (PVAc) [2, 3], are plasticized by water. IR spectra have revealed the interaction of water molecules with poly(vinyl acetate) [4] and vinyl acetate-vinyl pyrrolidone (VP) copolymers [5]. The modification of water protons monitored by H-NMR proved that as the water/VAc-VP copolymer ratio increases two types of water result: bound water and free water [5]. The plasticizing of the copolymer

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becomes important over the concentration range where free water emerges. When these polymers are obtained by emulsion polymerization, the latex particles are certainly plasticized. Therefore, the state of latex particles differs from that in a dry state, while the real concentration of the continuum (water) is modified to an extent which depends on the degree of plasticization.

The analysis of these phenomena is difficult. The specialists in polymer and colloid sciences [6] distinguish among different varieties of non-covalent interaction in polar media, like water. The specialists in water [7] draw the attention upon the numerous errors associated with the establishing of polymer-bound water owing to the "popular interpretation of non-freezing water".

The studies on water-polymer systems have shown three types of water: non-freezing, intermediate and free [8].

The first investigation on polar polymer-water interaction in latexes was carried out by Donescu *et al.* [9]. It was shown that during a semicontinuous process the amount of polymer-bound water decreases with the increasing of polymer/water ratio.

In the case of hydrophobic latexes, the existence of a non-freezing water layer on particle surface was proved [10]. The thickness of this "interlayer" depends on the nature of the surfactants and on the electrolytes.

Two types of vicinal water structure around particles were determined by differential thermal analysis in polystyrene latexes obtained without emulsifier: one adsorbed on the hydrophobic part and another one on so_4^- hydrophilic groups resulted from the initiator [11].

In the present work, we have studied the influence of the modification of PVAc latex particles polarity on the bound water. The polarity modification was carried out by copolymerization of vinyl acetate (VAc) with maleic diesters: dimethyl maleate (DMM), diethyl maleate (DEM), dibutyl maleate (DBM) and di-2-ethylhexyl maleate (DEHM).

EXPERIMENTAL

Materials

Vinyl acetate, dimethyl maleate, diethyl maleate, dibutyl maleate, di-2-ethylhexyl maleate, butyl acrylate (BuA) commercial reagents, were purified by rectifying. The initiator-potassium persulfate (KPS)-LOBA CHEMIE product, was utilized without subsequent purification. The surfactant, the sodium salt of sulfo-

succinic semiester with nonylphenol ethoxylated with 25 moles ethylene oxide (NPEO₂₅SS) was utilized without previous purification.

Procedure

A semicontinuous procedure, identical with that previously developed by Donescu *et al.* [12], was utilized. It consists of a batch step and a semi-continuous one. In the batch step 185 g water, 12 g NPEO₂₅SS and 1/10 of the whole monomer amount were introduced under continuous stirring.

When the temperature reached 65°C, 0.7 g KPS dissolved in 35 g water were introduced. The reaction was allowed to advance one hour, then the remaining monomer and 0.7 g KPS dissolved in 35 g water were added throughout 5 hours. The mixture was then heated to 80°C in one hour, and afterwards allowed to cool.

Analyses

The conversion of monomers was established gravimetrically, while that of the initiator by ceriometric titration of unreacted KPS [13].

The amounts of bound and free water were determined by means of a DuPont 2000 instrument. The DSC analyses were carried out by cooling the latexes (30 mg) at a 5°C/min rate down to -30°C. To determine the amount of water which crystallizes, the subcooling temperature dependence of crystallization enthalpy was taken into account [7]. TGA was carried out by programmed heating the latexes (40 mg) at a rate of 5°C/min up to 160°C. The bound water was considered that which evaporates above 100°C.

The particle diameters were determined with a NICOMP 270 instrument by dynamic light scattering.

RESULTS AND DISCUSSION

The first evaluations of bound water were carried out in latexes with various polymer contents. The polymer particles were of PVAc or VAc-DEHM (80/20 wt) copolymer. Under these circumstances, the amount of bound water depends linearly on water/polymer ratio (Figure 1).

Note the difference between the absolute values resulting from the two methods. The results are different because of the different accuracies of the methods and of temperature ranges. Regarding the DSC the enthalpies of crystallization of two types of water were taken into account: 0 ÷ -5°C (free water, I); -10 ÷ -30°C

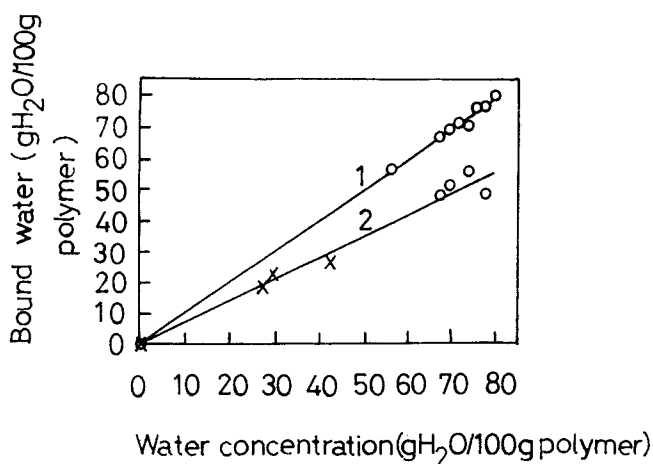


Figure 1. Modification of the amount of bound water versus water/polymer ratio (1-DSC, 2-TGA; swelled x-films, O-latexes).

(freezing bound water, II). The amount of non-crystallizable bound water (non-freezing water, III) was calculated making use of the known overall water content. The bound water for 100 g polymer corresponds to (II+III) sum.

The amount of water evaporated at temperatures above 100°C was calculated for TGA. Under these circumstances, one could expect that the percentage of polymer-water non-covalent bonds is lower than the values resulted from DSC measurements. The amounts of bound water for the films obtained from latexes were also evaluated. They agree well with those previously obtained for latexes.

Consequently, if only the modification of the amount of non-freezing water (III) was studied as a function of water/polymer ratio, the nature of the polymer in latex is very important (Figure 2). Poly(vinyl acetate), the most polar polymer studied (Figure 2) contains the maximum amount of bound water. The amount of non-freezing water for VAc-BuA copolymers is larger than that bound to VAc-DEHM copolymers. This is a normal result, because the DEHM structural units are more hydrophobic than BuA ones.

It is also established by TGA analyses that there are two types of bound water (Figure 3). The PVAc water evaporated at temperatures higher than 100°C exhibits a small shoulder at about 110°C, while VAc-DEHM copolymers prove the existence of two types of water which are above 100°C, that is, bound water.

These results prove, for the first time, that there are three kinds of water in polar latexes of PVAc and copolymers. In this contribution, we approach the overall

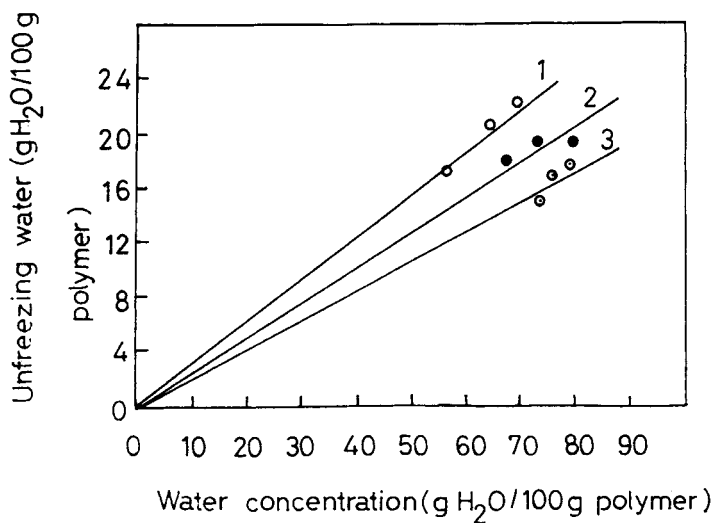


Figure 2. The amount of non-freezing water versus the nature of latex particles and water/polymer ratio (1-PVAc; 2-VAc-BuA (80/20 wt) copolymer; 3-VAc-DEHM (80/20 wt) copolymer).

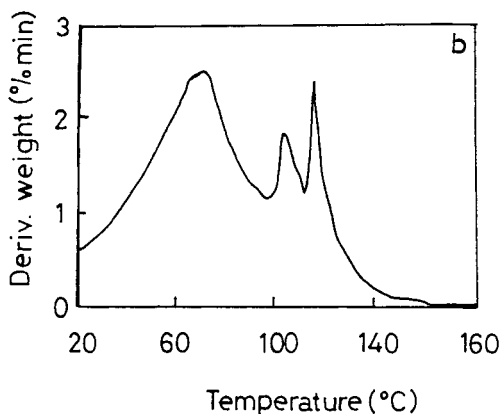
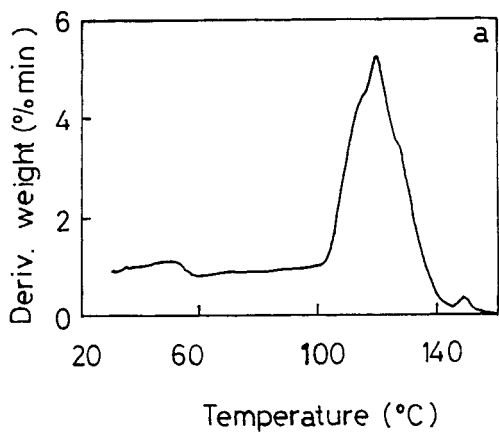


Figure 3. TGA curve for PVAc (a) and VAc-DEHM copolymer, $f_2 = 0.22$ (b).

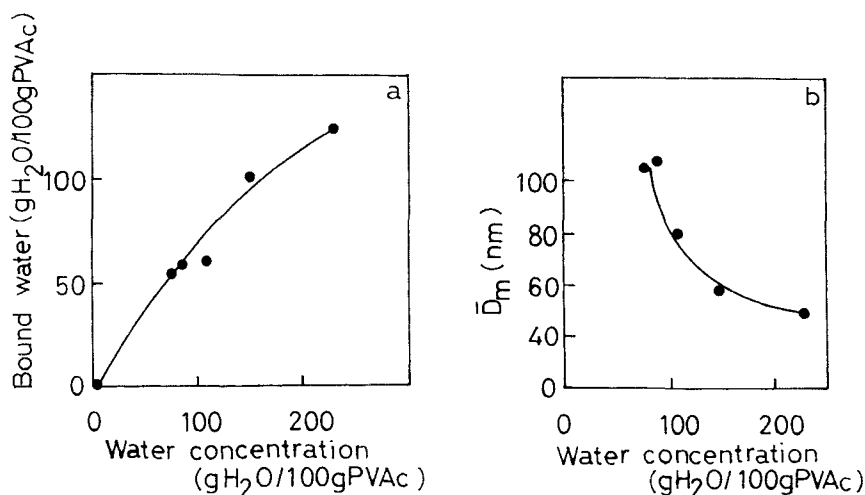


Figure 4. Modification of the amount of bound water (a) and average diameters of particles, (b) during semicontinuous polymerization of VAc.

effect of bound water. The bound water discussed here is estimated as the sum of two types evaporated above 100°C shown in Figure 3.

The linear dependence of bound water on water/polymer ratio was established for latexes resulting from a semicontinuous process. To explain the evolution of this process, it is very important to know the evolution of the amount of bound water and where it goes. Therefore, we added various amounts of VAc monomer to the continuous phase and obtained latexes of water/polymer ratios more diverse than those in Figure 1. The results are shown in Figure 4. At the beginning of the process, there is a large excess of water and the amount of bounded water does not depend significantly on water/polymer ratio. PVAc is a polar polymer, yet it has a limited value of water absorption. Therefore, as the amount of polymer increases, the polymer particles of higher diameter (Figure 4b) possess a decreasing quantity of bounded water.

These results are in good agreement with the previously published data [9]. The linear dependence in Figure 1 can be assigned to the domain in Figure 4a with a water/100 g PVAc ratio less than 100.

The results in Figure 4 suggested that we accept that new models of emulsion polymerization of PVAc-type polymers have to be developed, because latex particles are hydrated from the first steps of the process. The idealized theoretical approach which assumes that water does not dissolve either in particles or

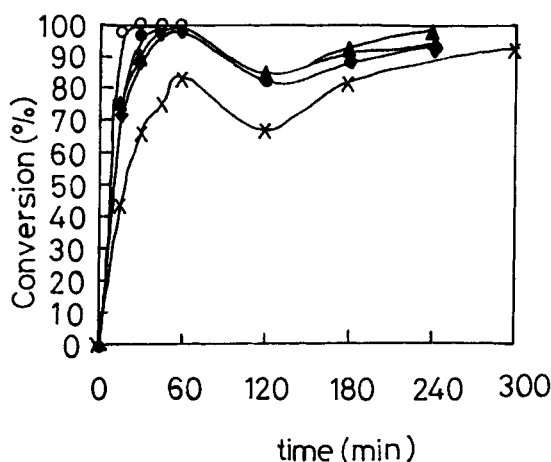


Figure 5. Monomer conversion during semicontinuous copolymerization (◆— VAc/DBM; ▲— VAc/DMM; ●— VAc/DEM; ×— VAc/DEHM; ○— VAc).

in monomer [14] is unacceptable in the case under study. The physico chemical properties of particles should be those corresponding to the degree of plasticization with water.

In order to determine the influence of the polarity of particles on the bound water, some copolymer latexes of vinyl acetate with maleic diesters have been used. To avoid the influence of the different water contents, all latexes contained 57.5-58% wt polymer. The mole fraction of maleic derivatives in the comonomer initial mixture was 0.22. Emirova *et al.* [15] have shown that this concentration ensures a maximum rate for DBM in emulsion copolymerization with VAc. One can assume that the nature of alkyl radicals does not alter the reactivity of maleic diesters. This is the case of C_1 - C_4 alcohol esters (Figure 5).

The reactivity of the comonomer, and virtually the whole system, is diminished by a substituent which is longer and more branched than 2-ethylhexyl maleate.

The bound water determined by TGA for the synthesized copolymer particles depends on the nature of the substituents of maleic derivatives (Figure 6).

The largest amount of bound water is in PVAc and decreases in the sequence: DMM, DEM, DBM. In the case of DEHM, the amount of bound water is minimum, but split into two peaks (Figure 3b).

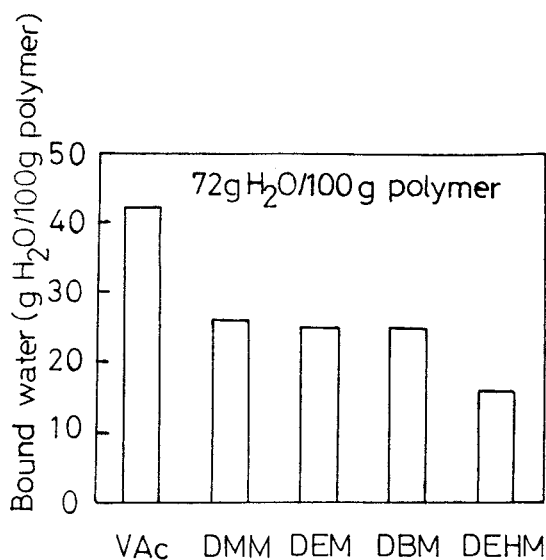


Figure 6. The variation of bound water in the copolymers with various comonomer units

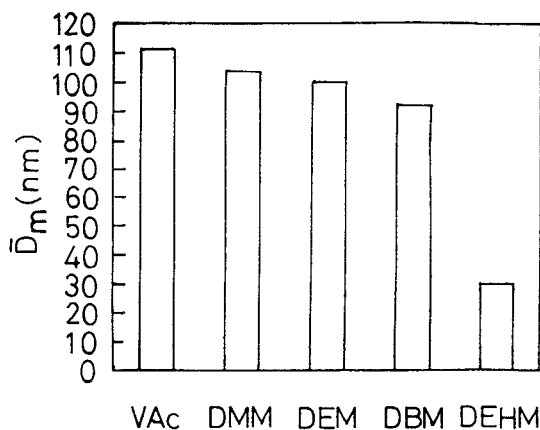


Figure 7. The dependence of particle diameter on the comonomer units.

The particles possess a different degree of hydration, and the first effect is the modification of particle size (Figure 7). The least hydrated copolymer (VAc-DEHM) consists of particles of minimum size, while PVAc and VAc-DMM copolymer of largest particles.

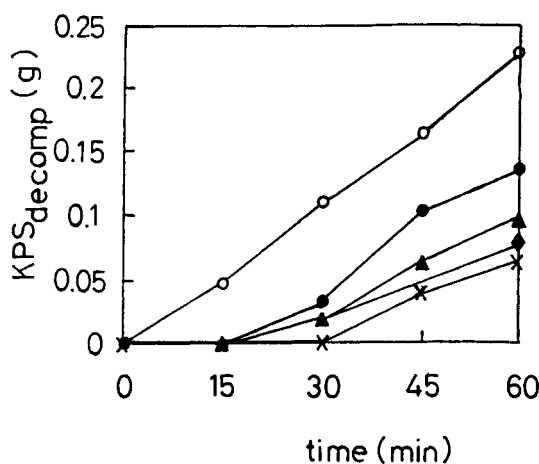


Figure 8. The evolution of the amount of initiator decomposed during the discontinuous step (\blacklozenge -VAc/DBM; \blacktriangle -V Ac/DMM; \bullet -VAc/DEM; \times - VAc/DEHM; \ominus -VAc).

Vijayendran *et al.* [16] have proved that the amount of surfactant which ensures the stability is different and depends on the polarity of latex particle surface area. These results could be accounted for in terms of the discussion above. The particles of hydrated polar polymers do not require a high surfactant concentration at interface to ensure stabilization. Therefore, in the case of some polar polymer latexes, the concentration of the free surfactant is higher than in less polar polymers. These concentrations are increased because the amount of free water which contains the surfactants not adsorbed on particles is much smaller in polar polymers.

The diminishing of free water and the increase of surfactant concentration determine an increase of KPS initiator decomposition rate in case of vinyl acetate copolymerization with the maleic diesters studied in this contribution (Figure 8).

KPS decomposition rate is maximum at VAc homopolymerization and minimum at its copolymerization with DEHM.

The modification of KPS decomposition kinetics, depending on the polarity of particles, demonstrates the usefulness of simultaneously monitoring the two major reactions in the system studied: those of the monomer and of the initiator. These conditions allow for the development of a correct kinetic model.

The reactant concentration should be referred to the free water, not to overall water. Under the conditions of this study, the concentrations of reactants referred to

free water are higher than the theoretic values: 2.4 times for PVAc, 1.75 for VAc-DMM copolymer, 1.71 for VAc-DBM copolymer, 1.6 for VAc-DEM copolymer and 1.4 for VAc-DEHM copolymer.

CONCLUSION

One can state that the degree of interaction with water of latex particles decreases with the increasing of the hydrophoby of maleic diester type comonomers. The increase of the amount of bound water for more polar particles lowers the free water concentration, and increases the actual concentration of reactants with respect to that referred to total water. Therefore, the rate of persulfate type initiator decomposition increases with the increase of latex particle polarity.

REFERENCES

- [1] S. T. Eckersley and A. Rudin, *J. Appl. Polym. Sci.*, **48**, 1369 (1993).
- [2] F. D. Blum J. E. Dickson, and W. G. Miller, *J. Polym. Sci. Physics Ed.*, **22**, 211 (1984).
- [3] M. Chuu and R. Meyers, *J. Appl. Polym. Sci.*, **34**, 1447 (1987).
- [4] E. P. Kalitskaia and S. S. Gusev, *Visokomol. Soedin, (A) XXIV*, **11**, 2416 (1982).
- [5] A. O. Grigorov, E. K. Podvalnaia, L. L. Suljenko, and N. V. Meia, *J. Priklanii Him.*, **6**, 1385 (1986).
- [6] C. J. van Oss, *J. Disp. Sci. Technol.*, **12**, 201 (1991).
- [7] F. Franks, in "Water, a Comprehensive Treatise", Plenum Press, New York, London, F. Franks, Ed., Vol. 7, 1982, p. 264.
- [8] S. Takigami, T. Kimura, and Y. Nakamura, *Polymer*, **34**, 604 (1993).
- [9] D. Donescu, A. Ciupituiu, K. Gosa, and I. Languri, *Rev. Roum. Chim.*, **38**, 1441 (1993).
- [10] O. G. Kiseleva and R. E. Neuman, *Koloidnii J.*, **4**, 799 (1985).
- [11] P. Staszczuk, M. A. Cabrerizo-Vilche, and R. Hidalgo-Alvarez, *Coll. and Polym. Sci.*, **271**, 759 (1993).
- [12] D. Donescu, L. Fusulan, and K. Gosa, *Journ. Mac. Sci., Pure & Appl. Chem.*, **A32**, 563 (1995).
- [13] I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, **25**, 298 (1953).
- [14] J. L. Gardon, *J. Polym. Sci.*, **A1**, **6**, 2859 (1968).

- [15] I. V. Emirova, N. I. Grisko, Z. I. Varonkina, I. N. Kobulova, and A. E. Kiricenکو, *Visokomol. Soedin. Krat. Soob.*, 5, 369 (1977).
- [16] B. R. Vijayendran, T. Bone, and C. Gajria, in “*Emulsion Polymerization of Vinyl Acetate*”, Appl. Sci. Publ., London, J. W. Vanderhoff and M. S. El-Aasser, Eds., 1981, p. 253.

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