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Alkaline Hydrolysis of Aqueous Polymer Dispersions, Particularly Vinyl Acetate Copolymers

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Synopsis

The influence of comonomer species and concentration on the ease of alkaline hydrolysis of vinyl acetate copolymers in the aqueous dispersion form is reported. The comonomers studied include higher vinyl esters, acrylic esters, a fumaric diester, and ethylene. The significance of the emulsion polymerization formulation has also been considered. The rate of hydrolysis is reduced with increasing proportions of comonomers and with increasing length and branching of the alkyl side chain originating from such comonomers. Branched long-chain tertiary vinyl esters reduce not only the rate but also the extent of hydrolysis, being resistant to hydrolysis themselves and also protecting part of the more susceptible vinyl acetate; inhomogeneous copolymers, specially prepared, were less resistant than the more homogeneous copolymer of the same overall composition. The inclusion of quite small amounts, such as 1% by weight, of acid comonomers has a relatively large effect, increasing ease of hydrolysis. For comparison, the behavior of higher vinyl ester homopolymers and methyl methacrylate copolymers with acrylic esters is included. It is concluded that the major factors influencing ease of hydrolysis are steric and other environmental effects arising from the copolymer microstructure.

INTRODUCTION

The alkaline hydrolysis of polymers is a subject of both practical and theoretical interest. Where surface coatings are to be applied to alkaline substrates an adequate degree of resistance to hydrolysis is essential for satisfactory performance and durability. This is particularly true for situations of high humidity or exterior weathering.

The increasing use of aqueous polymer dispersions produced by emulsion polymerization has made it desirable to gain a better understanding of the factors influencing alkaline hydrolysis, and among these are polymer composition and emulsion formulation. The majority of polymer dispersions used for surface coatings are based on vinyl acetate as the principal monomer. Where comonomers are incorporated to provide internally plasticized copolymers, these are usually the esters of acrylic acid or the higher vinyl esters; the diesters of fumaric and maleic acids may also be employed, and more recently ethylene has begun to be exploited. In some systems it is advantageous to include a minor proportion of a more polar monomer, such as acrylic acid, to obtain better dispersion stability and improved adhesion, particularly in pigmented systems.

Several authors[1-3] have shown that the resistance to hydrolysis of a polymer is important if it is to be applied where highly alkaline conditions are encountered. The later workers[2,3] have sought to correlate the resistance of a polymer dispersion to hydrolysis by aqueous sodium hydroxide with resistance of the pigmented air-dried film to "lime burn" and have deduced that resistance to hydrolysis is dependent on steric effects in the polymer. Bruin et al.[2] dealt with the vinyl esters of branched long-chain tertiary monocarboxylic acids, while Florus[3] prepared an acrylic ester based on an undisclosed sterically hindering alcohol component which was found to give good resistance to alkaline hydrolysis. None of the published work has given any information on the formulae used for preparing the dispersions.

EXPERIMENTAL

Emulsion Polymerization

With the exception of the vinyl esters of capric/caprylic acids and Acid 810 (Imperial Chemical Industries, Ltd.),[4] all the monomers were from commercial sources and were used as supplied, but examined for adequate purity ($\nless 99\%$) by gas chromatography. Polymerization inhibitor, usually 10–60 ppm hydroquinone or monomethyl ether of hydroquinone, was not removed.

The vinyl esters of capric/caprylic acids and Acid 810 were prepared by interchange from vinyl acetate.[5] The mixture of vinyl esters of branched long chain tertiary monocarboxylic acids was obtained as VeoVa 911 (Shell).[6]

Dispersions 1–65 were prepared by conventional emulsion polymerization with thermal activation of free-radical initiator. The emulsion formula was specially selected to cover a wide variation in copolymer composition, and the stabilizing system comprised hydroxyethyl cellulose (2.5%), non-ionic surfactant (1%), and anionic surfactant (0.5%), where all percentages were by weight based on total monomer charge. Potassium persulfate (0.5%) was employed as initiator and sodium bicarbonate (0.28%) as buffer. Water was included to give a final solids content of about 56%.

For liquid comonomers, polymerization was carried out at 80°C. in a 1 liter flask equipped with stirrer, reflux condenser, thermometer, and dropping funnels, and heated or cooled by means of a water bath. For ethylene copolymers a stirrred, stainless steel-jacketed autoclave was employed, operating at pressures in the range 10–50 atm. The initiator and the monomers were added continuously over 4 hr., and the polymer dispersion was then held at 85°C. for 15 min.; air was purged from the system with nitrogen, and ferric chloride (4 ppm on monomers) and sodium formaldehyde sulfoxylate (0.1% on monomers) were added and the temperature maintained at 85°C. for a further 15 min. before finally cooling. Conversions of monomers to polymer was normally 97–99% as estimated from the solids content of the dispersions, but for polymers containing 90 or 100% VeoVa 911, vinyl caprate/caprylate, *n*-butyl acrylate, or 2-ethylhexyl acrylate, conversions were slightly lower.

Two procedural modifications of dispersion 26 were made to introduce copolymer inhomogeneity. In dispersion 26a the first half of the total monomers added was vinyl acetate only, while the second half comprised a 40/60 vinyl acetate–VeoVa 911 (w/w) mixture; in dispersion 26b this procedure was reversed. Thus dispersions 26, 26a, 26b all contained the same overall ratio of monomers, 70/30 vinyl acetate–VeoVa 911 (w/w).

Dispersions 66–74 were all copolymers of vinyl acetate with VeoVa 911, and all except dispersion 70 contained additionally copolymerized acid (1.45% molar). These were prepared with non-ionic surfactant (2.0%), anionic surfactant (1.0%), potassium persulfate (0.5%), and borax (0.5%) as buffer, by a process[7] published by the manufacturers of VeoVa 911.

Two further dispersions, 75 and 76, typical of commercial all-acrylic copolymers, were prepared for comparison. These employed methyl methacrylate with methacrylic acid (2.0%) and ethyl acrylate (63.0%) or *n*-butyl acrylate (56.0%), and were prepared by using a formula similar to that for dispersions 66–74.

For dispersions 66–74, particularly 72 and 73 where particle size modifications were effected by the inclusion of sodium sulfate during polymerization, weight-average particle size was determined by a light-transmission method calibrated against electron microscopy.

Aqueous Alkaline Hydrolysis

To approximately 3.5 g. of dispersion weighed accurately (approximately 2 g. of polymer) was added distilled water (25 ml.). The diluted dispersion was neutralized cold to the first pink color of phenolphthalein with 0.1*N* aqueous sodium hydroxide, then 1*N* sodium hydroxide (50 ml.) was added with thorough mixing, and the mixture maintained at 25°C. (thermostatically controlled water bath) without agitation. After the desired time for reaction the unreacted alkali was determined by titration with 1*N* hydrochloric acid. The degree of hydrolysis was calculated as milligrams KOH per gram polymer and expressed as a percentage of the theoretical hydrolysis possible. Complete hydrolysis was also determined experimentally for all the vinyl acetate copolymers, with the exception of those containing VeoVa 911 in excess of 30 wt.-%, by prolonged refluxing with alcoholic potassium hydroxide, and agreement with the theoretical value was obtained in all cases.

The hydrolysis procedure employed at least 100% excess alkali, and it was found that the size of sample was not critical within the range 3.2–3.8 g. dispersion, relative to the precision of the method (± 0.5 mg. KOH/g.).

For one series of results the extent of hydrolysis was determined for

TABLE I
Hydrolysis Related to Polymer Composition and Time

No.	Copolymer composition, wt.-%[a]	Hydrolysis, % of theoretical at various times							
		7 hr.	17 hr.	24 hr.	48 hr.	69 hr.	110 hr.	160 hr.	360 hr.
1	VA 100	50.3	—	91.0	98.0	—	100	—	—
12	VA/VCC 90/10	33.6	56.2	68.2	89.4	—	95.8	100	—
13	" 80/20	11.7	30.6	38.7	56.5	—	82.1	94.2	99.8
24	VA/VV911, 90/10	13.7	31.0	40.8	64.9	75.5	—	87.5	—
25	" 80/20	10.3	16.4	19.3	21.6	24.6	—	35.9	51.7
26	" 70/30	7.6	9.2	11.0	12.9	14.5	—	18.9	31.1
27	" 60/40	—	—	7.5	8.6	—	11.8	14.3	24.4
38	VA/BA 90/10	33.0	57.5	67.8	86.5	—	97.0	98.7	—
39	" 80/20	14.8	—	41.9	63.5	—	87.5	94.3	95.8
50	VA/EHA 90/10	26.5	—	55.3	81.7	—	94.0	96.5	98.0
51	" 80/20	14.0	—	28.1	43.6	—	81.5	92.1	95.7
75	EA/MMA/MAA 63/35/2	1.7	—	4.0	7.4	—	15.7	20.0	38.0
76	BA/MMA/MAA 56/42/2	—	—	1.5	—	—	—	—	12.6

[a] VA = vinyl acetate; VCC = vinyl caprate/caprylate; VV911 = VeoVa 911; MMA = methyl methacrylate; EA = ethyl acrylate; BA = *n*-butyl acrylate; EHA = 2-ethylhexyl acrylate; MAA = methacrylic acid.

periods ranging from 7 to 360 hr., while for general comparative purposes a fixed period of 24 hr. was employed.

RESULTS AND DISCUSSION

Factors likely to influence the ease of hydrolysis of vinyl acetate copolymers in aqueous dispersion include plasticizing comonomer species and concentration, copolymerized acid, dispersion formula, and particle size, and homogeneity of copolymerization.

The relationship of extent of hydrolysis with time for some of the copolymers is found in the results detailed in Table I, and presented graphically in Figure 1. It is seen that vinyl acetate homopolymer is rapidly hydrolyzed to 91% in 24 hr., whereas the methyl methacrylate copolymers are much more resistant. The latter behavior is in keeping with the great difficulty with which methyl methacrylate homopolymer is hydrolyzed by alkali.[8] The other copolymers are more readily hydrolyzed, but those containing 30% and 40% VeoVa 911 exhibit behavior somewhat similar to the methyl methacrylate copolymers, except that the rate of hydrolysis is greater during the first 50 hr.

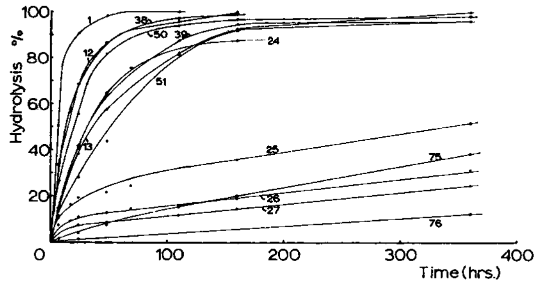

Fig. 1. Hydrolysis related to polymer composition and time. Reference numbers are to dispersions.

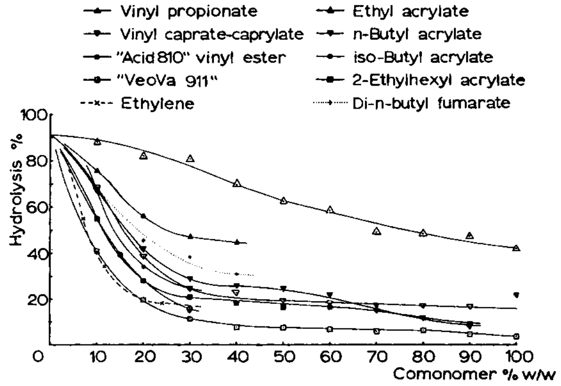

Fig. 2. Hydrolysis related to comonomer type and content.

TABLE II
24-Hr. Aqueous Alkaline Hydrolysis of Vinyl Acetate Copolymers

No.	Comonomer	Comonomer content Weight-%	Mole-%	Hydrolysis, % of theoretical
1	None[a]			91.0
	Vinyl propionate			
2		10	8.7	88.0
3		20	17.7	82.0
4		30	27.0	80.9
5		40	36.5	69.5
6		50	46.2	62.3
7		60	56.4	58.4
8		70	66.8	48.9
9		80	77.5	48.6
10		90	88.6	47.5
11		100	100.0	42.0
	Vinyl caprate/caprylate			
12		10	4.9	68.3
13		20	10.5	38.8
14		30	16.7	24.7
15		40	23.1	22.9
16		50	31.9	19.4
17		60	41.3	18.1
18		70	52.2	17.1
19		80	65.2	17.0
20		90	80.8	16.6
21		100	100.0	21.5
	Vinyl ester of Acid 810			
22		15	7.6	39.4
23		30	16.7	15.8
	VeoVa 911[b]			
24		10	4.6	40.9
25		20	9.7	19.3
26		30	15.8	11.1
26a		30	15.8	30.0
26b		30	15.8	21.7
27		40	22.6	7.5
28		50	30.4	7.3
29		60	39.6	6.2
30		70	50.3	5.8
31		80	63.6	6.2
32		90	79.6	4.7
33		100	100.0	3.5

For comparative purposes a fixed time of hydrolysis of 24 hr. was adopted. Hydrolysis effected in this period does not indicate the maximum degree of hydrolysis that could take place with a much longer reaction time, but any longer period is less discriminating and leads to figures approaching 100% for many of the vinyl acetate copolymers. Results obtained with 24 hr. hydrolysis are given in Table II, and presented graphically in

TABLE II (*continued*)

		Comonomer content		Hydrolysis, % of theoretical
No.	Comonomer	Weight-%	Mole-%	
	Ethyl acrylate			
34		10	8.7	75.8
35		20	17.7	56.2
36		30	27.0	47.1
37		40	36.5	44.8
	n-Butyl acrylate			
38		10	6.9	67.7
39		20	14.4	41.9
40		30	22.4	28.7
41		40	31.0	25.7
42		50	40.2	24.8
43		60	50.2	21.7
44		70	61.1	14.7
45		80	72.9	11.7
46		90	85.8	7.9
	Isobutyl acrylate[b]			
47		10	6.9	68.4
48		20	14.4	34.2
49		30	22.4	24.8
	2-Ethylhexyl acrylate			
50		10	4.9	55.3
51		20	10.5	28.1
52		30	16.7	20.9
53		40	23.1	18.3
54		50	31.9	16.3
55		60	41.3	16.4
46		70	52.2	14.5
57		80	65.2	12.2
58		90	80.8	9.5
	Di-*n*-butyl fumarate			
59		10	4.0	68.9
60		20	8.6	45.4
61		30	13.9	38.3
62		40	20.1	30.8
	Ethylene[b]			
63		7.1	19.0	55.0
64		11.7	28.9	34.4
65		24.0	49.2	18.1

[a] Vinyl acetate homopolymer.

[b] In these series hydrolyses were performed in duplicate and the mean value is quoted.

Figure 2. Here the effect of the various comonomers is very evident. A linear relationship between 0 and 100% comonomer would indicate that both monomer species are as easily hydrolyzed in the copolymer as in homopolymers, and that one does not protect the other; this is approximately true where the comonomer is vinyl propionate. With increasing length of the linear hydrocarbon side chain (vinyl caprate/caprylate) there

is greater protection; this is further improved for the case of an ester with a similar number of carbon atoms in the side chain, but where some branching occurs adjacent to the carboxyl group. (Acid 810 is reported to contain predominantly secondary acid structures.) VeoVa 911 confers slightly greater protection and is based on entirely tertiary carboxylic acids, with approximately the same chain length. From the vinyl ester comonomers it would appear that side chain length and branching are important factors contributing to increased resistance to alkaline hydrolysis.

The acrylic esters follow a similar pattern where the *n*-butyl chain gives more protection than ethyl acrylate, but branching not adjacent to the ester linkage, as with isobutyl acrylate and 2-ethylhexyl acrylate, does not have a dramatic effect. Di-*n*-butyl fumarate is intermediate between the ethyl and *n*-butyl esters of acrylic acid.

Ethylene stands in contrast to the other comonomers. It does not lead to the introduction of protective side chains, and yet, on a weight basis, affords almost as much protection as VeoVa 911. Since protection cannot be attributed to long or branched side chains, the function of ethylene must be considered from an alternative standpoint.

The proportion of comonomer incorporated is also relevant to the degree of protection afforded. In all the cases examined, most benefit has been achieved by the time the 30 wt.-% level has been reached. For practical purposes the protective effect must be related to the plasticizing efficiency of the comonomer, and this, for the ester types, increases with the length of the side chains but decreases with chain branching.

The introduction of copolymerized acid (Table III), comparing dispersions 67 and 70, results in a notable increase in sensitivity to alkaline hydrolysis. That this is not due to a change of polymerization formula is indicated by comparison of dispersions 26 and 70. Furthermore, the average particle sizes of dispersions 67 and 70 are very similar, and even when this factor is deliberately altered, as in dispersions 71–73, there is no significant change in hydrolysis behavior. Smaller particle size would be

TABLE III

Hydrolysis of Copolymers Containing Acid

No.	Acid	Copolymer composition VA	 VV911	 Acid	Average particle diameter, μ	Hydrolysis, % of theoretical
66	Acrylic	79	20	1	0.27	63.0
67		69	30	1	0.17	43.2
68		59	40	1	0.14	26.8
69		49	50	1	0.12	18.5
70		70	30	—	0.17	15.1
71		69	30	1	0.17	48.4
72			"		0.21	47.1
73			"		0.27	48.8
74	Crotonic	68.8	30	1.2	—	48.0

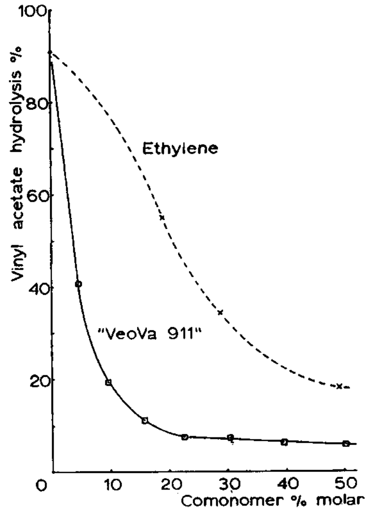

Fig. 3. Vinyl acetate hydrolysis related to molar content of ethylene and VeoVa 911.

expected to lead to easier hydrolysis, but in dispersions 66–69 such an effect is completely dominated by the influence of comonomer content.

Comparison of dispersions 25–28 and 66–69 shows that the benefit of 53% VeoVa 911 with 1% acrylic acid is no greater than 20% VeoVa 911 without acid. In dispersion 74 crotonic acid was incorporated in the same molar proportion as acrylic acid; the effect on ease of hydrolysis is virtually the same.

Where some inhomogeneity has been deliberately introduced, as with dispersions 26a and 26b, the protective action is diminished as compared with the more homogeneous copolymer, dispersion 26.

These various considerations focus attention on the mechanism of hydrolysis and on polymer microstructure; in turn, both these topics must be related to the protective influence of comonomers.

The initial point of attack by base in the hydrolysis reaction is at the carbonyl carbon atom which receives more protection arising from steric hindrance by the polymer backbone in the acrylate and fumarate ester copolymers, in which the carbonyl groups are adjacent to the polymer backbone, than in the case of vinyl esters. Thus with unbranched species of the same molecular weight (ethyl acrylate and vinyl propionate) acrylate esters are more resistant than vinyl esters.

The VeoVa 911 copolymers are not substantially hydrolyzed to a greater extent than can be attributed to the vinyl acetate content; in this context a study of the products of hydrolysis would be of interest. Thus VeoVa 911 can be regarded as a virtually nonhydrolyzable monomer like ethylene and methyl methacrylate when polymerized. While it is usually more appropriate in relation to the plasticizing function of comonomers to compare on a weight basis, from the standpoint of polymer structure it is valuable to consider the molar proportions of comonomers. In Figure 3 ethylene and VeoVa 911 are compared on a molar basis, the assumption being that only the vinyl acetate is hydrolyzable.

It is seen that, whereas on a weight basis ethylene affords as much protection as VeoVa 911, on a molar basis the latter is much more efficient. In the 24 hr. hydrolysis test 49 mole-% ethylene allows about 20% hydrolysis of the vinyl acetate; only 10 mole-% VeoVa 911 is needed to achieve the same effect. Vinyl esters are normally expected to copolymerize homogeneously and give random copolymers. Ethylene, on the other hand, copolymerizes with vinyl acetate under the emulsion polymerization conditions described above, such that virtually every ethylene unit in the polymer chain is bounded by two vinyl acetate units; thus the equimolar copolymer approximates to an alternating structure.

The protective effects of comonomers may arise from several possible modes of action. These include modification of local or overall water solubility or water insolubility of the macromolecule, steric protection by both side chains and the polymer backbone, and interruption of the sequence of hydrolyzable units in the copolymer.

If, in the heterogeneous dispersion system, hydrolytic attack occurs at the end of polymer chains or at intermediate segments that protrude from the polymer particle into the aqueous dispersion medium, or that are accessible to the aqueous base, then it seems reasonable to assume that groups offering increased water solubility would lead to easier hydrolysis. Such a result arises from the inclusion of quite small proportions of acid monomers, whose tendency to water solubility is greatly increased in alkaline media due to the formation of the carboxylate ion. Conversely, hydrocarbon segments would tend to reduce water solubility, thus leading to greater resistance to hydrolysis, and this is also substantiated experimentally.

Hydrolysis may proceed by random successive attack or by "chain" reaction in which hydrolysis spreads from one site to adjacent hydrolyzable units. On the former hypothesis it would be expected that alkyl side chains would provide protection for the ester link to which they are attached, and in the case of the more bulky long or branched side chains this protection would be increased, possibly to the extent of providing "umbrella" protection to adjacent units, particularly vinyl acetate, in the backbone. Such a mechanism would appear to predominate in the case of copolymers of the vinyl esters of tertiary carboxylic acids. On the second hypothesis, the interposition of nonhydrolyzable units in the polymer chain would be expected to retard hydrolysis, as is observed with ethylene copolymers. In such circumstances the tendency to alternation of comonomer species would lead to maximum interruption of vinyl acetate sequences, but at the same time the interrupting group would be of minimum size, namely, a single ethylene unit. In contrast, the interrupting effect of the nonhydrolyzable VeoVa 911 will be less efficient on account of the more random copolymerization characteristic of this monomer. However, on a molar basis, VeoVa 911 offers more protection than ethylene, suggesting that at most only part of the mechanism is an interrupting function, with steric and hydrocarbon effects predominating.

The plasticizing effect of ethylene is distinct from the more common comonomers. It functions by increasing the inherent flexibility of the backbone, as evidenced by pronounced depression of the glass transition temperature, rather than by the steric effect of bulky side groups such as are contributed by the majority of ester comonomers. It is possible that ethylene exerts some protection of vinyl acetate units by increasing the steric effect of the polymer backbone through more compact folding, thus leading to more efficient shielding of the hydrolyzable units.

CONCLUSION

The predominant factors influencing the ease of alkaline hydrolysis of vinyl acetate copolymer dispersions are comonomer type and concentration, and the incorporation of copolymerized acid.

Within the narrow range examined, dispersion formula and particle size are less significant. Inhomogeneous copolymer dispersions are likely to be more susceptible to hydrolysis than those in which copolymerization is more homogeneous.

The protective action of comonomers must depend to a considerable extent on whether the comonomer unit is hydrolyzable or not. Increased length of side chain and branching of side chain reduce ease of hydrolysis. Water solubility, steric, and interruptive effects all appear to be possible contributing factors to control of the rate of hydrolysis, and no one of these is adequate to explain all the phenomena observed.

In the consideration of this complex system the possible influence of polymer branching or grafting has not been taken into account at this stage. In the emulsion polymerization process employed these structural deviations are expected to be minimal.

Finally, in relation to practical applications, it is necessary to point out that both the monomeric and polymeric products of hydrolysis must be taken into account, particularly in terms of volatility and salt formation, especially with lime.

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Résumé

L'influence de la nature du comonomère et de la concentration de celui-ci sur la vitesse d'hydrolyse alcaline de copolymères d'acétate de vinyle en dispersion aqueuse est rapportée. Les comonomères étudiés comportaient des esters vinyliques supérieurs, des esters acryliques, un diester fumarique, et de l'éthylène. La signification de la polymérisation en émulsion a été également considérée. La vitesse d'hydrolyse est réduite avec des proportions croissantes en comonomères et avec une longueur croissante et une ramification des groupes alcoyles latéraux résultant des comonomères. De longues chaînes ramifiées d'esters vinyliques tertiaires réduisent non seulement la vitesse mais également le degré d'avancement de l'hydrolyse, étant résistante elle-même à l'hydrolyse et protégeant ainsi en partie les groupes d'acétate de vinyle les plus sensibles; des copolymères inhomogènes préparés intentionnellement étaient moins résistants que le copolymère le plus homogène de composition globale identique. L'inclusion de faibles quantités telles que 1% en poids de comonomères acides exerce un effet relativement considérable en accroissant la vitesse d'hydrolyse. A titre de comparaison on inclut dans cette étude le comportement d'homopolymères d'esters vinyliques supérieurs et de copolymères de méthacrylate de méthyle avec des esters acryliques. On conclut que les facteurs principaux influencant la vitesse d'hydrolyse sont de nature stérique et d'autres effets d'environnement résultant de la microstructure du copolymère.

Zusammenfassung

Es wird der Einfluss beschrieben, den die Art und die Konzentration des Comonomeren auf die Leichtigkeit hat, mit der eine alkalische Hydrolyse von Vinylacetat-Copolymeren in wässriger Dispersion erfolgt. Die untersuchten Comonomeren umfassen höhere Vinylester, Acrylester, einen Fumarsäurediester und Äthylen. Die Signifikanz der Formulierung der Emulsionspolymerisation wurde ebenfalls in Betracht gezogen. Die Hydrolysengeschwindigkeit wird durch steigende Anteile an Comonomeren und mit zunehmender Länge und Verzweigung der von diesen Comonomeren stammenden Alkyl-Seitenketten herabgesetzt. Verzweigte langkettige tertiäre Vinylester setzen nicht nur die Geschwindigkeit sondern auch das Ausmass der Hydrolyse herab, da sie selbst gegenüber einer Hydrolyse resistent sind und auch auf das empfindlichere Vinylacetat eine teilweise Schutzwirkung ausüben. Auf besondere Weise hergestellte inhomogene Copolymere waren weniger resistent als die homogeneren Copolymeren mit der gleichen Bruttozusammensetzung. Der Einbau von ziemlich kleinen Mengen an sauren Comonomeren, wie etwa 1-Gewichtsprozent, hat eine relativ grossen Einfluss im Sinne einer Erleichterung der Hydrolyse. Zum Vergleich wurde das Verhalten der Homopolymeren höherer Vinylester und der Copolymeren von Methylmethacrylat mit Acrylestern miteinbezogen. Daraus wird geschlossen, dass die Hauptfaktoren, die die Hydrolysentendenz beeinflussen, auf sterische und andere Nachbarschaftseffekte zurückgehen, die sich aus der Mikrostruktur des Copolymeren ergeben.

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