

Effect of Some Sodium Bisulfite Adducts of Different Chain Lengths on the Course of the Emulsion Polymerization of Vinyl Acetate

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SYNOPSIS

The emulsion polymerization of vinyl acetate using some bisulfite adducts of different chain lengths with potassium persulfate as the redox initiation system, in the absence of emulsifier, was studied. The effects of such adducts, which contain the same weight equivalent of bisulfite anion, on the rate of polymerization, maximum conversion, and stability of the produced polymer lattices as well as the morphological characteristics including volume-average diameters and the number of polymer particles per unit volume of water were investigated. The rate of polymerization was found to be dependent on the concentration of benzaldehyde, acetaldehyde, octyl aldehyde, methyl propyl ketone, and acetone sodium bisulfite adducts to the powers 0.54, 0.66, 0.95, 1.0, and 1.1, respectively. Also, it was found that increasing adduct chain lengths decreases the volume-average diameter, increases the obtained lattice stability, and improves the morphology of the polymeric particles, where a spherical morphology and extra stability were obtained in the presence of the octyl aldehyde adduct. © 1993 John Wiley & Sons, Inc.†

INTRODUCTION

The poly(vinyl acetate) emulsions produced in the present industrial scale are either stabilized by surfactant (if the particle size is between 0.1 and 0.2 μ) or with the use of protective colloid (if the particle size is between 0.5 and 3 μ) and prepared at relatively high temperatures with the production of polydisperse particle-size distributions.¹ Three major problems face the present industrial application of poly(vinyl acetate):

1. The polymeric chain branching (which increases with high temperature and with the presence of some emulsifiers).¹⁻³
2. The polydispersity of the produced particles.
3. The grafting copolymerization that may oc-

cur due to the reaction of vinyl acetate with some emulsifiers such as poly(vinyl alcohol) by chain transfer to emulsifier, which lowers the rate of polymerization and changes the properties of the produced poly(vinyl acetate).⁴ In recent years, many studies have been published on the emulsion polymerization of different monomers initiated by different redox systems,⁵⁻⁷ but most of these are performed at high temperatures (over 70°C) with the production of polydisperse particles and unstable emulsions.

The present study is an attempt to solve these industrial problems by polymerizing vinyl acetate monomer in the presence of a newly developed series of organic sodium bisulfite adducts having different chain lengths coupled with potassium persulfate as redox pair initiation systems in the absence of emulsifier at 40°C. Also, their effect on the kinetics of polymerization, on the morphological characteristics of obtained particles, and, finally, on the stability of the produced lattices were studied.

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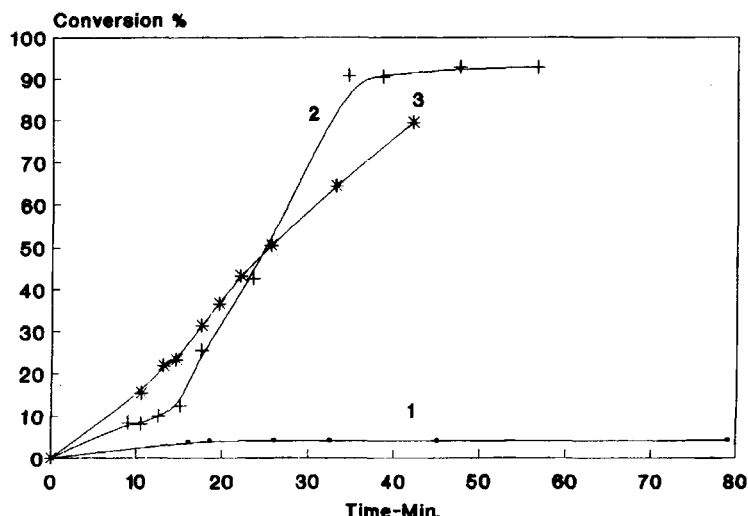


Figure 1 Rate dependence of methyl propyl ketone sodium bisulfite (MPKSBS) as reducing agent. $[KPS/MPKSBS] = (1) 3.125/6.25, (2) 6.25/12.5, (3) 12.5/25 \times 10^{-3}$. $[Monomer] = 1.083 \text{ mol/L}$ at 40°C .

EXPERIMENTAL

Vinyl acetate monomer (stabilized with 14 ppm hydroquinone) provided by BDH was redistilled before use and stored at -20°C , potassium persulfate was recrystallized from water by methanol, and the final

crystals were vacuum-dried. All water used was purified by distillation. The benzaldehyde, acetaldehyde, octyl aldehyde, methyl propyl ketone, and acetone sodium bisulfite adducts were prepared by the addition reaction of sodium bisulfite on the carbonyl group of benzaldehyde, acetaldehyde, octyl aldehyde, methyl propyl ketone, and acetone, respectively.

The polymerization technique and the number of polymer particles per unit volume of water were carried out as mentioned previously.^{8,9} The polydispersity of polymer particles were calculated by a computerized image analyzer equipment (Bildanalyze IBAS 1 and 2) to find the maximum diameter (D_{max}), circular diameter (D_{circle}), and area (A).

The stability of different emulsion lattices was measured by a kinetic sedimentation analysis technique using graduated analytical fine tubes. The lifetime of an emulsion is represented by $\tau = H/U$ (day), where H is the height of the emulsion under test (mm), and U , the rate of sedimentation (mm/day).

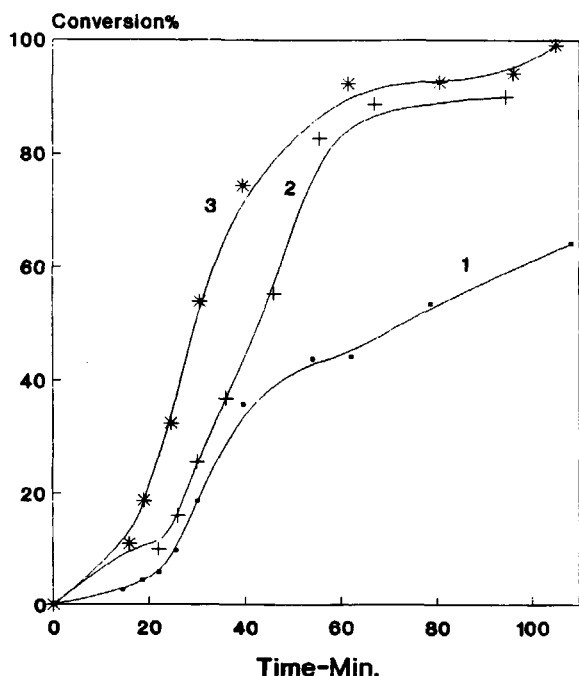


Figure 2 Rate dependence of octyl aldehyde sodium bisulfite (OASBS) as a reducing agent $[KPS/OASBS] = (1) 3.125/6.25, (2) 6.25/12.5, (3) 12.5/25 \times 10^{-3}$. $[Monomer] = 1.083 \text{ mol/L}$ at 40°C .

RESULTS AND DISCUSSION

Effect of Sodium Bisulfite Adducts of Different Chain Lengths on the Rate of Polymerization

Figures 1–4 demonstrate the conversion–time relationships for emulsifier free-emulsion polymerization of vinyl acetate at 40°C using some sodium bisulfite adducts of different chain lengths such as

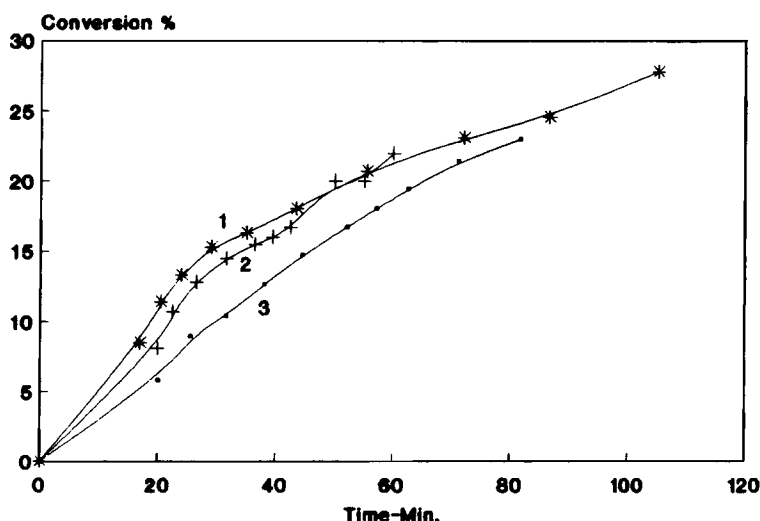


Figure 3 Rate dependence of acetaldehyde sodium bisulfite (ASBS) as a reducing agent. [KPS/ASBS] = (1) 12.5/25, (2) 9.375/18.75, (3) 6.25/12.5 $\times 10^{-3}$. [Monomer] = 1.083 mol/L at 40°C.

methyl propyl ketone, octyl aldehyde, acetaldehyde, and benzaldehyde sodium bisulfite together with potassium persulfate (KPS) as redox pair initiation systems. Also, a similar relationship was obtained using acetone sodium bisulfite as the adduct as mentioned previously.⁸ Figure 5 presents recaptulation of the data presented in this work.

The monomer concentration was kept at 1.0825 mol/L. From Figure 6 and Table I it is clear that the rate of polymerization (R_p) was found to be dependent on the used benzaldehyde, acetaldehyde, octyl aldehyde, methyl propyl ketone, and acetone sodium bisulfite adducts to 0.54, 0.66, 0.95, 1.0, and 1.1 powers, respectively. The rate equation with respect to initiator concentration is as follows:

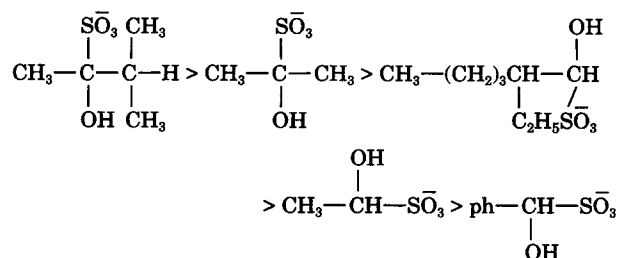
$$R_p \propto [I]^x$$

where I is the initiator concentration and X equals 0.54, 0.66, 0.95, 1.0, and 1.1 for benzaldehyde, acetaldehyde, octyl aldehyde, methyl propyl ketone, and acetone sodium bisulfite, respectively. In our previous work,^{8,9} it was found that the rate of polymerization was independent of the monomer concentration in the range of this study.

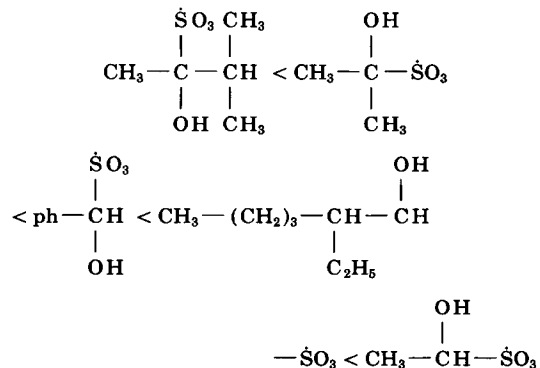
To explain the rate dependence on the sodium bisulfite adducts, we may postulate the following factors that may affect the free radical formation and the initial rates of polymerization:

1. The reducing ability of the adducts that depends on the inductive effect (+ I) of the

groups attached to the bisulfite anion, which decreases in the following order:



2. The steric hinderance of the bisulfite radicals, which control the activation energy of radical attack (the less the steric hinderance, the lower the activation energy of initiation), that increases as follows:



3. The solubility of the attacking bisulfite radicals in the monomer phase that increases by

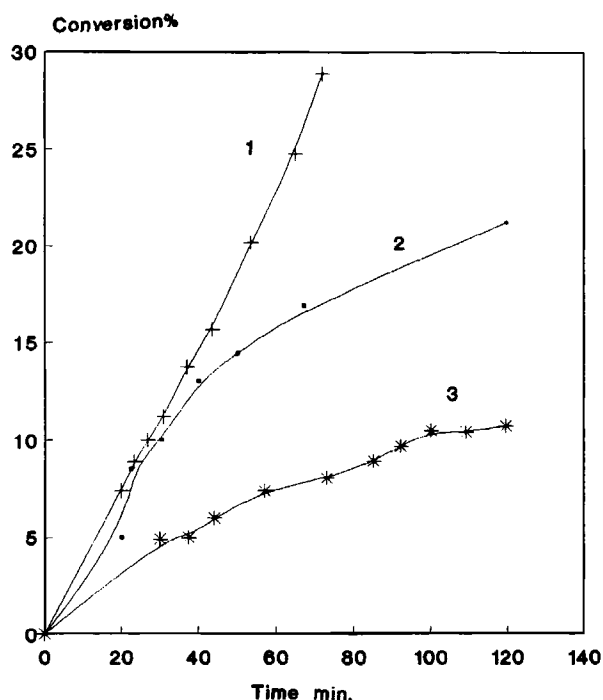


Figure 4 Rate dependence of benzaldehyde sodium bisulfite (BSBS) as a reducing agent. $[KPS/BSBS] = (1) 9.375/18.75, (2) 6.25/12.5, (3) 3.125/6.25 \times 10^{-3}$.

increasing the organic part of the attacking bisulfite radicals.

It is clear from Figure 7 and Table I that the ketonic sodium bisulfite adducts (acetone and

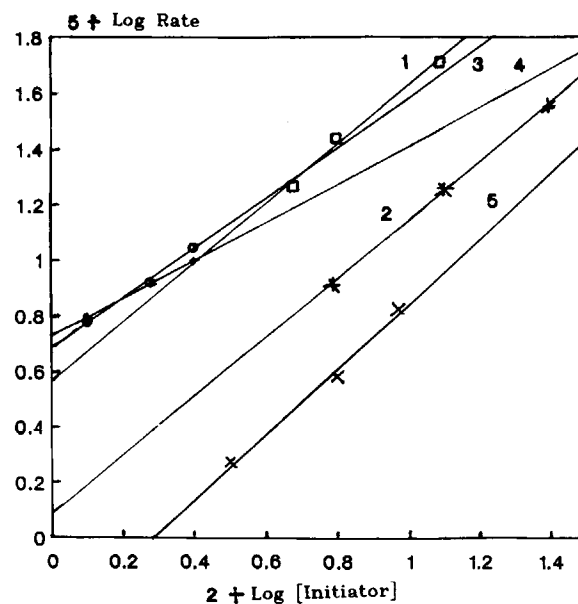


Figure 6 Log rate vs. $\log[\text{initiator}]$ for (1) acetone, (2) methyl propyl ketone, (3) octyl aldehyde, (4) acetaldehyde, and (5) benzaldehyde sodium bisulfite.

methyl propyl ketone) produce higher initial rates and maximum conversions than those of the aldehydic ones (acetaldehyde, benzaldehyde, and octyl aldehyde) due to the presence of two α -carbon atoms that have greater $+I$ than only one α -carbon atom. It can also be concluded that the acetone adduct gives a higher initial rate of polymerization and maximum conversion than does methyl propyl ke-

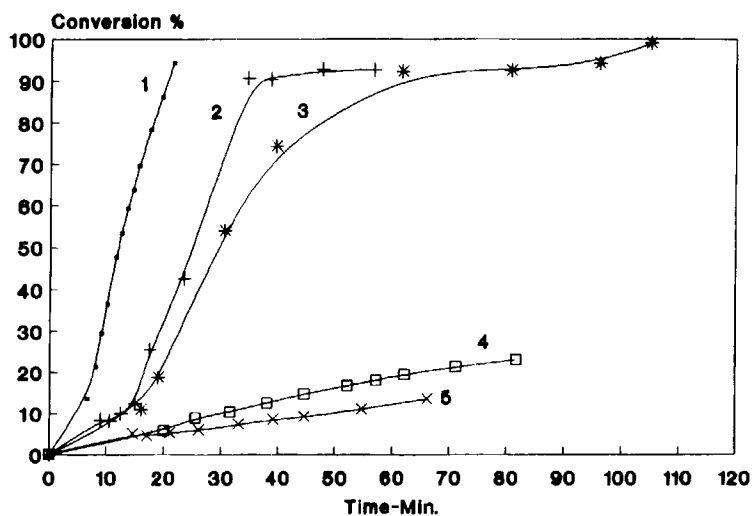


Figure 5 Conversion-time relationships in the presence of KPS of 6.25×10^{-3} concentration coupled with (1) acetone, (2) methyl propyl ketone, (3) octyl aldehyde, (4) acetaldehyde, (5) benzaldehyde sodium bisulfite of concentration 12.5×10^{-3} mol/L and $[\text{Monomer}] = 1.083$ mol/L at 40°C .

Table I Initial Rates, Particle Size, and No. Polymer Particles for the Emulsion Polymerization of Vinyl Acetate (1.083 mol/L) in the Presence of Different Bisulfite Adducts at 40°C with a Stirring Speed of 200 rpm

Initiation System Conc. $\times 10^3$ (mol/L)		Initial Rate $\times 10^5$ (mol/L s)	Conversion (%)	Particle Size (nm)	No. Polymer Particles $\times 10^{12}/\text{cc}$ Water
KPS	Bisulfite Adducts				
Adduct I					
12.5	25	3.838	38%	240	4.10
Adduct II					
12.5	25	10.280	90%	391	2.24
Adduct III					
12.5	25	11.400	100%	210	16.00
Adduct IV					
12.5	25	16.00	100%	340	3.79
Adduct V					
12.5	25	27.690	100%	266	3.05

Adduct I is benzaldehyde sodium bisulfite, Adduct II is acetaldehyde sodium bisulfite, Adduct III is octyl aldehyde sodium bisulfite, Adduct IV is methyl propyl ketone sodium bisulfite, and Adduct V is acetone sodium bisulfite.

tone due to the lower steric hinderance of the formerly formed radicals, whereas in the case of aldehydic adducts, octyl aldehyde produced the highest initial rate (Fig. 7) due to the presence of long hydrocarbon chain in its adduct with a relatively higher inductive effect. Finally, benzaldehyde sodium bi-

sulfite, although it has greater solubility in the monomer phase than that of acetaldehyde, produced the lowest initial rate and maximum conversion owing to its benzyl group that has $-I$ and the greatest steric hinderance. We can conclude that the steric hinderance of the ketonic adducts is predominant over the two other factors, whereas the chain length of aldehydic adducts is the predominant one.

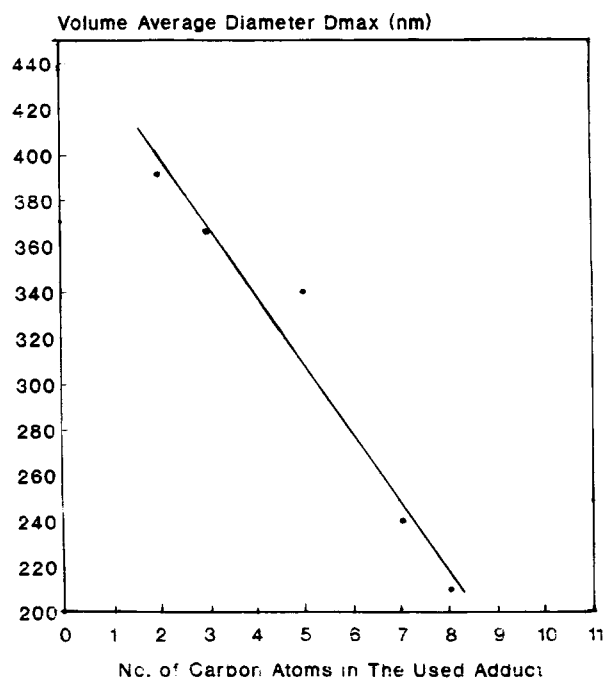
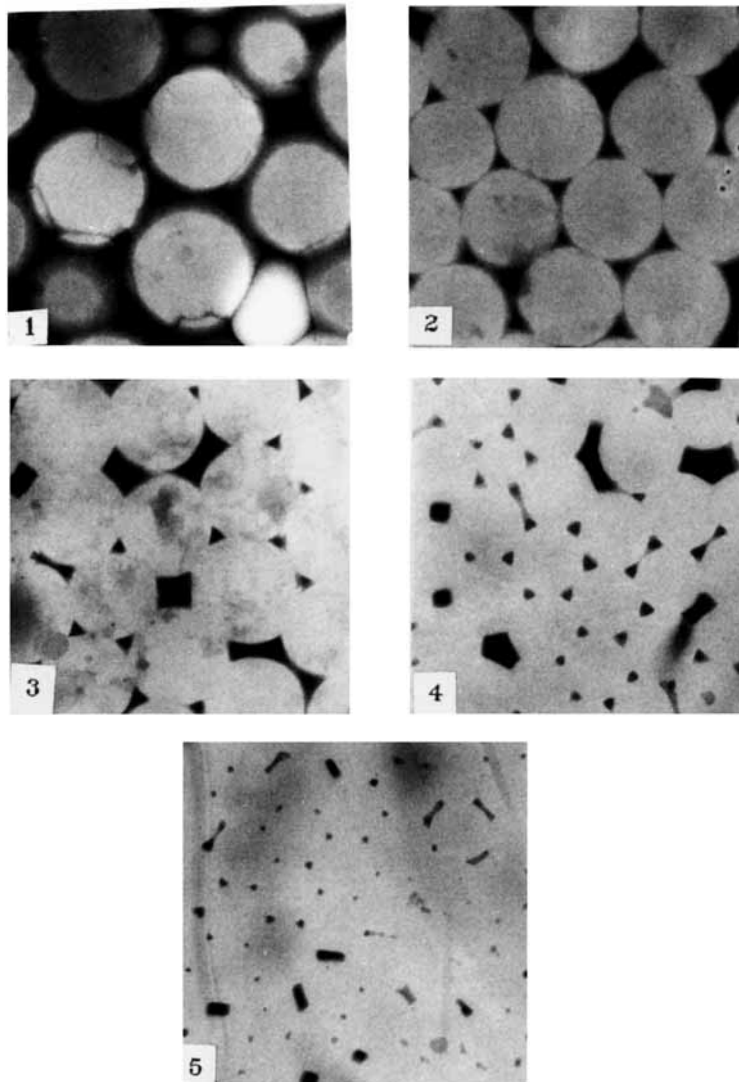


Figure 7 Relationship between no. carbon atoms of the adduct vs. volume-average diameter (D_{max}).

Effect of the Different Sodium Bisulfite Adducts on the Morphological Characteristics of the Obtained Lattices

Graphs 1–5 show the morphology of the obtained latex particles for the emulsion lattices prepared by potassium persulfate coupled with each of acetaldehyde, acetone, methyl propyl ketone, benzaldehyde, and octyl aldehyde sodium bisulfite adducts as redox initiation systems. Also, Tables II–VI show the maximum diameter (D_{max}), circular diameter (D_{circle}), area (A), center of gravity on the X axis ($C_{\text{Grav-X}}$), and center of gravity on the Y axis ($C_{\text{Grav-Y}}$) for the latex particles of Graphs 1–5 that were prepared according to the conditions of Table I. Furthermore, Figures 8 and 9 show the relationship between the number of carbon atoms of the used adducts vs. each of the average D_{max} of the produced latex particles and also the deviation from spherical morphology ($D_{\text{max}} - D_{\text{circle}}$), respectively. From Graphs 1–5, Figures 8 and 9, and Tables I–VI, it is obvious that the increasing of the chain



Graphs 1–5 Effect of bisulfite adducts of different chain lengths on the morphological characteristics of polymer particles with magnification 40,000 \times for (1) acetaldehyde, (2) acetone, (3) methyl propyl ketone, (4) benzaldehyde, and (5) octyl aldehyde sodium bisulfite.

length of the used adducts decreases the volume-average diameter, increases the number of polymer particles, and produces fewer polydisperse particles with more spherical morphology. Such behavior could be attributed to the emulsifying tendency of the used adducts that increases by increasing their organic chain length and, hence, decreases the volume-average diameter of the obtained latex particles and tends to produce smooth and spherical morphology. (A film prepared in the presence of octyl aldehyde and dried at room temperature for 24 h was found to be transparent and not subject to water spotting.)

Colloidal Behavior of the Emulsion Lattices Prepared by Some Sodium Bisulfite Adducts

The stability of the produced emulsion lattices, prepared in the previously mentioned bisulfite adducts, was investigated by applying the kinetic sedimentation analysis technique. Figure 10 demonstrates the relationship between the time elapsed through which the emulsions were tested vs. the corresponding rate of sedimentation of the dispersed phase. Also, Table VII clarifies the lifetime τ of each emulsion latex. From Figure 10 and Table VII, it is clear that increasing the chain length of the used adduct

Table II Morphology of Particles Prepared in the Presence of Acetaldehyde Adduct

No.	Area (mm ²)	D_{\max} (mm)	$C_{\text{Grav-X}}$	$C_{\text{Grav-Y}}$	D_{circle} (mm)	V_{sphere} (mm ³)
1	145.0	14.9	66.8	117.9	13.6	1313
2	163.3	15.6	57.7	130.3	14.4	1569
3	190.2	15.8	58.1	110.3	15.6	1973
4	166.4	15.5	66.0	90.0	14.6	1615
5	192.0	16.8	87.5	118.6	15.6	2001
6	188.4	16.0	90.4	97.8	15.5	1945
7	204.8	17.0	102.0	76.4	16.2	2204
8	186.4	14.4	101.2	106.7	14.4	1913
9	190.3	16.1	115.5	86.9	15.6	1974
10	187.3	15.8	154.8	77.2	15.4	1928
11	160.6	15.2	89.7	142.5	14.3	1531
12	159.2	14.8	77.0	136.8	14.2	1511

Table III Morphology of Particles Prepared in the Presence of Acetone Adduct

No.	Area (mm ²)	D_{\max} (mm)	$C_{\text{Grav-X}}$	$C_{\text{Grav-Y}}$	D_{circle} (mm)	V_{sphere} (mm ³)
1	197.4	16.9	99.1	71.1	15.9	2086
2	166.1	15.0	79.3	96.2	14.5	1610
3	163.9	15.4	117.2	78.5	14.5	1578
4	164.2	14.8	93.6	99.8	14.5	1583
5	137.0	13.7	119.5	93.6	13.2	1206
6	155.6	14.3	99.6	107.1	14.1	1460
7	159.4	14.2	91.0	96.5	14.2	1513
8	139.6	14.6	107.2	94.7	13.3	1240
9	155.5	15.4	84.6	96.6	14.1	1458
10	133.9	13.0	101.0	82.1	13.1	1165
11	160.8	15.0	105.9	81.2	14.3	1534
12	152.2	14.6	117.9	75.9	13.9	1412

D_{\max} , D_{circle} , area, and V_{sphere} are multiplied by 40,000.

Table IV Morphology of Particles Prepared in the Presence of Methyl Propyl Ketone Adduct

No.	Area (mm ²)	D_{\max} (mm)	$C_{\text{Grav-X}}$	$C_{\text{Grav-Y}}$	D_{circle} (mm)	V_{sphere} (mm ³)
1	143.9	13.9	97.4	66.6	13.5	1299
2	170.5	13.9	60.1	88.8	14.7	1674
3	131.4	13.1	92.7	94.3	12.9	1133
4	162.5	14.7	84.2	86.1	14.4	1558
5	144.6	14.0	92.3	80.2	13.6	1308
6	169.2	14.7	100.5	82.7	14.7	1655
7	139.9	13.8	135.4	74.6	13.4	1244
8	129.7	12.2	136.6	71.5	12.9	1111
9	150.9	14.2	119.5	97.5	13.9	1394
10	150.6	14.2	99.3	101.1	13.9	1390
11	164.9	16.5	88.3	101.6	14.5	1592
12	130.2	13.4	126.5	121.3	12.9	1117

Table V Morphology of Particles Prepared in the Presence of Benzaldehyde Adduct

No.	Area (mm ²)	D_{max} (mm)	C_{Grav-X}	C_{Grav-Y}	D_{circle} (mm)	V_{sphere} (mm ³)
1	73.1	10.2	57.2	118.1	9.6	470
2	72.3	10.0	55.6	112.9	9.3	463
3	67.2	9.1	46.7	120.8	8.8	415
4	61.0	9.2	49.8	111.7	9.8	358
5	75.1	9.3	60.2	127.7	9.2	490
6	67.0	9.6	65.6	98.2	11.5	413
7	74.0	10.6	43.4	108.6	9.7	479
8	56.2	8.5	64.8	92.9	8.5	317
9	60.6	9.1	43.6	114.0	8.8	355
10	73.8	10.3	55.9	118.6	9.7	477
11	58.4	8.9	57.5	111.7	8.6	336
12	70.2	9.6	55.4	99.5	9.5	442

D_{max} , D_{circle} , area, and V_{sphere} are multiplied by 40,000.

stabilizes the produced emulsion lattices, decreases its sedimentation rate, and, consequently, increases its lifetime (τ), giving maximum stability for the emulsion lattices prepared in the presence of the octyl adduct (the emulsion was stable for 9 months). It is quite clear that the sedimentation of emulsion latex particles possess two different kinetic stages for all cases except that prepared in the presence of acetaldehyde sodium bisulfite.

Finally, these results can be rationalized to the following:

1. The steric stabilization, which increases by the increase of the adduct's organic chain length.
2. The improvement of the morphological characteristics and the decrease in the size of the

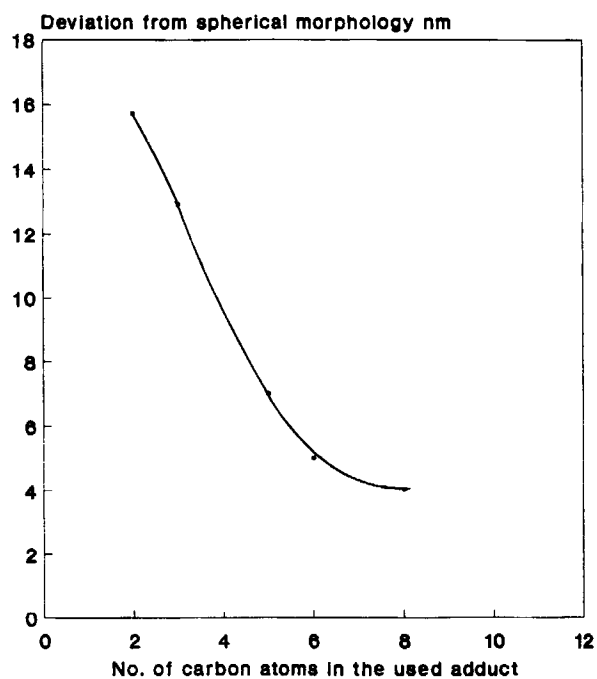


Figure 8 Relationship between no. carbon atoms in the used adduct vs. deviation from spherical morphology ($D_{max} - D_{circle}$).

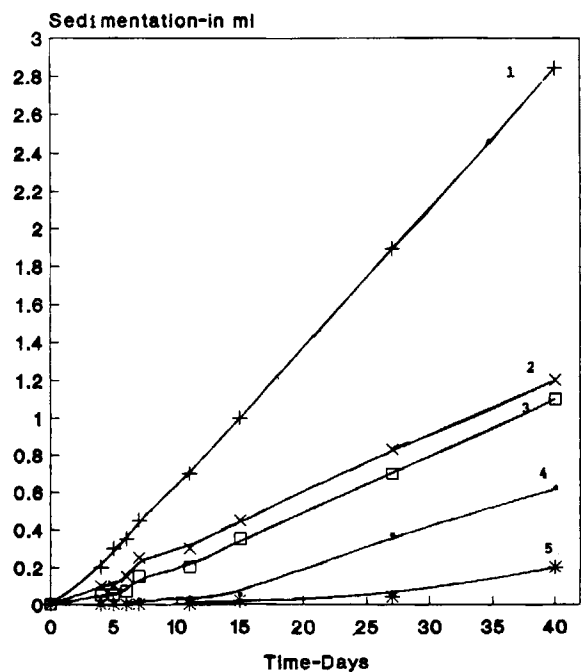


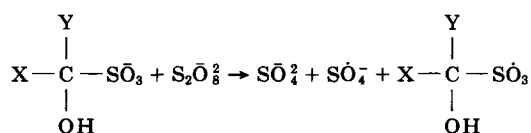
Figure 9 Relationship between time vs. sedimentation of different emulsion lattices where (1) acetaldehyde, (2) acetone, (3) methyl propyl ketone, (4) benzaldehyde, and (5) octyl aldehyde sodium bisulfite, respectively.

Table VI Morphology of Particles Prepared in the Presence of Octyl Aldehyde Adduct

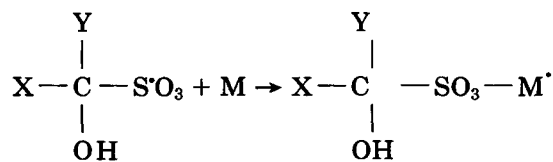
No.	Area (mm ²)	D _{max} (mm)	C _{Grav-X}	C _{Grav-Y}	D _{circle} (mm)	V _{sphere} (mm ³)
1	113.2	8.9	9.3	49.4	9.0	1280
2	109.1	8.8	14.7	54.9	8.3	1212
3	101.9	8.0	32.1	52.8	8.1	1095
4	111.6	8.7	39.0	49.5	8.4	1255
5	97.7	8.1	32.8	54.4	7.9	1028
6	124.1	—	19.2	75.2	8.9	1471
7	102.3	8.2	23.9	74.9	8.0	1100
8	108.6	8.0	27.7	66.1	5.5	1203
9	106.1	8.2	26.0	69.1	8.2	1165
10	105.6	8.0	41.3	66.4	8.2	1155

particles by increasing the chain length of the used adducts.

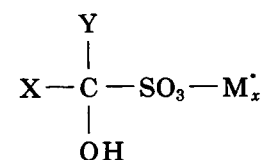
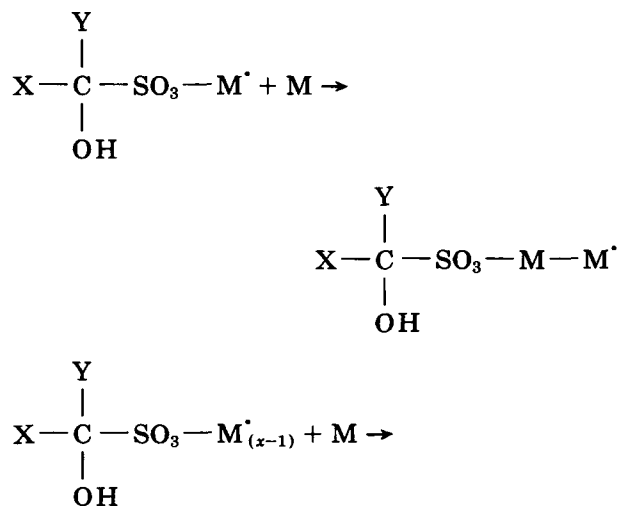
Mechanism of the Reaction



Initiation:



Propagation:



Termination:

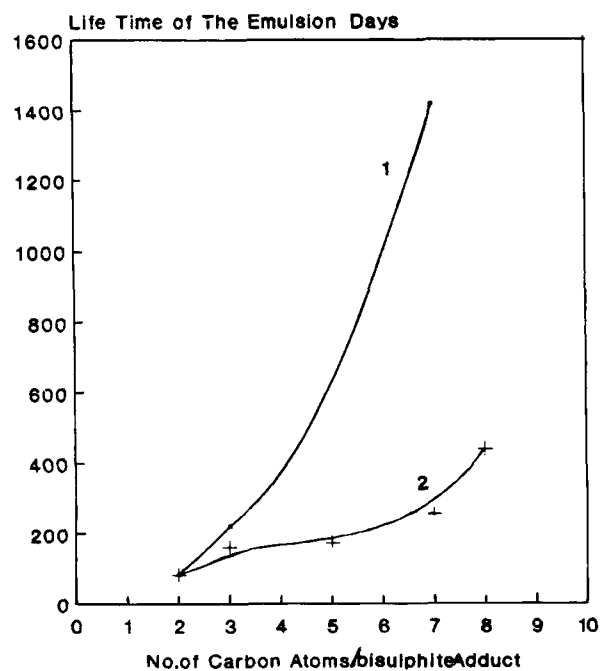
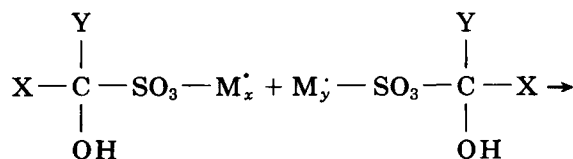
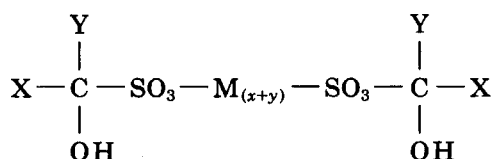


Figure 10 Relationship between no. carbon atoms/bisulphite adduct vs. lifetime of the emulsion latex: (1) first stage; (2) second stage.

Table VII Lifetime of Emulsion Latices (τ) Prepared by the Emulsion Polymerization of Vinyl Acetate (1.0825 mol/L) in the Presence of Different Bisulfite Adducts of the Same Concentration at 40°C

Adducts No.	No. Carbon Atoms/ Chain	First Stage		Second Stage	
		Time	Lifetime (τ)	Time	Lifetime (τ)
1-Adduct I	2	—	—	40	81.25
2-Adduct II	3	6	218.75	34	159.09
3-Adduct III	5	6	486.36	34	172.58
4-Adduct IV	7	10	1416.00	30	255.00
5-Adduct V	8	27	∞	13	437.50

Adduct I is acetaldehyde sodium bisulfite, Adduct II is acetone sodium bisulfite, Adduct III is methyl propyl ketone sodium bisulfite, Adduct IV is benzaldehyde sodium bisulfite, and Adduct V is octyl aldehyde sodium bisulfite.



where X = heptyl or methyl or phenyl and Y = hydrogen (for aldehydic adducts) or X = methyl or isopropyl and Y = methyl (for ketonic adducts).

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