

POLYMER COLLOID GROUP NEWSLETTER

Vol. 14 No. 2

12 October 1984

Two new members were elected at the 1984 Annual Business Meeting held during the Polymer Colloid Symposium in Montreal in June. They are:

Dr J. Lyklema, Laboratory for Physical and Colloid Chemistry, Agricultural University, de Dreijen 6, 6703 BC Wageningen, Holland	and Dr F. Candau, CNRS Centre de Recherches sur les Macromolécules, 6, Rue Boussingault, 67093 Strasbourg Cedex, France.
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Don Sunberg has a sabbatical year at the Swedish Institute of Surface Chemistry: his temporary address is
Ytkemiska Institutet,
Box 5607,
S-114 86 Stockholm,
Sweden.

We are sorry to hear that Professor Vrij has been in hospital and unable to contribute to this issue.

Future plans for Polymer Colloid Group meetings are that the 5th 'Polymer Colloids' Gordon Research Conference is scheduled for 8 - 12 July 1985 at Tilton School, New Hampshire with Ritchie Wessling as Chairman and Ron Ottewill as Vice-Chairman. The 1985 Annual Business Meeting will be held during this meeting. The 6th Gordon Conference will be held in the summer of 1987.

The 1986 meeting will be in Racine, Wisconsin at the invitation of Johnson Wax with cosponsorship by Lehigh University. It is hoped to arrange a 3rd N.A.T.O. Advanced Study Institute at Strasbourg in 1988.

The next event of interest to members will be the Plastics and Rubber Institute Conference 'Polymer Latex II' which is to be held in the Scientific Societies' Lecture Theatre, Savile Row, London on Tuesday and Wednesday 21-22 May 1985. Details from Mr M.D. Shuttleworth, Plastics and Rubber Institute, 11 Hobart Place, London SW1W 0HL.

The A.C.S. Division of Plastic Materials: Science and Engineering has scheduled a Symposium on Emulsion Polymerization for the 1986 Spring National Meeting at Atlantic City, 6 - 11 April.

I will have been editing the Group's Newsletter for 10 years by the time of the Tilton meeting next summer and I will be heavily involved with the affairs of the Macro Group UK as Programme Chairman for the following two years so the Annual Meeting should consider whether the time has not come to move the Secretariat elsewhere. In the meantime, copy for the Spring issue should be sent to reach me at Chemistry Department, UMIST, P.O. Box 88, Manchester M60 1QD, England by Monday 22nd April, 1985.

There is a proposal for the A.C.S. Division of Colloid & Surface Chemistry to sponsor a 'Polymer Colloids III' Symposium, possibly through the A.C.S. Macromolecular Secretariat at the 1987 Spring National Meeting at Denver, 5-10 April.

A. S. Dunn

D. C. Blackley, London School of Polymer Technology,
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Since completing the programme of work which was summarised in our paper presented to the 1933 Polymer Colloids Gordon Research Conference, we have carried out the following further investigations into aspects of the mechanical stability of natural rubber latex:

- i) further investigations of intermittent mechanical destabilisation;
 - ii) investigation of the effects of various synthetic hydrophilic polymers upon mechanical stability;
 - iii) further investigations of the effects of fatty-alcohol ethoxylates upon mechanical stability.
- i) Brief reference was made in our paper presented to the 1933 Polymer Colloids Gordon Research Conference to an interesting observation we had made when carrying out "split" mechanical stability tests on natural rubber latex. In the "split" mechanical stability test, the latex is sheared for a proportion of the time required for complete destabilisation, then allowed to stand undisturbed for a certain period, and then the test is resumed. We made the observation that, allowing the latex to stand for 24 hours at room temperature between the two stages of the test, the sum of the initial time of shearing and the time required to effect complete destabilisation during the second stage was almost constant regardless of the duration of the first stage. Furthermore, the sum was always almost exactly equal to the mechanical stability time as conventionally measured. It is as though the latex is able to remember quite precisely the extent to which it had been mechanically destabilised 24 hours previously, indicating that changes of some degree of permanence occur when natural rubber latex is subjected to mechanical shear, even although the latex has not been completely destabilised and appears visually to be unchanged. We have postulated that these changes take the form of the formation of loose aggregates of particles which entrap dispersion medium and so increase the effective volume fraction of disperse phase. This postulate is certainly consistent with many of the other observations reported at the 1933 Gordon Research Conference.

We have now made a more thorough investigation of the effect of intermittent mechanical destabilisation upon natural rubber latex. We have found that

- a) the "memory" effect seems to be quite general to ammonia-preserved natural rubber latices in that it is shown by HA latex, LA latex and HA substage latex;
- b) the "memory" is not affected by lengthening the time interval between the two stages, or by increasing the temperature at which the latex is stored;
- c) latex which has been partially mechanically destabilised retains its partial destabilisation when blended with fresh latex, and reduces the overall mechanical stability of the blend.

These further observations confirm that, whatever are the structural changes which are induced in partially-destabilised latex, they have a considerable degree of persistence.

ii) A range of synthetic hydrophilic polymers has been prepared and their effects upon the mechanical stability of natural rubber latex investigated. The object of this work has been to reveal correlations between the chemical structure of the polymer and its ability to enhance mechanical stability. The polymers investigated so far are all either copolymers of 2-hydroxyethyl methacrylate and methacrylic acid, or terpolymers of these two monomers and a hydrophobic monomer such as 2-ethylhexyl acrylate. The indications so far are that:

- a) The ability to enhance mechanical stability depends very much upon the balance of hydrophobic and hydrophilic groups in the polymer. Substantial enhancement occurs only if a proportion of the monomer units are hydrophobic in nature, presumably because such units encourage adsorption of the polymer at the rubber-water interface.
 - b) The ability of a given copolymer to enhance mechanical stability increases as the molecular weight of the copolymer increases.
- There is nothing very surprising about either of these observations, but it is interesting to have quantitative confirmation of one's expectations.

- iii) Our further investigations of the effects of fatty-alcohol ethoxylates upon the mechanical stability of natural rubber latex have been concerned with a more detailed examination than hitherto of the effects of small additions of these ethoxylates. As previously, we find that small additions bring about drastic reductions in mechanical stability. Experiments using ethoxylates containing the same hydrophobic moiety (derived from a mixture of cetyl and oleyl alcohols), but polyethylene oxide chains of different lengths have shown that
- a) the longer the polyethylene oxide chain, the sharper is the reduction in mechanical stability;
 - b) the longer the polyethylene oxide chain, the lower is the minimum mechanical stability attained;
 - c) the longer the polyethylene oxide chain, the lower is the level of addition of the ethoxylate at which the minimum in mechanical stability is observed.

One particularly interesting respect in which the present observations differ from those which we have made previously is that in this investigation we have not observed marked increases in mechanical stability at levels of ethoxylate addition which exceed those corresponding to the minimum in mechanical stability. The differences in behaviour are particularly marked in the case of the higher ethoxylates (45-mole and 60-mole). In earlier work, very marked enhancements of mechanical stability have been observed once the minimum has been passed, but in this investigation only very slight increases in mechanical stability have been observed. These differences in behaviour are almost certainly a reflection of the variability of ammonia-preserved natural rubber latex. One reason why the difference between the present and previous observations is interesting is that it suggests the possibility that the effect of long-chain ethoxylates upon mechanical stability might form a useful predictor to the behaviour of natural rubber latex in certain industrial processes. The variability in the colloid stability of natural rubber latex causes serious problems in industries which use this latex, and any simple test which can be used to predict processing behaviour would be very useful.

119 SEP Decd

EFFECT OF LATEX PROPERTIES ON THE BEHAVIOR OF NONIONIC
ASSOCIATIVE THICKENERS IN PAINT

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Introduction

Water soluble polymers are used in latex paint formulations to control the viscosity-shear rate profile to insure adequate resistance to sedimentation during storage and to provide suitable application characteristics. Cellulose ethers have been the dominant thickener over the past three decades, although they have serious deficiencies. Cellulose ethers efficiently thicken paint formulations and generally have predictable performance characteristics. The viscosity obtained is normally related to the specific amount of thickener employed, the molecular weight range of the thickener, and the volume solids of the formulation. However, the cellulose ethers fail to provide latex paints the viscosity-shear rate profile necessary to achieve good application characteristics when compared to the solvent borne paints they have been instrumental in replacing. Cellulose ether thickened paints exhibit poor leveling properties resulting in undesirable brush or roller patterns, heavy roller spatter during application, and over-spreading that results in thin films and poor applied hiding power. In addition, being cellulose derivatives, they are difficult to protect from enzymes of micro-organisms commonly found in water which relatively easily degrade the polymer.

Synthetic "associative thickeners" have been developed for paints that result in highly attractive application properties. These polymers are generally of lower molecular weight, and contain hydrophobes on a water soluble polymer backbone. These polymers have the ability to provide the viscosity-shear rate profile desirable in a paint, but their behavior can be drastically influenced by surfactants, dispersants, latexes and pigments.

The interactions between associative thickeners and surfactants and latexes in a paint are quite complex. While studying the behavior of two polyether polyurethane associative thickeners of differing molecular weight and hydrophobicity, we have observed relationships between latex particle size and associative thickeners that relate to the high shear viscosities of paints. The high shear viscosity measured on an I.C.I. cone and plate viscometer at 10,000 sec⁻¹ relates to the film thickness application characteristics of the paint by either brush or roller. In addition, the surface characteristics of the latex particles and the surfactants that may be carried in the latex serum also are major contributors to the viscosity shear rate profile of paints.

EXPERIMENTAL

The associative thickeners studied are hydrophobe-modified polyether polyurethanes, available from Union Carbide Corporation. The products will be referred to as T-1 and T-2. These thickeners were studied in an interior semigloss paint formulation (Table II). Latexes used in this study included commercial acrylate-methacrylates from Rohm & Haas (R-1, R-2, R-3), commercial styrene-acrylates from BASF (B-1), Hoechst (H-2), and Synres (S-3) and a commercial vinyl acrylate from Union Carbide Corp. (U-1). In addition, four latexes were prepared in our laboratories and are described in the text. The high and low shear viscosities of the prepared paints were measured with an I.C.I. cone and plate viscometer at 10,000 sec⁻¹ (Research Equipment Ltd.) and on a Stormer viscometer (Arthur H. Thomas Co.). The particle size of the latexes was measured on a Nicomp Instruments Laser Particle Sizer Model 200. The surface tension of associative thickeners in water was determined by the Wilhelmy Plate method.

RESULTS AND DISCUSSION

Data on the molecular weights of associative thickeners T-1 and T-2 have previously been published (1), and those values are shown in Table I. While T-2 has a higher molecular weight than T-1, it has a lower hydrophobe content that is reflected in the solubility of the polymer at low concentrations. Below 5% polymer T-1 is insoluble when diluted with water, while T-2 remains in solution to infinite dilution. The hydrophobe modification of these and other types of water soluble associative thickeners result in

TABLE I
THICKENER PROPERTIES

ASSOCIATIVE THICKENER	M _w	M _n	SOLUBILITY % IN H ₂ O
T-1	10.9 x 10 ³	8.7 x 10 ³	INSOLUBLE
T-2	9.4 x 10 ⁴	4.7 x 10 ⁴	SOLUBLE

paint thickeners that can provide excellent viscosity-shear rate profiles. The mechanism of the thickening action has been attributed to association of the hydrophobes on the water soluble polymer backbone with disperse phase solid surfaces, with other surface active molecules in solution, and with themselves (2). Associative thickeners do exhibit weakly surface active properties as indicated by the surface tension curve of T-2 in pure water as shown in Figure 1. It has been widely recognized that the efficiency of associative thickeners varies widely with different latex types, surfactants, dispersants and water soluble co-solvents used in typical paint formulations (3). It is widely believed that the latex surface characteristics and the surface active components of the formulation control the degree of association of the associative thickeners and account for the large differences in behavior observed. Using the paint formula in Table II, latexes R-1 and R-2 were employed with each of the two associative thickeners T-1 and T-2. The resulting viscosity data in Table III show how radically the viscosity of a paint can vary at both high and low shear rates by changing the latex or the thickener. Both commercial latexes have very similar bimodal particle size distributions that average about 0.1 and 0.5 microns. The polymer compositions of both are predominately the same butyl acrylate and methyl methacrylate ratios as indicated by I.R. analysis and minimum film formulation temperature. The more hydrophobic low molecular weight thickener T-1 demonstrates good thickening with R-2, but virtually none with R-1. The more hydrophilic and higher molecular weight T-2 demonstrates exactly the opposite response. In all examples the pigment volume content, latex volume content, volume solids and dry thickener loading (6.0 pounds per 100 gallons of dry thickener) are identical. In these

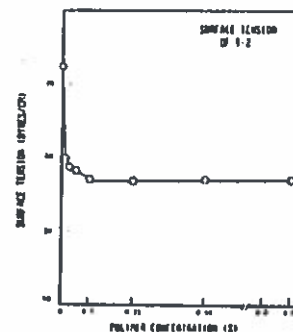


FIGURE 1. SURFACE TENSION OF ASSOCIATIVE THICKENER T-2

TABLE II
INTERIOR SEMIGLOSS

PIGMENT DISPERSION	GRAMS
Propylene Glycol	75.0
Tamol 5G-1	11.6
Defto 495	2.5
Mucsept 95	3.0
Zopaque RCL9	255.0
LET DOWN	
Latex, 50%	496.0
Tensol	20.0
Triton GRM	0.5
Propylene Glycol	20.0
Water	139.4
Thickener Solution 20%	30.0
Defto 495	2.5
28% Ammonia	2.0
	1057.5

TABLE III
PAINT VISCOSITIES
ACRYLIC LATEXES

PAINT VISCOSITIES	T-1		T-2	
	R-1	R-2	R-1	R-2
STORMER, K.U.	68	94	100	61
I.C.I., POISE	1.1	1.0	1.0	0.7
LATEX PROPERTIES				
COMPOSITION	← PREDOMINATELY BUTYL ACRYLATE-METHYL METHACRYLATE →			
PARTICLE SIZE	← 0.1/0.5 MICRON BIMODAL →			

examples the surface active materials in the latex serum and/or the characteristics of the latex particle surfaces must alter interaction of the associative thickeners in both the high and low shear rate range. Similar results were obtained when three styrene acrylic latexes were compared with both T-1 and T-2 in the same formulation (Table IV). Again all formulation parameters are the same as those used in the example above. These latexes all have a relatively narrow small particle size distribution of 0.14-0.15 microns, and have similar styrene and butyl acrylate compositions. Therefore the differences in low and high shear viscosity response shown on Table IV must reflect the influence of serum surface active materials or the latex surface characteristics on the ability of the associative thickeners to adsorb on surfaces or associate with themselves or other components in solution.

TABLE IV
PAINT VISCOSITIES
STYRENE ACRYLIC LATEXES

PAINT VISCOSITIES	T-1			T-2		
	R-1	S-3	M-2	R-1	S-3	M-2
STORMER, K.U.	78	104	106	129	112	90
I.C.I., POISE	0.9	1.4	0.9	1.7	1.5	0.9
LATEX PROPERTIES						
COMPOSITION	← STYRENE-BUTYL ACRYLATE →					
PARTICLE SIZE, MICRONS	0.15	0.14	0.14	0.15	0.14	0.14

Effect of Latex Particle Size

If the characteristics of latex surfaces are a factor in an associative thickener's performance then intuitively one must consider that the particle size of latexes, and consequently the surface area of the particles, should be a factor in determining the performance of associative thickeners. An evaluation of this concept was attempted by comparing the performance of T-1 and T-2 with acrylic latex R-3 and two experimental acrylic latexes of smaller particle size. Acrylic latex R-3 polymer composition is similar to R-2 and R-1. The major difference appears to be, by analysis, that it is stabilized by a relatively high level of an alkyl aryl ethoxylate nonionic surfactant, and has a narrow particle size distribution with a mean of 0.11 microns. This particle size closely corresponds to the small population in R-2 and R-1. As shown in Table V T-1 effectively thickens the R-3 paint with the viscosity-values being equal or better than the T-1/R-2 example. In an analogous fashion T-2 relatively poorly thickened the R-3 paint and the R-2 paint from the earlier example.

TABLE V
PAINT VISCOSITIES
ACRYLIC LATEXES

PAINT VISCOSITIES	T-1			T-2		
	R-3	EXP. A	EXP. B	R-3	EXP. A	EXP. B
STORMER, K.U.	100	102	102	78	88	90
I.C.I., POISE	1.0	1.5	2.3	0.9	1.2	1.5
LATEX PROPERTIES						
COMPOSITION	← BUTYL ACRYLATE-METHYL METHACRYLATE →					
PARTICLE SIZE, MICRONS	0.11	0.09	0.06	0.11	0.09	0.06

The experimental latexes have polymer compositions similar to that of the commercial R-3, but with minor constituent differences in the 1-3% range. Experimental latex A has a slightly smaller mean particle size than R-3 with an average size of 0.09 microns, and is stabilized with a 40 mole ethoxylate of nonyl phenol (TERGITOL NP-40). Experimental latex B has a narrow distribution with an average size of 0.06 microns, and like A contains the same nonionic surfactant type and level plus anionic surfactant necessary to achieve the desired particle size reduction. The T-1 thickener gave about the same Stormer viscosity with R-3 and both experimental latexes. However, the decreasing particle size of this latex series correlates with substantial increases in high shear viscosity. A similar significant trend to higher high shear paint viscosities was obtained with Thickener T-2 and the three latexes with decreasing particle size. With T-2 the increasing high shear viscosity was also accompanied with increasing low shear viscosity. The more hydrophobic lower molecular weight T-1 clearly responds more effectively in the paint formulation as the particle size is decreased. These viscosity increases are not due to interaction of the surfactants used to prepare the latex with the thickeners in the aqueous phase of the paint. Both the anionic and nonionic surfactant used to prepare these latexes when added to paints containing T-1 or T-2 at equivalent concentrations, can be expected to decrease both the high and low shear paint viscosity.

A similar latex particle size and paint viscosity relationship with the associative thickeners was found with a series of commercial and experimental vinyl acrylic latexes. Experimental latex C was prepared with a 40 mole ethoxylate of octyl phenol (Triton X405) and latex D with a 40 mole ethoxylate of nonyl phenol (TERGITOL NP40). Both latexes have a small narrow size distribution with each having an average diameter of 0.16 microns. These experimental latexes are compared in the semigloss paint formula to U-1, with both thickeners; the results are summarized in Table VI. U-1 is essentially a nonionic surfactant stabilized latex with an average particle size of 0.25 microns. Both experimental latexes interact effectively with T-1 as evidenced by substantially higher low and high shear viscosities. Thickener T-2 did not thicken the experimental latex paints any more effectively than it did the larger particle size U-1.

TABLE VI
PAINT VISCOSITIES
VINYL ACRYLIC LATEXES

PAINT PROPERTIES	T-1			T-2		
	U-1	EXP. C	EXP. D	U-1	EXP. C	EXP. D
STORMER, K. U.	72	90	90	70	70	70
I. C. I. POISE	0.9	1.2	1.2	1.1	0.6	0.6
<u>LATEX PROPERTIES</u>						
COMPOSITION	← VINYL ACETATE - BUTYL ACRYLATE →					
PARTICLE SIZE, MICRONS	0.25	0.16	0.16	0.25	0.16	0.16

CONCLUSIONS

Paint thickening studies using two associative thickeners with acrylic and styrene acrylic latexes illustrate how the efficiency of these thickeners can vary widely despite nearly the same particle size characteristics and latex particle surface chemistry contribution from the gross polymer composition. The varying thickening efficiencies probably are due to surface active materials used to stabilize the latex particle, some of which may be grafted to the surfaces of the latex particles. The inverse manner of the thickening efficiency relationship of the two associative thickeners of differing degrees of hydrophobicity tend to support the premise that association with surface active species is involved in the thickening mechanism. Studies with experimental acrylic latexes show that latex particle size below 0.1 microns promotes the efficiency of the associative thickeners in paints, especially in the high shear rate range. A similar observation can be made with the vinyl acrylic latexes although the particle size of the latexes tested may not be sufficiently small to generate a response as large as was obtained with the acrylic latexes. The lower molecular weight, more hydrophobic, thickener T-1 yields a much greater increase in thickening efficiency as the particle sizes of the latexes decreased.

REFERENCES

1. Glass, J. E., Eglund-Jongewaard, Susan K., *Polymeric Materials Science and Engineering Proceedings*, 50, 485, National ACS Mtg., St. Louis, 1984.
2. U.S. Patent 4,426,485 (Union Carbide Corporation).
3. Warson, Henry, *Gloss Emulsion Paints*, Second Edition, p. 39-40, Solihull Chemical Services, Solihull England.

Contribution from the Centre de Recherches sur les Macromolécules
6, rue Boussingault, 67083 Strasbourg-Cedex, France

by F. CANDAU

POLYMERIZATION OF ACRYLAMIDE IN INVERSE MICROEMULSION (Y.S. Leong)

The radical polymerization of acrylamide in inverse microemulsions stabilized by Aerosol OT emulsifier and initiated with azobisisobutyronitrile (AIBN) or potassium persulfate ($K_2S_2O_8$) has been investigated. The inverse polyacrylamide latexes formed are clear and highly stable. The structure of the microemulsions prior to polymerization and of the final latexes was studied by elastic and quasi-elastic light scattering, ultracentrifugation, and viscometry experiments. The dimensions of the micellar particles increase with water or acrylamide contents, whereas the size distribution is not affected. Addition of acrylamide to the AOT/water/toluene system leads to an enhancement of the attractive interaction forces between particles, due to the localization of the monomer at the W/O interface.

Owing to a particle growth during the polymerization process the final dispersions are shown to consist of two species of particles in equilibrium: polymer particles ($d \sim 400 \text{ \AA}$) with a narrow size distribution and small AOT micelles ($d \sim 30 \text{ \AA}$). The interparticular interactions are decreased after polymerization as most of the polymer is strongly collapsed within the particles.

A dilatometric technique was used to follow the conversion of monomer at $T=45^\circ\text{C}$. The rate of polymerization is first order with respect to initial monomer concentration in the presence of AIBN, and is 1.5 order with $K_2S_2O_8$. An inverse relationship between molecular weight and emulsifier concentration is found which suggests participation of the emulsifier in the initiation reaction. This is confirmed by the independence of the molecular weight of polyacrylamide on the concentration of the initiators. Aerosol OT evidently plays the major role in generating free radicals, probably by forming bisulfite ion which is known to initiate the polymerization of acrylamide. High values of the rate of polymerization are obtained combined with high molecular weights (up to 10^7).

An important and novel feature of this microemulsion process is that each final latex particle consists of one single molecule of polyacrylamide in a collapsed state. This suggests kinetics which do not follow the Smith and Ewart theory but are characterized by continuous particle nucleation.

MODIFICATION OF POLYACRYLAMIDE MICROLATEXES BY USING A SEEDING PROCEDURE

(C. Holtzscherer)

The polyacrylamide content in the microlatexes prepared by polymerization in microemulsion does not exceed 7% by weight. Higher solid contents are usually desirable in most major applications of water soluble polymers. A seeding procedure is presently applied to our systems in order to increase the polyacrylamide concentration. The first results indicate that, as in conventional emulsion polymerization, the polymerization in the seed particles is accompanied by growth of the latter.

EXTENSION OF THE MICROEMULSION POLYMERIZATION PROCESS

(C. Holtzscherer, Z. Zekhnini)

We are pursuing our study in order to generalize the microemulsion polymerization process to systems containing different monomers and stabilized by another class of surfactants. The synthesis of sodium acrylate-acrylamide copolymers which present interesting properties in tertiary oil recovery processes is also in progress.

RECENT PUBLICATIONS IN PRESS

"Inverse microemulsion polymerization of acrylamide : characterization of the water-in-oil microemulsions and the final microlatexes"

F. Candau, Y.S. Leong, G. Pouyet and S. Candau
J.Coll.int.Sci.

"Kinetic study of the polymerization of acrylamide in inverse microemulsion"

F. Candau, Y.S. Leong and R.M. Fitch
J.Pol.Sci.

COLLOID RESEARCH AT MCMASTER UNIVERSITY - RECENT DEVELOPMENTS

-2-

by

Archie Hamielec

1. McMaster Institute for Polymer Production Technology (MIPPT)
Search for sponsor companies for the Institute (\$15,000 U.S./year for a minimum of 3 years) is continuing. To date, 13 companies have joined and the target number for steady-state is 15 companies. It is now felt that the staff and facilities of MIPPT can adequately service 15 member companies at most.
2. Bulk and solution polymerization of p-methyl styrene
Extensive experimentation on the kinetics of the free radical synthesis of poly(p-methyl styrene) at MIPPT and at the University of Heidelberg has permitted the development of effective process models for batch and continuous reactors for the production of crystal poly(p-methyl styrene). Two publications are in press.
O. Chiantore and A.E. Hamielec, "Thermal Polymerization of p-Methyl Styrene at High Conversions and Temperatures", in press POLYMER (1984).
H. Mutschler, U. Schröder, E. Fahner, K.H. Ebert and A.E. Hamielec, "Free Radical Polymerization of p-Methyl Styrene", in press POLYMER (1984).
3. Bulk copolymerization of p-methyl styrene (PMS) with comonomers styrene, methyl methacrylate and acrylonitrile.
Experimental investigations of the free radical copolymerization of PMS with comonomers styrene and methyl methacrylate have been completed and two papers submitted for publication, and with comonomer acrylonitrile investigation is in progress. Diffusion-controlled termination and propagation have been modelled using the free-volume theory.
4. Aqueous solution polymerization of acrylamide with diffusion-controlled termination.
Aqueous solution polymerizations with high monomer concentrations and up to high conversions have been done. The very high molecular weight macroradicals ($M \sim 10^7$) become entangled at moderate conversions giving diffusion-controlled termination. A publication covering this work follows.
C.J. Kim and A.E. Hamielec, Polymer 25, 845 (1984).
5. Semi-batch emulsion copolymerization of styrene/butadiene.
Work is continuing with no progress to report.

6. Batch emulsion copolymerization of styrene/acrylonitrile.

An experimental study has been completed and a rate model developed. A paper is being prepared for publication.

7. High temperature thermal bulk co and terpolymerization to form very low molecular weight polymers.

An experimental program has been initiated to investigate the kinetics of synthesis of styrene/acrylic acid in the temperature range 250-300°C. Weight-average molecular weights in the range 1000-3000 are expected.

Some of the work reported herein is being done in collaboration with Dr. J. F. MacGregor, McMaster University.

Activities in the field of polymer colloids, Lab. for Physical & Colloid Chemistry of the Agricultural University, Wageningen

1) Dielectric study of polystyrene latices

We measured the dielectric permittivity of a number of emulsifier-free homodisperse polystyrene as a function of frequency ($200-10^6$ Hz) and salt concentration (HCl, KCl, LiCl). To this end, a special cell with variable electrode distance was constructed and a transformer ratio arm bridge method was developed. The latices show very high low-frequency dielectric increments $\Delta\epsilon'$, of over 1000. The Cole-Cole plots are circular but the origin is not on the ϵ' axis, although the homodispersity of the latices is very good (uniformity parameter $a_{32}/a_{10} \approx 1.002$). Publication: M.M. Springer, A. Korteweg, J. Lyklema, J. Electroanal. Chem. 153 (1983) 55.

As a corollary, we developed a theory for such dispersions, profiting from the help of the Russian School Publication: J. Lyklema, S.S. Dukhin, V.N. Shilov, J. Electroanal. Chem. 143 (1983) 1.

At present we are in the process of applying the theory to the experiment. The most important conclusion of the theory, viz., that the relaxation is dominated by the diffuse part of the double layer rather than that due to bound ions has been corroborated. However, for a quantitative description we must assume that the surface charge of the latex, σ_0 , is much higher than the value found conductometrically. Moreover, the lyotropic sequence predicted by the theory is just the opposite of that observed experimentally. These last two points have not yet been solved, perhaps they have to do with some idiosyncracies of the latex surface.

2) Electrokinetic study of polystyrene plugs

We improved and extended a method of measuring simultaneously the streaming current, streaming potential and electric conductivity of plugs of the same latices as used under 1). For a publication on this method, see A.G. van der Put and B.H. Bijsterbosch, J. Colloid Interfac. Sci. 92 (1983) 490.

It appears that variations in the ionic strength cause a maximum in the ζ -potential and that the surface conductivities are much higher than those calculated from the Bikerman equation. In the low frequency range (0.1-1000 Hz) an additional relaxation in the conductivity shows up. Most of these anomalies gradually disappear when tetraalkylammonium ions are adsorbed at the polystyrene surface. The combined evidence seems to indicate that on the surface of the polystyrene particles a "halvy layer" is present, the thickness of which increases upon decreasing the ionic strength.

- 3) Polyoxymethylene (POM) crystals. Modifying a procedure originally proposed by Roe, we prepared batches of stable POM crystals as a model substance for studies in the adsorption of proteins (emphasizing reversibility effects) and polyelectrolytes (with as the main aim the verification of the theory of polyelectrolyte adsorption, developed in our Department). The preparation and characterization of the POM-crystals has recently been published: J. Papenhuijzen and G.J. Fleer, J. Colloid & Interfac. Sci. 100 (1984) 561.

14

15

POLYMER COLLOIDS AT THE UNIVERSITY OF SYDNEY

Reporters D. H. Napper and R. G. Gilbert

20 SEP Recd

1. Periodic Nucleation in Emulsion Polymerization

Wulf Heller many years ago discovered that Liesegang ring type of phenomena can be observed in suitable emulsion polymerization systems. When the monomer is not dispersed as droplets but merely layered on the surface of an unstirred aqueous system, a series of bands of particles, separated by order of 1 mm, may be observed. It is most unlikely that the classical nucleation theory of micellar entry can explain such a curious observation. This simple observation casts considerable doubt upon the validity of micellar entry as the mechanism of latex particle nucleation.

Mr. P. J. Feeney has now developed a theory of periodic nucleation in emulsion polymerization systems based upon coagulative nucleation. This theory suggests that in order for periodic nucleation phenomenon to be observed, the particle production rate must be an increasing function of time for much of the nucleation period. Such a requirement appears to preclude both the micellar entry and homogeneous nucleation mechanisms from being operative in systems displaying Liesegang rings (e.g., SDS/styrene system). Both would give a monotonically decreasing particle production rate. Coagulative nucleation, on the other hand, predicts the requisite increasing particle production rate curve.

2. Termination Rate Constants from Emulsion Polymerization

Relaxation studies for methyl methacrylate seeded emulsion polymerizations allow the termination rate constant to be estimated over a wide range of polymer volume fractions. If chain transfer agent is added to the seed latex particles, it is possible to determine the values of k_t in systems in which only the chain length of the growing chains is varied. This permits the recent theories of the chain length dependence of k_t to be tested. The results obtained to-date are in good agreement with the theories of Sundberg and coworkers. They also confirm quantitatively his theory for residual chain termination, first postulated by Gardon.

1 - Preparation of polystyrene latexes in presence of a sulfonated-type zwitterionic emulsifier (H. ESSADAM)

Kinetics of emulsion polymerization of styrene using zwitterionic emulsifiers (such as ${}^{-}O_3S(CH_2)_nNCOCH_3$ $\begin{matrix} + \\ | \\ N-CH_3 \\ | \\ CH_3 \end{matrix}$ or ${}^{-}O_3S(CH_2)_n$ $\begin{matrix} + \\ | \\ N-CH_2R' \\ | \\ CH_3 \end{matrix}$) prepared by the organic chemistry group (P. Le Perchec, S. Brunel) are currently investigated. Stable and monodisperse latexes were obtained with particle size ranging from 100 to 500 nm.

2 - Batch emulsion copolymerization of acrylonitrile with n-butyl acrylate (L. SABATIER)

Extensive work has been investigated to understand the influence of various parameters on the kinetics: composition of the initial emulsion (monomer composition, monomer/water ratio); nature and amount of surfactant (anionic and nonionic surfactants); initiator concentration and the initiating radical production; the temperature. It is found that the initial comonomer composition plays a major role on the variations of the copolymer composition as well as on the particle morphology. The composition drift is always very low up to 70 % conversion.

3 - Azeotropy in batch emulsion copolymerization of acrylonitrile-styrene J. GUILLOT

Abstract of a paper to be published in the special volume of Die Makromolekulare "Emulsion Copolymers and Copolymerization".

While in solution or bulk radical polymerization, only one azeotropic copolymerization can be observed at the best-if reactivity ratios are both > 1 or < 1 , on the contrary in emulsion batch copolymerization, many more such azeotropic copolymers can be synthesized. Monomer partitioning between droplet, water and particle phases is at the origine of this behaviour of a practical interest, hence water solubility of the monomers plays a determining role. Experimental works confirm the theoretical predictions derived from an

16
pproach, based on partition coefficient and thermodynamics, which allows to compute the optimum monomer/water ratio to be used in order to get, in a batch process, a copolymer of constant composition up to high conversion. The optimum depends upon reactivity ratios, monomer water solubility, monomer feed composition. Examples are given of acrylonitrile, methylacrylate copolymerizations. It appears that it is not any more necessary that they are both greater or lower than unity ; for instance, batch emulsion copolymerizations of acrylonitrile-butylacrylate ($r_{AN} = 0.89 - r_{BuA} = 1.2$) result in homogeneous copolymers at the optimum monomer/water ratio, on the whole range of monomer feed. The approach can also be applied to semi-continuous process to select the best experimental conditions to "tailor" the copolymer.

4 - Inverse emulsion polymerization of acrylamide

Abstract of two papers to be submitted to J. Polymer Science.

I - Mechanistic aspects of the homopolymerization of acrylamide- C. GRAILLAT - C. PICHOT - A. GUYOT

The inverse emulsion polymerization of aqueous solution of acrylamide in toluene has been studied at 40°C, using a blend of surfactants as emulsifying system and oil soluble azo initiators. The azo compound partition between the phases has been measured as well as the effect of their nature and amount on the polymerization kinetics. The influence of other parameters such as the nature and the amount of the emulsifier system, the stirring rate and the presence of oil soluble inhibitor has been also investigated. The particle size analysis through electron microscopy or dynamic light scattering methods showed the presence of two families of particles in the initial monomer emulsion and in the inverse latex : the first one is a very large number of tiny particles (around 20 nm) and the second one consists of larger particles (80-400 nm) highly polydispersed. The average size of these large particles undergoes a sharp decrease at a conversion depending upon the stirring rate which might result from an equilibrium

17
between coalescence and shear dispersion. It is also suggested that the aqueous phase is probably not homogeneous (polymer particles with different conversion levels are present).

Concerning the initiator process, the very low solubility of the azo compound in the aqueous solution, together with the effect of the stirring rate and of the presence of an oil soluble inhibitor on the polymerization kinetics, as well as the high surface area of the tiny particles, lead to conclude that most of the initiation originates from the capture of radicals produced in the oil phase or in the interfacial layer.

II - Synthesis and characterization of copolymers with methacrylic acid

V. GLUKHIKH - C. GRAILLAT - C. PICHOT

Abstract emulsion copolymerization studies of acrylamide (Am) with methacrylic acid (MAA) are reported. Aqueous monomer solutions were emulsified in toluene with a blend of two surfactants (sorbitan sesquioleate - C₁₈ terminated acrylamid oligomers). Polymerization kinetics in presence of an oil soluble initiator (AIBN) were determined at 40°C as function of methacrylic acid content and aqueous phase pH. Polymerization rates were found to be faster at basic pH than at acidic pH, which appeared to be related to the actual concentration of methacrylic acid in aqueous phase. Monomer reactivity ratios have been derived as $r_{AM} = 0.58 \pm 0.02$ and $r_{MAA} = 4.40 \pm 0.10$ at pH = 4 and $r_{Am} = 0.56 \pm 0.005$ and $r_{MAA} = 0.15 \pm 0.03$ at pH = 10. These differences were found to have an effect on the molecular characteristics of the copolymer. Initial emulsion and final inverse latexes displayed the same broad size distribution ; under basic pH the particle size is relatively insensitive to the ionic comonomer concentration. Poor latex stability is characteristic of copolymer latexes prepared under acidic conditions. Based on these experimental results, some aspects of the polymerization mechanism are discussed.

Submitted by I. Piirma

18
-2 OCT Recd

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September 1984

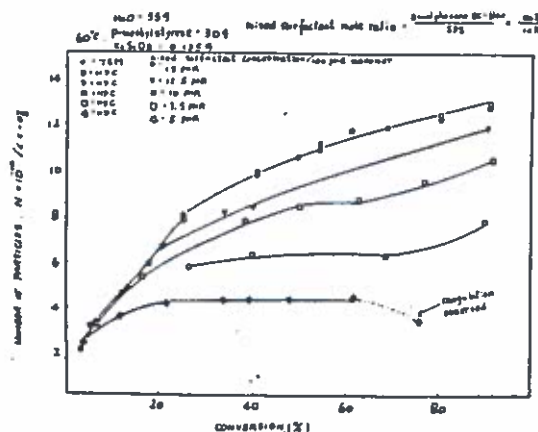
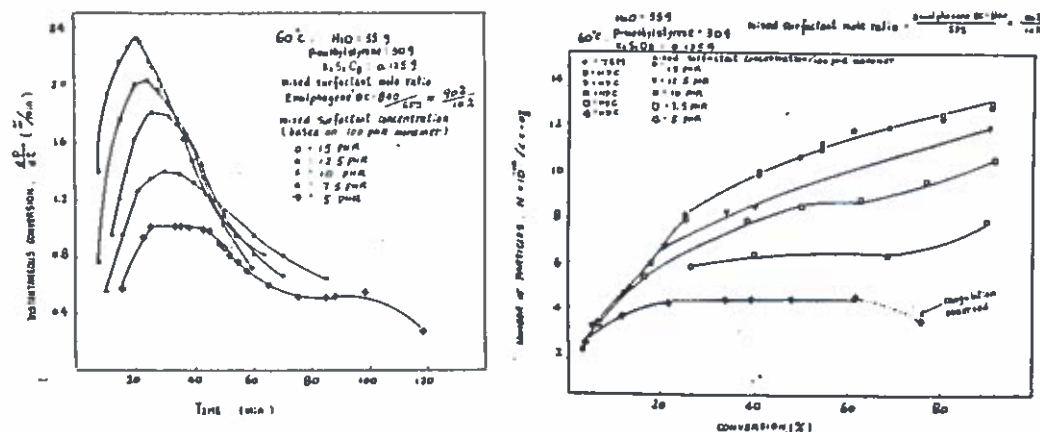
114 SEP Recd

1. Emulsion polymerization of p-methylstyrene. Work carried out by Shang Lee

The polymerizations of p-methylstyrene were carried out at 60°C using three different surfactant systems, sodium dodecyl sulfate (SDS), tridecyloxy poly(ethyleneoxy) ethanol (Emulphogene BC 840), and a mixture of the two. As expected, the SDS stabilized polymerizations showed constant rate regions in the rate curves between 27% and 50% conversion. This constancy in rate was further proven to be due to constancy in number of particles in that region.

Two constant rate regions and bimodal particle size distributions appeared in the reactions with BC 840. This unusual polymerization behavior has been observed with other monomers, (a paper published on this subject in Polymer Bulletin 11, 497 (1984) is available upon request).

The results with a mixture of the two surfactants in a ratio of 90/10 BC 840/SDS are shown in Figures 1 and 2. It is obvious that with increasing total concentration of surfactant the constancy of both the rate of polymerization and the number of particles disappears completely.



Formation of polymer particles from monomer droplets in emulsion polymerization has often been neglected when compared with micelle and homogeneous nucleation. The reasons most often cited for the lack of significant droplet nucleation are the small number of droplets compared to the polymer particles formed and the distribution of emulsifier within the reacting mixture. The monomer droplets produced by moderate agitation of a conventional recipe will be in the range of 2 to 20 μ m in diameter. The total surface area associated with these droplets will normally accommodate only a fraction of the added emulsifier; leaving the remainder dissolved in the continuous phase and/or in the form of micelles. In addition, continuum transport theory predicts that the small micelles and dissolved emulsifier will be more effective in capturing water-borne free radicals; thus leaving an even smaller fraction to diffuse into the large monomer droplets.

Formation of polymer particles from monomer droplets has been reported by a number of workers. Ugelstad, El-Aasser and Vanderhoff (1) used mixed emulsifier systems to generate emulsions comprised of small monomer droplets. Their work clearly demonstrated that droplet nucleation could effectively compete with other mechanisms when the total surface area of the droplets became large enough to adsorb a large fraction of the emulsifier. Durbin et al. (2) carried out a series of bottle polymerizations with conventional styrene recipes. They reported that the number of large particles produced (presumably from monomer droplets) increased with the intensity of the mixing process prior to charging the pre-emulsion to the reaction bottles. In no case, however, was the weight ratio of large to small particles greater than 10. Thus, the number of small particles was much greater (by a factor of about 10 to 1) than the large particles measured.

Hansen and Ugelstad (3,4) developed quantitative models for comparing the relative importance of micelle, homogeneous and droplet nucleation. They presented the results of model predictions to illustrate the increase in droplet nucleation expected when smaller droplets were produced. They also carried out experiments with a fixed recipe but various degrees of monomer pre-emulsification. These results also illustrated the potential importance of monomer droplet initiation.

The purpose of this brief paper is to demonstrate, via the use of approximate calculations, that every monomer droplet in the reaction mixture during interval 1 (the particle nucleation period) will, in the absence of flocculation, become a polymer particle. The

calculations presented will provide estimates of radical diffusion into the droplets and show that these droplets are likely to produce larger particles than those formed by other nucleation mechanisms. A single example of styrene emulsion polymerization will be analyzed to examine these phenomena.

SIMULATION EXAMPLE

The computations presented will be based on the recipe and reaction parameters listed below.

Continuous water phase	= 1 dm ³ H ₂ O
Monomer charge	= 0.3 dm ³ M
Emulsifier concentration	= 0.02 gmoles/dm ³ H ₂ O
Radical generation rate	= 10 ¹⁶ radicals/dm ³ H ₂ O-sec
Monomer/polymer volume ratio in the particle	= 2:1
Adsorption area per emulsifier molecule	= 50 Å ²
Polymerization propagation rate constant	= 300 dm ³ /mole-sec
Monomer droplet radius	= 5 μm
Termination rate constant	= 115 × 10 ⁶ dm ³ /mole-sec

EXAMPLE CALCULATION RESULTS

1. Emulsifier Distribution

Total potential adsorption area of the charged emulsifier = $a_s[S]N_A = 6.02 \times 10^{21}$ nm²/dm³ H₂O. The 0.3 dm³ of monomer is dispersed in droplets of radius 5 μm. This yields 5.73×10^{11} droplets per dm³ of H₂O with a total surface area of 1.8×10^{20} nm²/dm³ H₂O which represents 3% of the emulsifier charged.

2. Free Radical Distribution

Two models have been used for the calculation of free radical transport rates from the aqueous phase into micelles, particles and droplets. The "lower limit" particle nucleation model of Smith and Ewart (5) is based on the assumption of distribution in direct proportion to interfacial area. A theoretical basis for this model was presented by Gardon (6). This model predicts, for the present example, that 3% of the free radicals will enter the droplets. The radical flux per droplet is given by:

$$\frac{0.03 \rho_i}{N_0} = 524 \text{ radicals/droplet-sec}$$

The continuum diffusion model is based on molecular transport theory. This model predicts that the rate of absorption of radicals will be proportional to radius (in contrast to r² of the area model). Hansen and Ugelstad (4) have developed a particle nucleation theory based on continuum

diffusion concepts. They computed the probability of a given radical entering a 5 μm radius droplet, for a recipe very similar to the present example, to be 0.019. This model yields the following value for radical flux to the droplets.

$$\frac{0.019 \rho_i}{N_0} = 332 \frac{\text{radicals}}{\text{droplet-sec}}$$

3. Computation of S-E Particle Nucleation:

The above computations demonstrate that all the monomer droplets are likely to absorb a large number of radicals and, therefore, form polymer particles. The Smith-Ewart nucleation models are used to predict the number of particles formed via aqueous phase mechanisms for comparison with droplet nucleation. The first step in this particle number computation is to estimate the duration of interval I. This, assuming 100% capture efficiency, is given by:

$$t^* = 0.4 \frac{(a_s[S]N_A)^{0.6}}{\rho_i^{0.6} \mu^{0.4}} = 113 \text{ sec.}$$

An estimate of the number of particles formed yields,

$$N = 0.97 \rho_i t^* = 1.10 \times 10^{18} \text{ particles/dm}^3 \text{ H}_2\text{O}$$

The ratio of particles nucleated in the aqueous phase (micelles) to those formed from monomer droplets is

$$\frac{N}{N_D} = \frac{1.10 \times 10^{18}}{5.73 \times 10^{11}} = 1.92 \times 10^6$$

Clearly, the number of particles formed from droplets is a very small fraction of the total particle population.

4. Volume of Monomer and Polymer at the End of Interval I:

The total calculated particle volume at t* is given by

$$V(t^*) = \rho_i \mu t^* / 2 = 0.02235 \text{ dm}^3/\text{dm}^3 \text{ H}_2\text{O}$$

$$\text{Volume of polymer in particles} = 0.00745 \text{ dm}^3/\text{dm}^3 \text{ H}_2\text{O}$$

$$\text{Percent of original monomer in the particles} = 0.02235/0.3 \times 100 = 7.45\%$$

$$\text{Percent of original monomer converted} = 0.02235/(0.3)(3) \times 100 = 2.48\%$$

The polymerization rate within individual monomer droplets is given by:

$$R_p V_D = k_p [M]_D [R\cdot] V_D$$

where $[R\cdot] \cong \sqrt{J_i/k_t V_D}$, J_i is the radical transport rate into the particles (moles/particle-sec) and $[M]_D \cong 9 \text{ moles dm}^{-3}$, is the monomer concentration in the droplets.

$$\begin{aligned} R_p V_D \text{ (CONSTANT FLUX MODEL)} &= 0.537 \times 10^{-17} \text{ moles/sec} \\ R_p V_D \text{ (CONTINUUM MODEL)} &= 0.424 \times 10^{-17} \text{ moles/sec} \end{aligned}$$

Polymer produced per droplet in Interval 1 is:

$$P \text{ (CONSTANT FLUX MODEL)} = (0.537 \times 10^{-17}) (113)(104) = 0.632 \times 10^{-13} \text{ grams/droplet}$$

$$\text{Total Polymer in Droplets (CFM)} = 0.0362 \text{ gms}$$

$$P \text{ (CONTINUUM MODEL)} = 0.5 \times 10^{-13} \text{ gm/droplet}$$

$$\text{Total Polymer in Droplet (CM)} = 0.0286 \text{ gms}$$

$$\% \text{ of original monomer in droplets} = 100 - 7.45 = 92.55\%$$

$$\% \text{ of original monomer as polymer in droplets}$$

$$\text{(Constant Flux Model)} = 0.0127\%$$

$$\text{(Continuum Model)} = 0.010\%$$

Ratio of the polymer per monomer droplet to the polymer per particle is given by:

$$R = \frac{(0.632 \times 10^{-13}) / (0.95 \times 10^3)}{(0.00745) / (1.10 \times 10^{18})} = 9820 \text{ (CONSTANT FLUX MODEL)}$$

$$R = 7945 \text{ (CONTINUUM MODEL)}$$

5. Conclusions:

Monomer droplets will be a source of polymer particle formation even in systems in which the monomer is not finely dispersed. When the monomer droplets are large at the beginning of Interval 1 they will capture a large number of free radicals during the nucleation period. At the end of Interval 1 the average monomer drop will contain substantially more polymer than the average polymer particle. The number of particles, however, will be much greater than the number of droplets and the particles (in total) will contain a very large fraction of polymer.

During Interval 2 the droplets will continue to shrink as monomer is transported to the major polymerization sites in the polymer particles. This shrinkage will stop when the polymer concentration in the monomer droplets approaches that in the monomer-swollen particles. At this point the particles formed from droplets will be larger than those formed from micelles.

If the monomer is dispersed in smaller droplets more particles will be formed via the droplet initiation mechanisms. These particles will, however, be smaller than those formed from the 10 μm diameter droplets used for this illustration.

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CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

Submitted by F. L. Saunders, Dow Chemical Co., Midland, MI - U.S.A.

- 2 OCT Recd

KINETICS OF QUATERNIZATION OF VINYL BENZYL CHLORIDE COPOLYMER LATEXES

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The kinetics of the reaction of tertiary amines with vinyl benzyl chloride (VBC) copolymer latexes have been investigated. In this reaction, benzyl chloride groups on the latex particles are converted in high yield to quaternary ammonium groups. With proper design of the starting latex, the process can be used to make latexes stabilized by high levels of bound cations (1, 2).

Latexes stabilized by strong acid or base groups, chemically attached to the particles, are of value as model colloids (3). However, latexes of this type are difficult to prepare by emulsion copolymerization of ionic and nonionic monomers because of large differences in the monomer solubilities in H₂O. Copolymerizations in aqueous media generally lead to a mixture of water-soluble ionic polymer and latex particles containing relatively low ionic content. Separation of the mixture in order to obtain a "clean" latex can be very difficult (4).

Latexes stabilized by bound strong acid or base groups are easily obtained by an indirect route (5, 6). A functional copolymer latex is first prepared from nonionic monomers of similar low water solubility by emulsion copolymerization. The functional latex can then be converted to the desired ionic derivative by reactions that do not destabilize the latex.

VBC has been effectively utilized in this process (6). It is easily copolymerized by emulsion polymerization techniques and the latexes can be converted directly to a variety of derivatives under mild reaction conditions. A large number of ion-forming reactions are known for VBC (7, 8). Cation-forming reactions are most commonly used, but VBC latexes have also been converted to sulfonic acid derivatives (5, 9).

This study shows that quaternary ammonium functional latexes are easily prepared by reaction of VBC copolymer latexes with tertiary amines. The course of the reaction is determined by amine reactivity rather than amine water solubility. The kinetics are complicated by a severe rate retardation effect developing at conversions in excess of 30%. The limiting conversion appears to be associated with the maximum charge density that can be tolerated on a hydrophobic particle. A surface reaction model is invoked to explain the results.

The study leads to some general observations about the conditions needed to produce surface limited reactions on latex particles.

1. If the latex particle T_g is lower than the temperature of the quaternization reaction, the reaction will penetrate into the particle at a rate dependent on the VBC content in the copolymer, the nucleophilicity of the amine and the proximity of the chloromethyl groups to the latex particle surface.
2. If the particle T_g is higher than the quaternization reaction temperature, the reaction will penetrate into the particle only if the latex particle is plasticized in the process.

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NOTE: The material covered in this report was presented in part at the International Symposium on Emulsion Copolymers and Copolymerization, Lyon, France (March, 1984). To be published in Makromolekulare Chemie.

STUDY OF WETTING OF SOLID SUBSTRATES BY POLYMERIC SURFACTANTS

D. M. Pickelman, D. L. Schmidt, and R. A. Wessling

To be presented at Polymeric Surfactant Symposium at the
Spring, 1985 ACS Meeting in Miami BeachSUMMARY

Copolymers of methyl methacrylate/vinylbenzyl chloride have been prepared using a solution polymerization process and characterized on the basis of their surface activity as water-soluble onium derivatives (1). Cationic polymeric surfactants (CPS) were prepared using an emulsion polymerization process and studied in the same manner. (2) Subsequent attention was focused upon finding CPS compositions which could be most successful in wetting solid substrates. Spreading potential of aqueous surfactant solutions was obtained through surface tension and contact angle measurements. Comparisons were made with conventional low molecular weight soaps. A technique was established by which surfactant solutions could be ranked in terms of wettability. Four substrates were studied and found to wet in the following order: Glass > Mylar®; Polystyrene > Polyethylene. Unlike the lower-energy substrates, it was difficult to obtain accurate measurements of contact angle on glass because of its hydrophilic character. Hydrophobic polyethylene is very difficult to wet with aqueous surfactant solutions, however, methylmethacrylate/vinylbenzylsulfonium chloride copolymers over a broad charge density range wet better than conventional cationic low molecular weight soaps.

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LATEX FACTORS AFFECTING BLADE COATER RUNNABILITY*

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Earlier work has shown that both latex particle-size and vinyl acid type, level and position play a major role in the blade runnability of the styrene (S) butadiene (B) latexes which are used in coating colors.

Recent investigations have revealed the significance of latex particle-size distribution on the high shear rheology blade coater runnability of the corresponding coating colors. In particular the blade runnability of high solids coating colors can be improved by using a carboxylated S/B latex with a bimodal rather than a mono-disperse particle-size distribution. This improvement results in a superior coat weight application control as a function of inverted blade tube pressures and less tendency for blade coater runnability defects at a higher coating color solids level. High shear coating color rheology determinations also have shown that the bimodal as compared to a polydisperse latex particle-size distribution is superior. The details of the above findings will be discussed.

*Presented at TAPPI Blade Coating Seminar, Sept. 24-26, 1984; Portland, ME.

THE INFLUENCE OF LATEXES ON ROTOGRAVURE PRINTABILITY *

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A B S T R A C T

In addition to their traditional binding role, latexes can influence the rotogravure printability of coated papers in a variety of ways. Being soft and compressible, they can influence the compressibility of coated papers and thus improve the contact between the surface of coated papers and the printing plate at the nip. Being solvent-sensitive, they can help reproducing halftone dots sharply and accurately by preventing ink from spreading. More importantly, they can influence the colloidal and rheological properties of coating colors by adjusting their interactions with pigment particles and thus control the immobilization of coating colors, which is largely responsible for improved coating holdout and rotogravure printability. This paper will describe in more detail how latexes can improve the rotogravure printability.

*Presented at the Panel Discussion on Rotogravure Printability Improvement through Coating Immobilization and Pigment Selection for the 1984 TAPPI Coating Conference.

28 SEP Recd

The Effect of Polymer Molecular Weight
Upon Reaction Rates in Emulsion Polymerization

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INTRODUCTION

It has been clear for some time that the Tromsdorff gel effect causes not only accelerating reaction rates but also simultaneous and dramatic increases in polymer molecular weight. Balke and Hamielec (1) have presented a wide range of data which clearly show these effects in the bulk polymerization of methyl methacrylate (MMA). More recently researchers such as Marten and Hamielec (2) and Son and Sundberg (3) have offered descriptions of termination rate constants which are chain length dependent. While all of this work has been applied to bulk polymerization, there have been no detailed studies of the inter-relationship of the reaction rate and polymer molecular weight in latex systems. It is also of interest to note that the use of some chain transfer agents used to substantially change the molecular weight of emulsion polymers have also appeared to have caused reductions in the reaction rate. Occasionally these chain transfer agents are then labeled as non-ideal by producing free radical groups with less inherent reactivity than those of the monomer and polymer. With this as background, the present study was undertaken to provide some experimental evidence of this effect in emulsion polymerization. The system chosen for study was that of MMA because it has such a strong gel effect which would offer a good chance to observe such effects. The technique used was to prepare several seed latices of widely different molecular weight (by using chain transfer agents in the base latex formulation) but at the same particle size, and then to observe the polymerization rate behavior of subsequently added monomer under the exact same reaction conditions.

2

The basic premise of this study was that the termination rate constant is chain length dependent and that higher molecular weight polymer chains entangle more extensively than shorter ones, thereby leading to lower values of k_t . In turn, the lower value of k_t should lead to higher radical populations in the particles (i.e. higher values of \bar{n}) and thus to higher reaction rates. However, it must also be recognized that if the molecular weight is changed by adding a chain transfer agent, it is likely that desorption of short, chain transferred radicals will increase and lower \bar{n} . This result has recently been reported for small particle sized latices (ca. 600-700 Å) by Lee and Poehlein (4). In order to avoid this simultaneous effect, the present study made use of larger particle sized seed latices (1100-2000 Å) whose surface to volume ratio is such that radical desorption has no effect upon the reaction kinetics. This would place these systems in the area of Ugelstad's (5) \bar{n} vs. α' plot (for negligible water phase radical termination) in which α' is greater than about 0.10. It is acknowledged that if water phase radical termination is very significant, then one would have to consider both radical desorption and molecular weight effects.

EXPERIMENTAL

Seed latices were prepared by using standard batch and semi-continuous feed reaction techniques. Sodium lauryl sulfate was used as the only surfactant and potassium persulfate was used as the initiator. At the end of the seed latex preparation (carried out at 50°C), the batch was heated to 95°C for about an hour to deplete the unused initiator. The seed latices were produced at the same particle size but at differing polymer molecular weight by the use of tertiary dodecyl mercaptan (t-dm) as a chain transfer agent. These seed latices were subsequently swollen with fresh MMA monomer to the extent of 150 parts per hundred parts polymer. The swelling was carried out under batch conditions with moderate agitation for periods of time long enough to prevent the formation of a

separate oil layer when the latex was left in a quiescent state for an hour or so. These latices were then cooled from room temperature to 5°C to prevent any polymerization from occurring when the initiator solution was added (this also at 5°C). Latices prepared in this fashion were added to tubular glass reactors (5 mm O.D. and 3 mm I.D.), sealed under vacuum and plunged into a water bath at 50°C to carry out the reaction. Each tube contained enough latex to provide a solids level determination (for measuring conversion level) and to yield polymer for molecular weight determination via dilute solution viscometry. The use of these tubular reactors ensured excellent temperature control even for very rapid reaction rates.

The experimental space studied may be best viewed in matrix form. The seed latices were made at three different polymer molecular weights (High - 5.8 million, Medium - 1.2 million, and Low - 0.4 million) and the polymer subsequently formed also produced at these three molecular weights. This gave a possibility of nine separate experiments and are designated below by the notation;

High M.W. polymer formed in High M.W. seed; H/H
 Low M.W. " " " " " " ; L/H
 etc.

The experimental matrix appears as

H/H	H/M	H/L
M/H	M/M	M/L
L/H	L/M	L/L

with columns representing experiments utilizing the same seed latices in the presence of which polymer of varying molecular weight is produced, and rows representing different seed latices in the presence of which polymer of the same molecular weight is formed. All of these reactions were carried out under the same exact conditions of solids and initiator levels, and temperature (50°C).

One unfortunate aspect of the use of t-dm was that it could not be stripped out of the M and L seed latices after their preparation. This prevented the formation of high molecular polymer in the presence of a low molecular weight seed. Thus the actual experimental matrix was

H/H		
M/H	M/M	
L/H	L/M	L/L

RESULTS AND DISCUSSION

Matrix experiments were carried out for seed particle sizes at 1100 Å and 2000 Å. The swollen particle diameters were roughly 26% larger than the seed particles and together with the other experimental parameters yielded values of α' of 1.0 or greater at the beginning of the reaction. Due to the presence of the gel effect in each experiment the value of α' increased with conversion and thus assured that radical desorption need not be considered in assessing the reaction kinetics.

The reproducibility of the experimental data can be assessed from Figure 1 which shows duplicate runs of the H/H experiment at the 1100 Å seed particle size. Since some of the differences in conversion profiles for the 1100 Å seed latices may not be too great, this level of reproducibility is important.

In general terms it was anticipated that the reaction rates would be slower as one moves down a column of the experimental matrix and as one moves to the right along a row of the matrix. Thus the H/H run should be the fastest and the L/L run should be the slowest. Figure 2 shows the results for column 1 using the high molecular weight seed latex producing post-formed polymer at high, medium and low molecular weights. The lower molecular weights were produced by adding t-dm to the monomer used to swell the H seed latex. As expected the

rates decreased as the post-formed polymer molecular weights decreased. Although polymer fractionation was not performed prior to measurement of molecular weight, the combined viscosity average molecular weight of the resultant L/H emulsion polymer was 2.1 million vs. the 5.8 million of the H seed polymer.

The bottom row experiments represented the formation of equivalent molecular weight post-formed polymer in the presence of various molecular weight seed polymer. In these experiments the same level of t_{dm} was used in each. The conversion profiles are displayed in Figure 3 and again show that lower rates are associated with lower molecular weights, although the differences in the row experiments are more subtle than those in the column experiments.

The combined effect of varying seed molecular weight and post-formed molecular weight can be seen from the diagonal set of experiments H/H, M/M and L/L. Here the post-formed and pre-formed molecular weights were measured to be the same. Figure 4 displays the conversion profiles and shows a very significant dependency of rate upon molecular weight. In another diagonal set of experiments, M/M and L/H, one can see the combined effect of pre-formed and post-formed molecular weight in a different way. Here the respective changes between pre-formed and post-formed polymer vary in opposite directions. One might then expect some sort of compensating effect between the two changes. Figure 5 shows a rather fortuitous situation in which these competing effects appear to completely counteract one another.

Larger sized seed latices were also made in order to increase the difference in the rates seen as molecular weight was changed in the smaller sized latices. Here, an H seed was produced at 2000 Å and 5.7 million molecular weight and a L seed was produced at the same particle size but at 0.34 million molecular weight. The resultant conversion profiles are shown in Figure 6 where the difference in the two curves is quite dramatic. Another interesting way to view these data is

to compare the conversion profiles for two latices of the same molecular weight but at different particle sizes (where rate differences are clearly expected) and simultaneously for two latices at the same particle size but at significantly different molecular weight. Such a comparison is presented in Figure 7 where H/H runs at 1100 Å and 2000 Å are compared to H/H and L/L runs at 2000 Å. Obviously the effect of polymer molecular weight can be nearly as significant as latex particle size.

CONCLUDING REMARKS

The data presented in this study indicate that there appears to be no doubt that the polymer chain length environment can substantially affect emulsion polymerization kinetics. In seed latex polymerization of a single homopolymer it is suggested that the chain length of the seed polymer and that of the developing post-formed polymer exert independent effects which combine to give a unique overall result. Due to these observations it appears that one should be careful not to necessarily conclude that rate reductions seen when chain transfer agent is added to an otherwise high molecular weight system are caused by "slow radicals" resulting from chain transfer fragments.

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LIST OF FIGURES

- | | |
|----------|--|
| Figure 1 | Reproducibility of rate data |
| Figure 2 | Conversion profiles for column 1 experiments, H/H, M/M and L/H |
| Figure 3 | Conversion profiles for last row experiments, L/H, L/M and L/L |
| Figure 4 | Conversion profiles for main diagonal experiments, H/H, M/M and L/L |
| Figure 5 | Conversion profiles for cross-diagonal experiments, L/H and M/M |
| Figure 6 | Conversion profiles for large particle sized latices, H/H and L/L |
| Figure 7 | Conversion profiles for latices at varying particle size and molecular weight. |

FIGURE 1

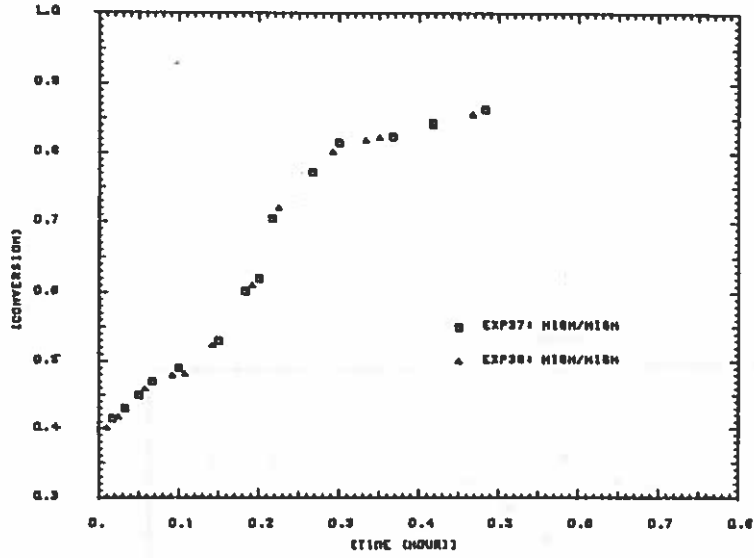


FIGURE 2

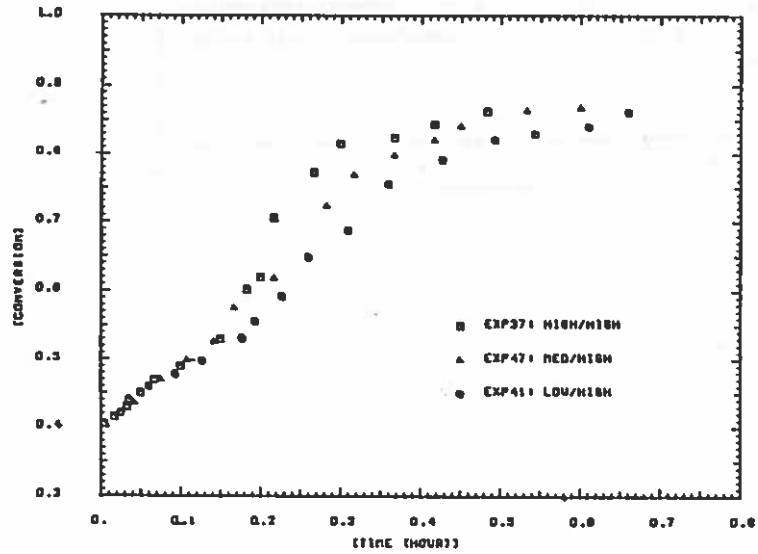


FIGURE 3

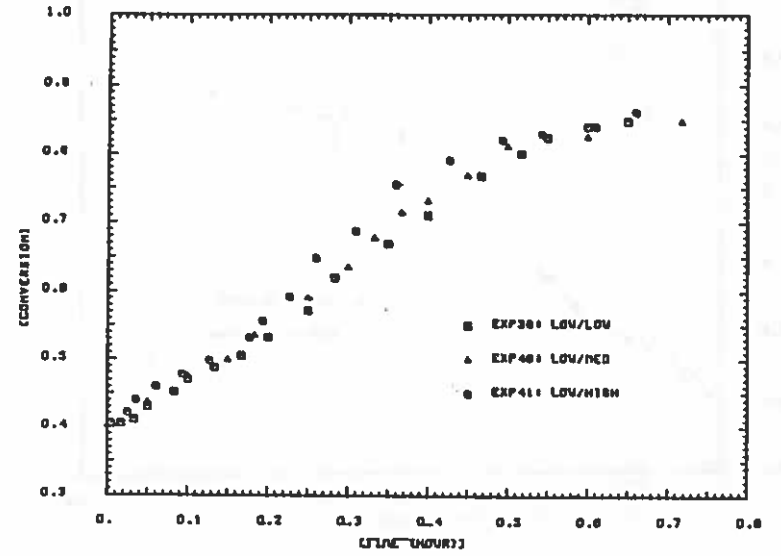


FIGURE 4

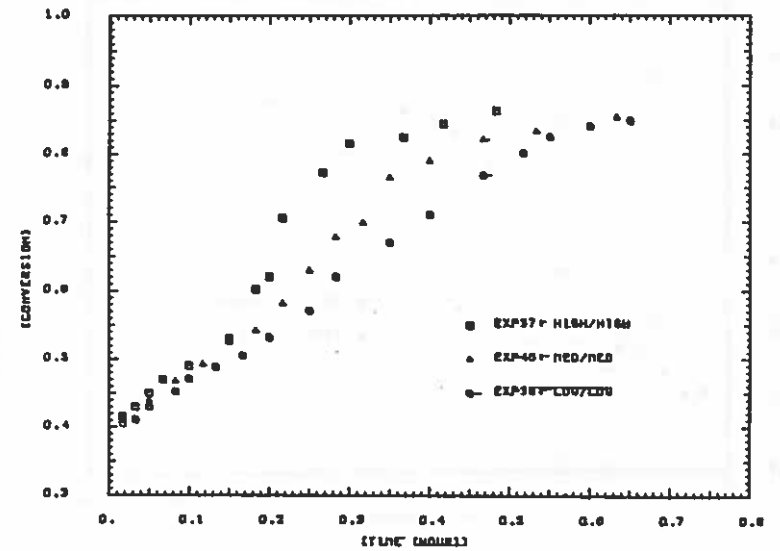


FIGURE 5

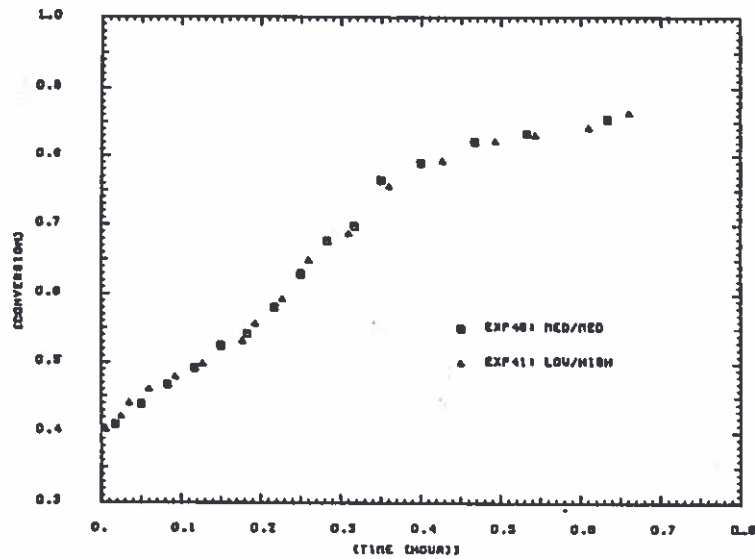


FIGURE 6

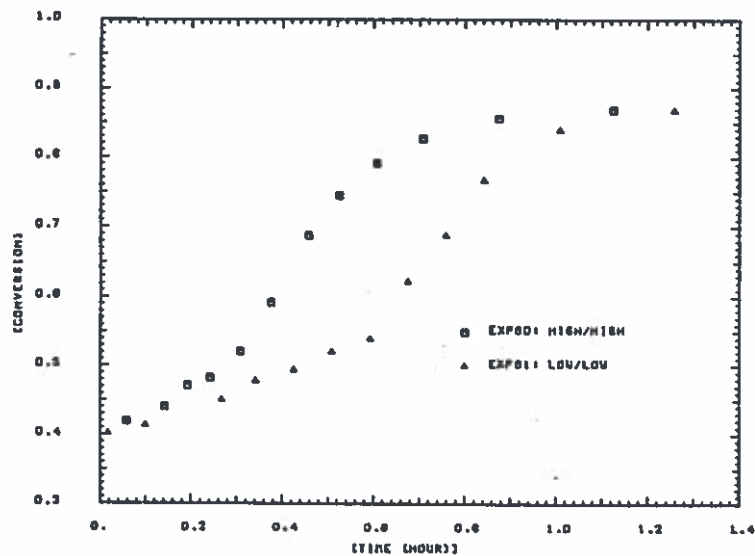
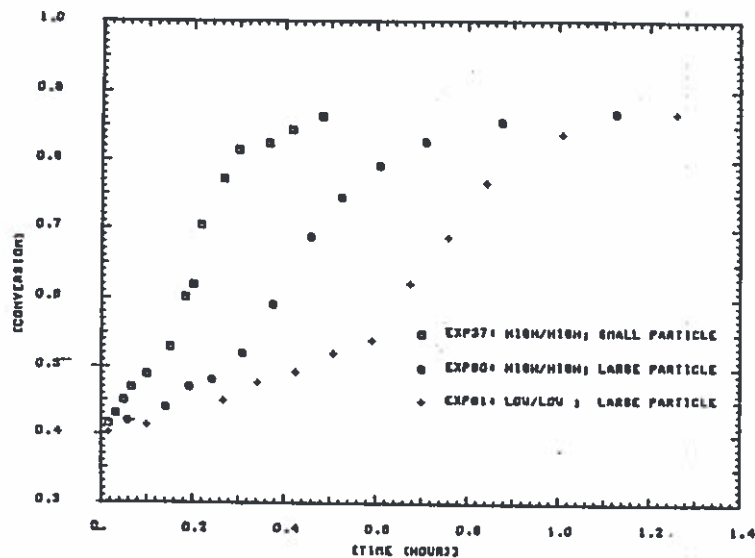


FIGURE 7



Work at Department of Industrial Chemistry, University of
Trondheim, and at SINTEF.

John Ugelstad.

39
28 SEP Recd

1. Magnetic particles.

The work at the group in Trondheim has lately been concentrated on the preparation of magnetic particles. Since the publication of the results in London on the application of our magnetic particles for clinical use in removal of neuroblastoma cells from bone marrow we have got requests from a very large number of institutes and hospitals around the world for these particles. Clinical treatment of children with neuroblastoma with these particles have already for some time also been carried out in Lyon and several other hospitals at different places are building up the magnetic equipment necessary for the procedure.

The particles used for neuroblastoma have been our 3 μm porous magnetic particles with a relatively large surface. Beside having the disadvantage that they use a lot of antibody of which a large part is ineffective as it does not take place in the binding to the cells it has turned out that the particles also show a relatively high nonspecific binding. That means that they will also tend to adhere to some extent to other normal cells which do not possess antigen corresponding to the antibody adsorbed on the particles. We have ascribed these disadvantages to the high porosity of the particles.

Quite recently we have therefore developed particles which has the same monodispersity and the same magnetic properties, but with a smooth surface. The one we have developed to the point that we can deliver them commercially are particles with a hydrophobic surface. This means that we have to bind the antibody by physical adsorption. However, the nature of the surface and the fact that the surface is very low has led to that they when covered with antibody shows an extreme selectivity for the cells they are meant to interact with.

Investigation with these new particles are now carried out at a number of places and their ability selectively to remove T-lymphocytes from bone marrow are very promising. This opens up the possibility for nonautologous bone marrow transplantation.

We have also made compact magnetic particles for covalent coupling including particles with -OH, $-\text{CH}^{\text{O}}-\text{CH}_2$ and -NCO groups. These particles we expect to be the best particles because we do not risk any leakage of antibody from the particles and because the activity of chemically bound antibody seem to be higher than for physical bound antibody.

A special particle we are working with is a magnetic particle with a relatively thick shell of polymer with functional groups around it. We cooperate in this research with the European Molecular Biology Laboratories in Heidelberg, Germany, who have found magnetic particles especially suitable for isolation and studies of organelles and viruses. The method they have developed necessitates magnetic particles which are monodisperse both as regards size and content of magnetite. Our patent application on preparation of magnetic particles has now become available and as you may have seen the method is extremely simple, and involves preparation of the magnetic iron oxides in situ.

I have believed that we by our process get magnetite, Fe_3O_4 . After having lectured at MIT last month I am not quite sure. It may be that what we finally get is $\gamma\text{Fe}_2\text{O}_3$. We will cooperate with MIT about this problem and also in construction of the most suitable magnetic equipment.

2. Transport of material between particles (droplets).

In several papers we have written the equilibrium equation for transport and distribution of a compound (1) between a (b) phase and an (a) phase by

$$\Delta\bar{G}_{1a}^P + 2\bar{V}_{1a}\gamma_a/r_a = \Delta\bar{G}_{1b}^P + 2\bar{V}_{1b}\gamma_b/r_b$$

where $\Delta\bar{G}_1^P$ stand for partial molare free energy in the case that we have $r = \infty$ (plane surface).

As we have pointed out in several papers the distribution of (1) between the phases will depend upon both the composition of the two phases and the size of the particles (droplets) of the two phases.

In the "Piirma book" we made the obvious point that if we par example has pure 1 in the (b) phase, we would in principle be able to swell any particle infinitely provided we had a sufficient low value of r_b . Also we pointed out the effect of r_b on the rate of transport from (b) to (a), again stressing that also in this expression the effect of an increase in activity due to a reduction of r_b comes into play.

We also demonstrated the effect of subdivision of phase (b) experimentally both on the rate of swelling and the degree of swelling of the (a) particles. In our patent on the two step swelling of polymer particles from 1977 we described in detail the use of fine dispersions of the swelling compounds for achieving an effective swelling and also especially included this in our patent claims. From some recent publications we have got the impression that these facts seem to have been overlooked.

Most often if one homogenize monomer (phase b) to get a more effective swelling, one will find that one during the swelling process experience that the monomer droplets instead of diminishing in size becomes larger apparantly due to interdroplet transport. We have shown previously that the presence of a small amount of a Y compound (relatively low molecular weight water insoluble compound) in the monomer during homogenization will prevent such a degradation. In this case we get an interesting system. If we consider a system consisting of an (a) phase with a polymer P and a Y compound and a (b) phase consisting of a (1) compound and an Y compound which may be the same or different from that in the (a) phase we will have a transport of (1) from (b) to (a) untill the equilibrium

$$\ln \phi_a + (1-m_{1Y})\phi_{Yb} + \phi_{Pa} + \phi_{Ya}^2 x_{1Y} + \phi_P^2 x_{1P} + \phi_{Ya} \phi_{Pa} (x_{1Y} + x_{1P} - x_{YP} m_{1Y})$$

$$+ 2\bar{v}_{1a} \gamma_a / r_a RT = \ln \phi_b + (1-m_{1Y})\phi_{Yb} + \phi_{Yb}^2 x_{1Y} + 2\bar{v}_{1b} \gamma_b / r_b RT$$

Obviously the activity of (1) in the (b) phase and thereby the swelling of the (a) phase in this case will depend upon the two counteracting effects in the (b) phase, the presence of Y which will decrease the activity and the increase in activity due to the

low value of r_b which may be obtained because of the presence of a Y compound in the (b) phase. It turns out that one in this case may obtain so small droplets of (b) that the activity will be considerably higher than for pure (1) in bulk despite the decreasing effect of Y on the activity. Also such a system may under given conditions ("infinite" amount of (b) with sufficiently high activity of (1) bring about an "infinite" swelling of phase (a)).

With a limited amount of the (b) phase the size of the (b) droplet will decrease due to the transport of (1) from (b) to (a). This will in principle tend to increase the activity of (1) in the (b) phase. This effect will usually be more than counteracted by the decrease in activity due to the increase in concentration of Y in the (b) droplets as the compound (1) is transported from (b) to (a).

Even more interesting for a theoretical study are the systems El-Asser and I discussed in Lyon, namely systems where we use monosized a and b particles, both containing Y compounds so that they might pick up quite a lot of (1) compounds. Such systems would allow very interesting studies to be carried out, as f.i. the effect of amount and type of the Y compound on the distribution of (1) between the particles. Also it would be an interesting system for measuring the rate of transport of a compound 1 from one phase to another. And especially one would if one started with different (1) compounds in the particles get an exchange of (1) compounds which would be interesting to follow. Even if this may seem to have mostly theoretical interest it has also some practical consequences which I will return to later.

University of Trondheim, 20.09.1984


John Ugelstad

25 SEP Reed

The following are abstracts (slightly extended) of two papers (to be) submitted for publication:

1. Electrically Induced Changes in Latex Structure (M. Tomita and T.G.M. van de Ven)

Electrically induced changes in latex structure have been studied experimentally and theoretically. Bragg diffraction intensity curves obtained from ordered lattices subjected to an electric field shifted to longer and shorter wavelengths depending on the polarity of the electric field. Examples are shown in Fig. 1. The magnitude of the shift was nearly proportional to the electric field strength, and depended on volume fraction and ion concentration of the suspending medium. The electric field effect was larger for lattices of lower volume fraction and lower ion concentration. A semi-quantitative explanation has been given for the observed phenomena, which in essence consists of a balance of two forces exerted on a reference particle: a force due to the external electric field and a colloidal force due to the interaction with the asymmetrically distributed surrounding particles.

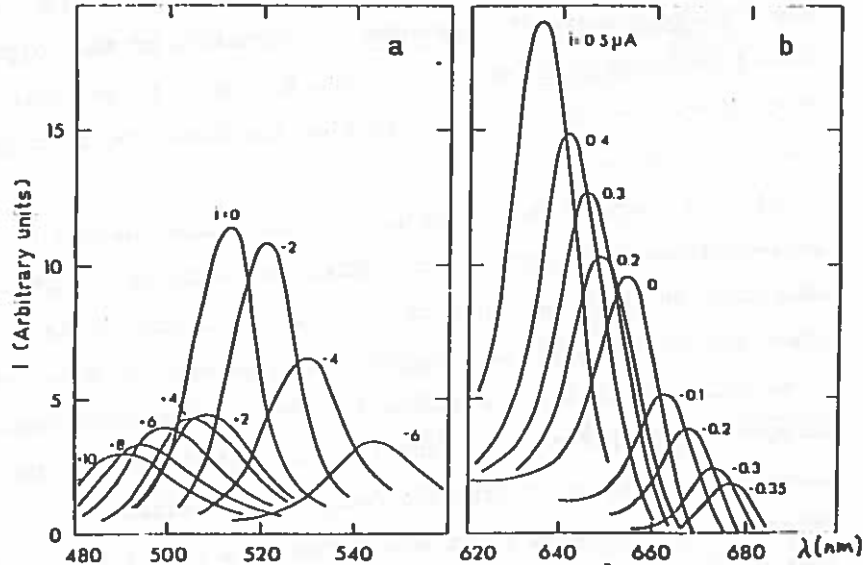


Fig. 1 - Examples of experimentally observed diffraction curves (intensity of back scattered light vs wavelength) for various electric currents. The maxima correspond to the spacing between layers of latex particles near the transparent electrode.

II. Rheo-optics of Suspensions of Anisometric Particles. I. Monodispersed Ellipsoids. (D.S. Jayasuriya and T.G.M. van de Ven)

Rheo-optical behavior of a single ellipsoid in a simple shear flow, calculated using extensions of Jeffery's equations and modified Rayleigh-Debye theory, clearly indicates the presence of an ordered structure underlying its complicated modes of motion. Calculations were extended to an ensemble of randomly oriented monodisperse ellipsoids using a dynamic simulation method. The results, obtained for the ensemble, reveal the occurrence of well-defined periodic transient rheo-optical oscillations provided the ellipsoids are not too far from axisymmetric. An example is shown in Fig. 2. This indicates that transient rheo-optical measurements provide a suitable experimental method to study suspensions of anisometric particles.

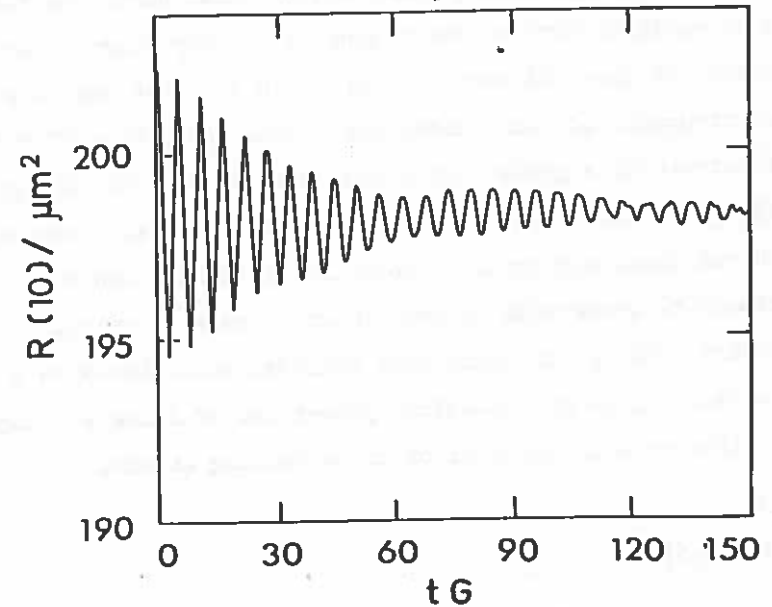


Fig. 2 - Rayleigh ratio (at a scattering angle of 10°) of ellipsoids with axes 473, 334 and 249 nm subjected to a simple shear flow of gradient G , as a function of time t (non-dimensionalized by G).

REGULATION OF PARTICLE STRUCTURE DURING LATEX POLYMERIZATION OF MONOMER COMPOSITIONS

31 AUG Recd

Eliseeva V.I., Titova N.V.

Summary

The present work deals with the influence of methods of performing semicontinuous emulsion polymerization of given monomer compositions on polymer structure and morphology. It is shown that during seed polymerization latex particles form as a result of heteroflocculation of primary polymer particles of various chemical composition, which explains the complicated structure of final latex particles. Properties of films of latexes of a given brutto composition obtained through copolymerization, separate and seed polymerization are described and their differences shown. It is established that at incomplete conversion of seed latex polymer, a transition layer appears between the segregated polymers which leads to a substantial change of mechanical properties of films as compared to films made of mixtures of corresponding latexes.

Introduction

A series of works dedicated to two-stage latex polymerization of monomer 1/2 systems point out the substantial difference in polymer structure /1,2/ and particle morphology /3-6/ depending on the method of monomer introduction, their polarity /3,6/, hydrophilicity /4,5/, and polymerization temperature.

Some conditions lead to phase inversion in particles in the second stage of polymerization /3,5,6/; in other cases phase inversion was observed in films obtained from latexes after heating /7/. Most works /4,5/, for the purpose of attaining maximum separation, describe such monomers 1 and 2 which imply thermodynamic incompatibility of their polymers, with polymerization in both stages continued to deep conversion. Thus, final latexes were compositions of homopolymers 1 and 2 which are close to latex mixtures of polymers 1 and 2.

More complicated systems are considered in the present paper - for the purpose of increasing thermodynamic compatibility of polymers 1 and 2, seed latex conversion was left incomplete, with part of monomer 1 introduced into composition 2. It was thereby expected to preserve the structure of the polymer formed in latex films particles, and thus make it possible to exert purposeful influence over the film-forming properties of latexes.

It is a characteristic feature of the studied method of semi-continuous polymerization, which is conducted by gradual introduction into the reaction of monomer and emulsifier in a specified ratio, that the monomer phase, as well as micelles (emulsifier concentration during this process is lower than CCM), are absent. This ruled out the possibility of drop and micellar mechanisms of particle formation; particles are generated in the water phase and formed as a result of flocculation of newly formed particles.

Results and discussion

Polymer structure and particle morphology of the same brutto composition were changed via different methods of polymerization:

- A. Copolymerization of all monomers.
- B. Separated polymerization of monomers 1 and 2.
- C. Seed polymerization of monomer 2 on monomer 1 latex (or vice versa).

To increase thermodynamic compatibility of polymers, seed latexes were brought to 90-96% conversion; in some experiments, part of monomer 1 was introduced into monomer 2.

The structure and morphology of latex particles and films were studied by electron microscopy and dielectric relaxation. Mechanical properties of films were established on a Polanyi-type device with an automatic recorder of stress-deformation curves. Mechanical strength of films was determined with respect to their mean cross-section at breaking point. Mechanical properties of films were determined after a month of storage under normal conditions and exiccator conditioning, and also after prolonged (several years) storage under normal conditions.

Table 1 contains the recipes and conditions of polymerization, as well as the physico-chemical characteristics of latexes based on monomer compositions I-III. The Table shows that, given the same brutto composition, the latexes obtained according to different methods are different in colloido-chemical properties; this is evidently due to differences in chemical nature and adsorption capacity of particle surface in various stages of the process.

It was shown that in the process of polymerization according to methods A and B, particles form as a result of flocculation of newly formed particles with the old ones /8/.

Fig. 1 show that during method C polymerization, the introduction of new monomer quantities into the seed latex leads to the formation of new particles. Insufficient stability of these particles leads to their heteroflocculation with seed latex particles /9/. As a result, they form a single particle with a complicated inner structure - the seed latex core is surrounded by copolymer globules which form the shell.

Fig. 2 describes the kinetics of particle number change in the second stage of composition III polymerization, method C, according to electron microscopy data. It is clear that the net number of particles as compared to the seed latex hardly changes regardless of the flocculation observed. This leads to the conclusion that heteroflocculation of particles formed in the second stage occurs in such a way that the overall number of particles remains the same. A similar situation is observed during polymerization of composition II.

Therefore, particles of final two-stage latexes (method C) have the "core-shell" type structure.

As seed particles contain residual monomer due to incomplete conversion, diffusion of new monomers into them in the second stage may lead to some copolymer formation, enriched with monomer links from the seed latex. This copolymer acts as a transition layer, by means of which seed and new particles are brought into contact. The presence of such a copolymer is confirmed by a temperature dependence study $\text{tg} \delta$ (angle of dielectric loss) for films of the investigated latexes. Fig 3 a

cites temperature dependence $tg\delta$ curves at a frequency of $f = 1$ kHz of samples B, C 1/2 and B-2, (Table 1) obtained during polymerization of composition I.

The Figure shows that the region $tg\delta_{max}$ is symmetrical and coincides in temperature with the same region of B-2 copolymer. The region of dielectric relaxation of sample C1/2 is shifted, as compared to samples B-2 and B, towards high temperature, and has a non-symmetrical form, which may be an indicator of a third phase present in the sample. At a frequency of $f = 1$ kHz (Fig. 3b), the curve for the film dried under normal conditions, has a non-symmetrical form (curve C); during heating of this film at 70°C (curve C'), asymmetry is enhanced; the dissolution of the film in an organic solvent and subsequent drying leads to the separation of the $tg\delta_{max}$ region into two peaks (curve C''). Heating and dissolution of the film makes composition polymer phase separation easier. That is why the process in the temperature range 23-26°C (curve C) may be assumed to go on due to the co-existence of the copolymer phase of the transition layer with higher MMA formed in the second stage

Fig. 4 shows temperature dependences of $tg\delta$, taken at 1-kHz, for composition III films obtained according to methods B and C. Latex mixture (method B), not unexpectedly exhibits properties of a two-phase heterogeneous system - two $tg\delta_{max}$ regions are observed, one of which corresponds by temperature to the α -transition of PMA (B-1), and the other - to P/BA-MAA/ (B-2). For the latex film obtained according to method C two $tg\delta_{max}$ peaks were also discovered that are close in temperature to the α -transition of latex polymers obtained according to method C. Nevertheless, both transitions observed for this polymer, are shifted towards each other. This provides grounds for

the belief that, first, latex C polymer is heterogeneous as its components have their own glass transition temperature; and second, the volume of this polymer contains a noticeable amount of mixed intermediate structure.

On the basis of the above data, structure and organization of the polymer in particles of latex polymers obtained through polymerization of monomers 1 and 2 according to three different methods, may be schematically described as follows (Fig.5):

Method A: particles consist of statistical copolymer globules.

Method B: latex comprises a mixture of polymer 1 and 2 particles,

Method C: a) Latex particles consist of polymer 1 core and polymer 2 shell. Transition layer of intermediate composition lies in between core and shell.

b) Latex particles are of the same morphology as "a", but with inverted polymer location.

As seen from Table 2, latex films of one and the same brutto composition are radically different in their mechanical properties depending on the method of latex synthesis. The difference is observed not only in statistical copolymer and composition polymers, but also in composition polymers that do or do not contain a transition layer. For instance, for compositions I, II, III the initial strength of latex films synthesized by seed polymerization is 1.5-2 times greater than the strength of films synthesized from a mixture of corresponding latexes (a comparison of methods B and C). This confirms the presence of the transition layer that provides contact between the segregated

polymers. A comparison of experiments 1C 1/2 and 1C 2/1 indicates also considerable influence of the order of segregated polymer location in particles on the mechanical properties of films. We may therefore believe that the structure of particles that form in the process of polymerization remains in the latex films. Observed improvement in film properties during prolonged storage under normal conditions (Table 2) is explained by specific conditions of film formation from latexes of linear polymer which are connected to coalescence of neighbouring particles and governed by inter-particle macromolecule diffusion. The greatest change in properties in case of copolymer and mixture latexes (strength grows 1.5-3 times) is evidently connected to the least suppressed diffusion in these cases, while in latex films, synthesized via seed polymerization II C and IIIC, this is probably prevented by the presence of the intermediate layer. The trends established in this work allow to control the structure of latex particles that are obtained from the same monomer composition, and therefore to exert a guided influence on film properties.

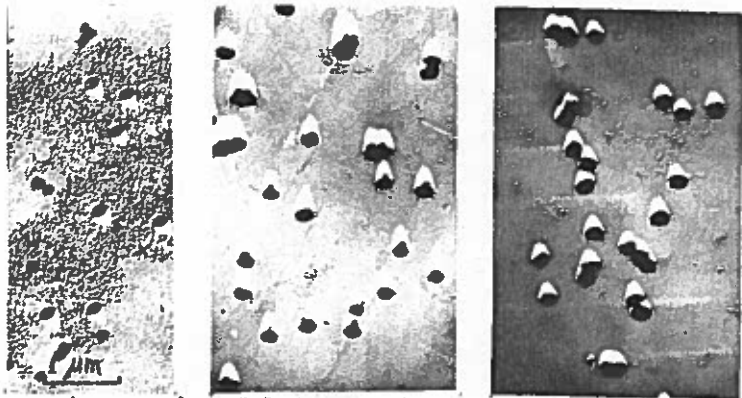


Fig.1 Electron micrographs of latex synthesized according to method C, composition III : a - seed latex PMA, b,c -- latexes in the process of synthesis and final, respectively

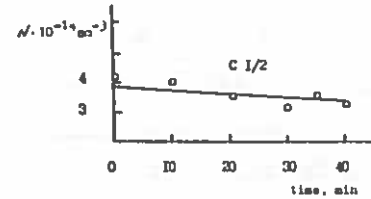


Fig.2 Kinetics of the change in the number of particles in the second stage of composition III polymerization according to method C

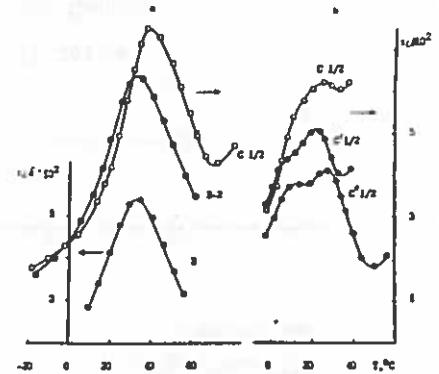


Fig.3 Dependence of $\text{tg } \delta$ on temperature for samples a - B, b and b-2, obtained during polymerization of composition I at 40°C; a - B, c' - C' at 40°C

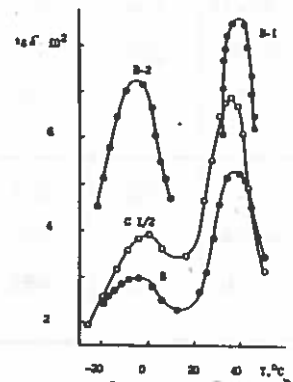


Fig.4 Dependence of $\text{tg } \delta$ on temperature for film samples B-1, B-2, C, composition III at 40°C

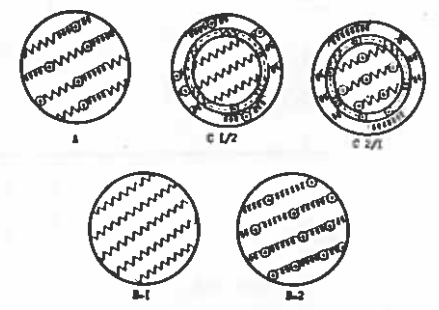


Fig.5 Schemes of structure of polymer and particle morphology in latexes obtained according to various methods (broken line signifies MA links, spiral - MA, cross - MA)

Table 2

Mechanical properties of films before and
after prolonged storage.

Composition	Methods	$\sigma \cdot 10^7$, N/m ²		ϵ , %	
		before	after	before	after
I MMA-BA-MAA 57.4:39.3:3.3	A	continuous film fails to form			
	B	2.90	9.50	160	430
	C 1/2	4.47	5.27	180	210
	C 2/1	3.50	7.50	110	170
II St-BA-LAA 45:50.4:4.6	A	3.70	10.15	230	420
	B	2.97	6.60	300	350
	C	6.90	6.70	470	370
III MA-BA-MAA 62:35:3	A	0.94	2.05	1500	900
	B	3.03	4.74	470	570
	C	3.90	4.60	580	630

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