SOME ASPECTS OF INVERSE EMULSION

COPOLYMERIZATION OF ACRYLAMIDE WITH

METHACRYLIC ACID

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ABSTRACT

        Inverse emulsion copolymerization studies of acrylamide (Am) with
methacrylic acid (MAA) are reported. Aqueous monomer emulsions in toluene
were prepared with a blend of two surfactants (sorbitan sesquioleate - C18
- terminated acrylamide oligomers). Polymerization kinetics in presence of
an oil soluble initiator (AIBN) were determined at 40°C as function of MAA
content and aqueous phase pH : monomer reactivity ratios have been derived
as rAm = 0.58 $\pm$ 0.02 , rMAA = 4.40 $\pm$ 0.10 at pH 4 and rAm = 0.56 $\pm$ 0.005 ,
rMAA = 0.15 $\pm$ 0.03 at pH 10. Particle size and stability of inverse monomer
emulsions and final latexes were found to depend upon the aqueous phase pH,
as well as the intrinsic viscosities of the copolymers ; this suggests
differences in polymerization mechanism versus the pH.

INTRODUCTION

        In recent years, the preparation of acrylamide polymers has re-
ceived increasing interest because of their use in many practical appli-
cations (flocculants, water treatment, tertiary oil recovery, etc). Among
the different polymerization processes which are generally carried out,
inverse emulsion polymerization is particularly attractive, due to the
colloidal nature of this type of process, which associates a high polymeri-
zation rate with a high average degree of polymerization.

        Since the pioneer works of VANDERHOFF (1) and KURENKOV (2), a few
studies have been reported concerning the inverse emulsion polymerization
process. In the last years, much effort has been focused in this area,
mainly in the case of acrylamide, with the purpose of elucidating the poly-
merization mechanism (3, 4, 5, 6). Several features of this reaction are

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similar to the conventional emulsion polymerization, some others are quite specific of the inverse emulsion process (effect of interfacial area, nature of reaction loci, type of initiation).

Furthermore, it is noteworthy that, very often, polymers are in fact copolymers, and in the case of water soluble polymers, the comonomer is generally selected in order to impart an ionic character to the macromolecule, depending upon the desired functionality. In this objective, carboxylic acids, such as acrylic or methacrylic acids, have been widely used but no fundamental work has been reported on the inverse emulsion copolymerization of these systems.

Thus, the purpose of this paper is to highlight some specific aspects of the acrylamide (Am)-methacrylic acid (MAA) copolymerization by inverse emulsion process. The study deals with the stabilization of aqueous monomer emulsions, the kinetics and the molecular and colloidal characteristics of final emulsion copolymers as a function of methacrylic acid content at two different pH.

EXPERIMENTAL

* Materials

Acrylamide (PROLABO reagent grade) was used as received ; the methacrylic acid (from FLUKA) was distillated under vaccum before use. Toluene was distilled and purged with nitrogen. Deionized water was boiled under nitrogen. The initiator, $2,2'$-azoisobutyronitrile (AIBN) was recrystallized from methanol solution (from MERCK).

The low-HLB emulsifier (MONTANE 83 from SEPPIC) a sorbitan sesquioleate, was used as received. Two high-HLB emulsifiers were used as cosurfactants : a poly(oxyethylene) sorbitan trioleate (MONTANOX 85 from SEPPIC) and a C18 - mercapto terminated acrylamide oligomer (C18 - $(Am)_{20}$)prepared in the laboratory by a radical oligomerization process described elsewhere (7).

* Preparation of aqueous monomer emulsions

Aqueous monomer emulsions of acrylamide or (acrylamide-methacrylic acid) mixtures were obtained by emulsification of a fixed amount of aqueous monomer solutions in toluene containing emulsifier blends of various composition using magnetic type stirrer (300 rpm). An exemple of such a w/o emulsion is given in Table I.

<div align="center">

TABLE I

Inverse Latex Recipe[a]

</div>

	Part/Weight
Dispersion medium (toluene)	66
Aqueous monomer solution (weight ratio of monomer/water 2/3)	22
Surfactant (weight ratio of montane 83/C18 mercapto terminated acrylamide oligomers 95/5)	9.5
Initiator (AIBN)	0.02

[a] Temp.: 4o°C

* Stability study

        The stability of these inverse emulsions was determined by measu-
ring the average droplet size variation as function of the amount and
composition of the emulsifying system. Coulter Nanosizer (from Coultronics)
was used as a rapid technique to estimate the average droplet size of the
emulsions. In order to prevent coalescence of droplets due to the required
dilution for the measurement, it was necessary to dilute with toluene
containing Montane 83 (10 % W/W). The total particle number $N_{t=o}$, at time
t=o was calculed from the relation $N_{t=o}$ 6 Φ/π $(D_v)^3_{t=o}$, where Φ is the
volume fraction of aqueous solution and $(D_v)_{t=o}$ the volumetric mean parti-
cle diameter at time $_{t=o}$. As reported by REDDY et al. (8), the ratios
$(N_t/N_{t=o})$ at different times were determined as $N_t/N_{t=o}$ $(D_{v\ t=o}/D_v t)^3$.

- Polymerizations

        The polymerization procedure was as follows : a one-liter round
bottom reactor was used, equipped with steel paddle - type stirrer, nitro-
gen inlet, temperature control and sampling tube. The aqueous monomer
emulsion was prepared as described above and then purged with purified
nitrogen during 30 minutes ; agitation rate was fixed at 250 rpm and
temperature was maintained at 40°C. Then the initiator, previously dissol-
ved in toluene, was added to the reaction mixture, starting the polymeriza-
tion. A standard recipe of the polymerization conditions is listed in
Table I.

The kinetics of monomer consumption were determined by gas chroma-
tography analysis of reaction medium aliquots periodically withdrawn   from
the bottom of the reactor. Polymers were precipitated by methanol or ace-
tone, solubilized in water, again precipitated and then dried under vaccum.

– Partition study of the two monomers between organic and aqueous phases

Partition behavior of acrylamide and methacrylic acid between a-
queous and organic phases in absence of emulsifier were determined by gas
chromatography analysis as function of pH and composition of the comonomer
feed mixture.

Mixtures of toluene, water and comonomers, prepared under similar
conditions of polymerization experiments, were submitted to centrifugation
to separate the two phases which were further analyzed. pH of the aqueous
phase was adjusted by adding either hydrochloric acid or sodium hydroxide.
Calibration curves were established from analysis of standard solutions of
the two monomers in toluene or water phases.

– Particle size analysis

Droplet sizes of initial monomer emulsions and final latexes were
determined using three different methods : (i)Coulter Nanosizer ; (ii)dyna-
mic light scattering (equipped with MALVERN autocorrelator) ; (iii)trans-
mission electron microscopy using a freeze fracture technique. Viscosity
was measured with a capillary automatic viscometer at 25°C on solutions of
0.1g/dl of neutralized polymer in 0.1N NaCl water ; the intrinsic viscosity
$[\eta]$ was obtained by extrapolation to zero concentration.

RESULTS AND DISCUSSION

1) Partition behavior of the monomers between aqueous and organic phases

The data given in Table II show that in the case of acrylamide, a
small amount of the monomer is solubilized in toluene phase (2 mole-%) when
acrylamide is used alone. When methacrylic acid is introduced in the como-
nomer feed, under acidic form, there is a three-fold increase of the
acrylamide amount solubilized in toluene ; it becomes negligible at basic
pH.

TABLE II

PROPORTION OF ACRYLAMIDE MONOMER IN TOLUENE pHASE (*)

COMONOMER COMPOSITION (mole-% Am)	pH	PROPORTION OF ACRYLAMIDE DISSOLVED IN TOLUENE (mole-%)	PARTITION COEFFICIENT K o/w
100	–	2 %	0.02
50	4	5-6.3 %	0.052-0.067
50	10	∿ 0 %	0

(*) Proportions of toluene, water, monomers are the same than reported in Table I.

In the case of methacrylic acid, a more detailed study on the partition behavior was carried out due to the relatively hydrophobic nature of this monomer when it is under acidic form.
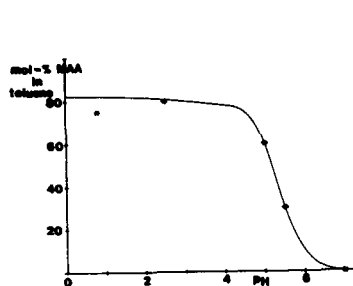
Figure 1 .
PROPORTION OF METHACRYLIC ACID
(MAA) SOLUBILIZED IN TOLUENE
VERSUS pH OF AQUEOUS PHASE
(Experimental conditions :
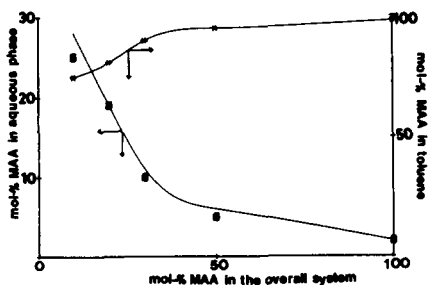Toluene : 150 g,   Water = 30 g,
 MAA = 7,19 g , Am = 13,7 g

Figure 2 .
PARTITION OF METHACRYLIC ACID
(MAA) BETWEEN ORGANIC AND AQUEOUS
PHASE AS FUNCTION OF MAA CONTENT
IN THE COMONOMER MIXTURE

Figure 1 shows that with a comonomer mixture containing 30 mole-%
of MAA, a high proportion of MAA is located in the toluene phase at pH
below 4 (75-80 mole-%). Whitin a short range of pH (5 to 6), a sharp
decrease is observed, and at pH 7, all MAA has been transferred back in the
aqueous phase due to the hydrophilicity of the ionized molecules at a pH
higher than the pKa of MAA such as pKa 4,2.

This former study was completed taking account of the effect of
the overall MAA amount in the system. All the range of MAA concentrations
has been investigated ; the corresponding variation of pH being not too
important (between pH 2.5 and to pH 3.0).

Figure 2 shows the variation of the MAA partitioning in both
phases versus the overall acid concentration in the system. A complex
variation law is in fact pointed out : a continuous increase of MAA
amount in toluene phase occurs as the total amount of MAA increases ,
whereas the proportion in aqueous phase drastically decreases from 25 mole-
% at 10 mole-% MAA, to reach only 2 % at 100 mole-% MAA.

This partition study, carried out in absence of emulsifier, shows
that under basic pH, all methacrylic acid and acrylamide molecules are
essentially located in the aqueous monomer droplets. Conversely, under
acidic conditions, a large amount of MAA is solubilised in toluene phase,
with the consequence that the comonomer composition in the droplets is
greatly dependent on the methacrylic acid concentration. However, it has to
be kept in mind that the presence of emulsifier (10 wt-% based on toluene)
would probably affect the actual partition behavior of the two monomers.

2) Stability studies of aqueous monomer emulsions

The preparation of stable water in oil emulsions is somewhat more
difficult than in the case of oil in water emulsions, and is generally
controlled by the following factors : nature, concentration and composition
of the emulsifying system, nature of the oil and aqueous phase effect of
comonomer(s). Different routes have been reported in the literature to
prepare stable acrylamide emulsions : selection of a blend of a low-HLB
emulsifier with a high-HLB emulsifier (9) - choice of a particular emulsi-
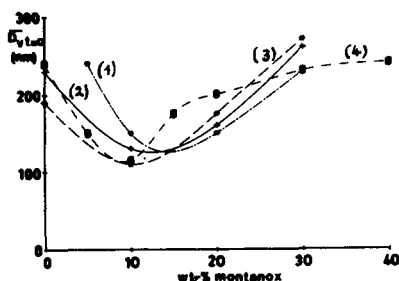fier providing multiple emulsion droplets (10).

Figure 3 .
INITIAL DROPLET SIZE OF ACRYLA-
MIDE (Am) - METHACRYLIC (MAA)
INVERSE EMULSION VERSUS MONTANOX
CONCENTRATION IN THE EMULSIFIER
MIXTURE FOR DIFFERENT AMOUNTS OF
MONTANE (WT-% RELATED TO THE
ORGANIC pHASE)
(1) = 3 % ; (2) = 5 % ;
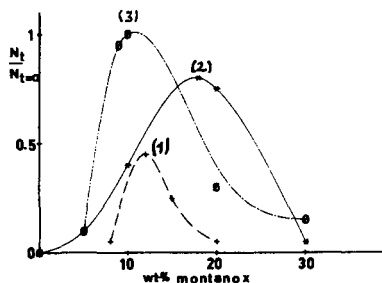(3) = 8 % ; (4) = 10 % ;
((Am)/(MAA) = 70/30 - pH 10)

Figure 4 .
EFFECT OF MONTANOX CONCENTRATION
IN THE EMULSIFIER MIXTURE ON THE
RATIO $N_{t=1h}/N_{t=o}$ OF ACRYLAMIDE
(Am) METHACRYLIC ACID (MAA)
INVERSE EMULSION FOR DIFFERENT
AMOUNTS OF MONTANE (WT-% RELATED
TO THE ORGANIC PHASE)
(1) = 5 % ; (2) = 8 % ; (3) = 10%
((Am)/(MAA) = 70/30, pH 10)

We tried to optimize a suitable emulsifier system in the case of
acrylamide and acrylamide-methacrylic acid mixtures as function of pH. At
first, the effect of montane and montanox concentration was investigated.
In the Figure 3 which reports the variation of the initial droplet size
of emulsion versus montanox concentration, it can be seen that $\overline{D}_v$ goes
through a minimum value within a short range of montanox concentration (10
wt-% based on montane) and then increases, an indication that efficient
stabilization is imparted, as expected (9) in the low HLB range (4 to 6).

Figure 4 which gives the variation of $(N_{t=60\ min}/N_{t=o})$ confirms
this optimal stability ; it also points out that a correct stabilization of
the monomers emulsions is provided by using at least 10 wt-% (based on
toluene) of the low HLB emulsifier (montane).

Stability experiments were also performed, using 10 wt-% of mon-
tane, but varying the nature of the monomer mixture and the aqueous phase
pH. Figure 5 shows that, for acrylamide emulsions, $\overline{D}_v$ is not significantly
affected by the montanox concentration up to to 30 wt-% in the blend. A

different trend is observed with the MAA-acrylamide mixture, showing a minimum value (100 nm) at 10 wt-% of montanox under basic pH, and markedly higher (230-250 nm) under acidic pH. In the case of acrylamide oligomer as cosurfactant (Figure 6), the stability behavior is quite different. It provides stability within a shorter range of concentration about 5 wt-% based on montane). Poor stability is conferred under acidic pH, which is confirmed by larger droplet size than at basic pH and rapid phase separation upon ageing.
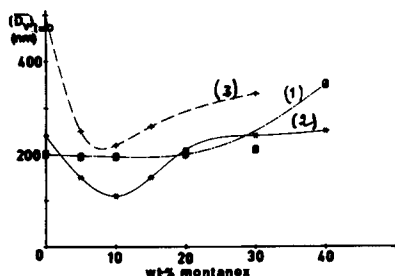

Figure 5 .
EFFECT ON MONTANOX CONCENTRA-
TION IN THE EMULSIFIER MIXTURE
ON THE INITIAL DROPLET SIZE OF
DIFFERENT MONOMER EMULSIONS
(1): ACRYLAMIDE ;
(2):ACRYLAMIDE METHACRYLIC
ACID , (Am)/(MAA) = 70/30
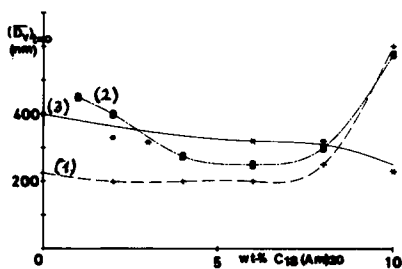pH 10, (3): ACRYLAMIDE METHA-
CRYLIC ACID, (Am)/(MAA) = 70/30,
pH 4

Figure 6 .
EFFECT OF C18 -(Am) 20 CONCEN-
TRATION IN THE EMULSIFIER MIX-
TURE ON THE INITIAL DROPLET SIZE
OF DIFFERENT MONOMER EMULSIONS
(1):ACRYLAMIDE ; (2): ACRYLAMIDE-
METHACRYLIC ACID , (Am)/(MAA) =
70/30 pH 10 ; (3) ACRYLAMIDE-
METHACRYLIC ACID,(Am)/(MAA)=
70/30,pH 4

Interpretation of enhanced stability with mixtures of emulsifiers is usually referred to packing conditions in the interfacial layer due to interaction forces between the hydrophobic parts of the two emulsifiers (10). Change in stability behavior versus pH in our systems, could be an indication that the methacrylic acid molecules would interfere in the formation of surfactant layers. Under acidic conditions (where a large amount of MAA is solubilized in the external phase), a loose packing would occur at the oil-water interface, whereas under basic conditions, the

presence of MAA inside the aqueous droplets would result in a more conden-
sed film, perhaps due to specific associations between the ionic monomer
and the hydrophylic part of the emulsifiers. It was found that interfacial
tension measurements do not well correlate the stabilization behavior of
these systems, which suggests that other physical methods have to be per-
formed to characterize the nature of the steric barrier.
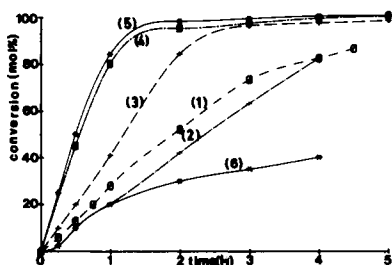
3) Kinetic studies of inverse emulsion copolymerization

Figure 7 .
ACRYLAMIDE (Am) - METHACRYLIC
ACID (MAA) inverse emulsion
copolymerization kinetics at
pH 10.Mole-% MAA in comonomer
mixture (1) = 10 % , (2) = 20 %
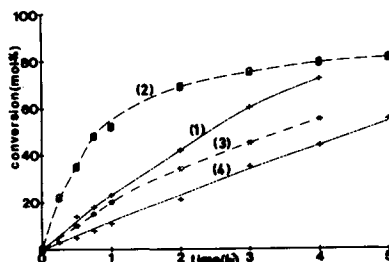(3) = 30 % , (4) = 50 % ,
(5) = 75 % , (6) = 100 %

Figure 8 .
ACRYLAMIDE (Am) - METHACRYLIC
ACID (MAA) inverse emulsion co-
polymerization kinetics at pH 4.
Mole-% MAA in comonomer mixture
  (1) = 10 % , (2) = 20 % ,
  (3) = 30 % , (4) = 50 %

    Kinetics of inverse emulsion copolymerization of acrylamide with diffe-
rent methacrylic acid concentrations are reported respectively in Figure
 7 for the series carried out under basic pH, and Figure 8 for those
carried out under acidic pH.

        In the case of the basic pH series, it is found that the overall
rate of polymerization increases with the MAA content in the initial como-
nomer feed, the highest rate being observed in the range of 50-70 mole-% of
MAA. This kinetic behavior might be the result of drastic changes in the
polymerization kinetic parameters, due to the increased concentration of

MAA in the aqueous monomer droplets where polymerization is supposed to take place. That would cause a corresponding increase of the macroscopic viscosity, early in the polymerization. This explanation was already proposed by KABANOV et al.(11) in the case of MAA homopolymerization versus pH, and consequently chain termination probably becomes diffusion-controlled as polymerization proceeds.

In the case of the acidic pH series, it is observed (Figure 8) that the variation of the overall polymerization rate with the MAA content in the comonomer feed, follows a different trend, a maximal rate being observed around 20 mole→% MAA ; the Rp values decrease with further increase in the (MAA) concentration. In addition, the polymerizations were not completed. This kinetic behavior can be related to the actual concentration of MAA in the aqueous phase as described above in the previous section. Figure 9 shows the good correlation between the actual MAA concentration in aqueous phase and Rp values ; the higher the MAA concentration in aqueous phase is, the higher the overall polymerization rate.
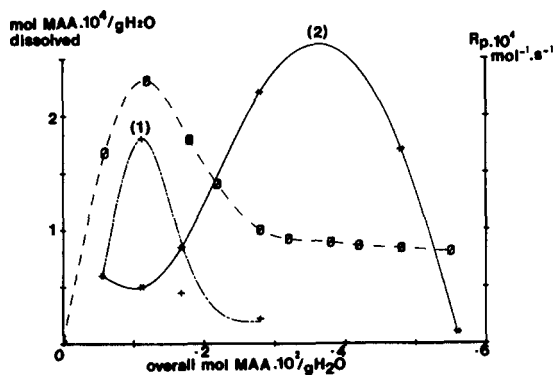

Figure 9 . Concentration of methacrylic acid (MAA) in aqueous phase (---) and polymerization rate (Rp) versus the overall MAA concentration in the system. (1): Rp at pH 4 ; (2): Rp at pH 10

Using these kinetic data as well as the correction of the MAA concentration in the aqueous monomer droplets and the contribution of polymerization in the case of acidic pH series, monomer reactivity ratios were derived from different classical methods.

TABLE III

MONOMER REACTIVITY RATIOS
FOR ACRYLAMIDE (Am) - METHACRYLIC ACID (MAA)
INVERSE EMULSION COPOLYMERIZATION
T = 40°C

pH	rAm	rMAA	Conditions	Reference
4	0.20 $\pm$ 0.069	2.80 $\pm$ 0.44	Solution, 30°C	S. PONTRAMAN et al. (12)
4	0.58 $\pm$ 0.02	4.30 $\pm$ 0.20	Inverse emulsion	This work
10	0.57 $\pm$ 0.06	0.34 $\pm$ 0.05	Solution 30°C	S. PONTRAMAN et al. (12)
10	0.56 $\pm$ 0.005	0.15 $\pm$ 0.03	Inverse emulsion	This work

Values are reported in Table III and compared with literature values corresponding to solution conditions (12). As expected, there is a strong pH effect on the monomer reactivity ratios, especially on the rMAA values, an indication that the reactivities of MAA monomer and MAA-ended macroradical are affected.

4) Characterization of Am-MAA inverse emulsion copolymers

Concerning the particle size of inverse emulsions, using the transmission electron microscopy and a freeze fracture technique, it was found that the initial monomer emulsions display (13), as reported in the Figure 10 , a wide range of droplet size (from 15 nm to 2000 nm). In the final latexes, the same broad size distribution is still obtained with always a background of tiny particles (15-20 nm), but with an average particle size depending on pH, degree of conversion and in some cases on
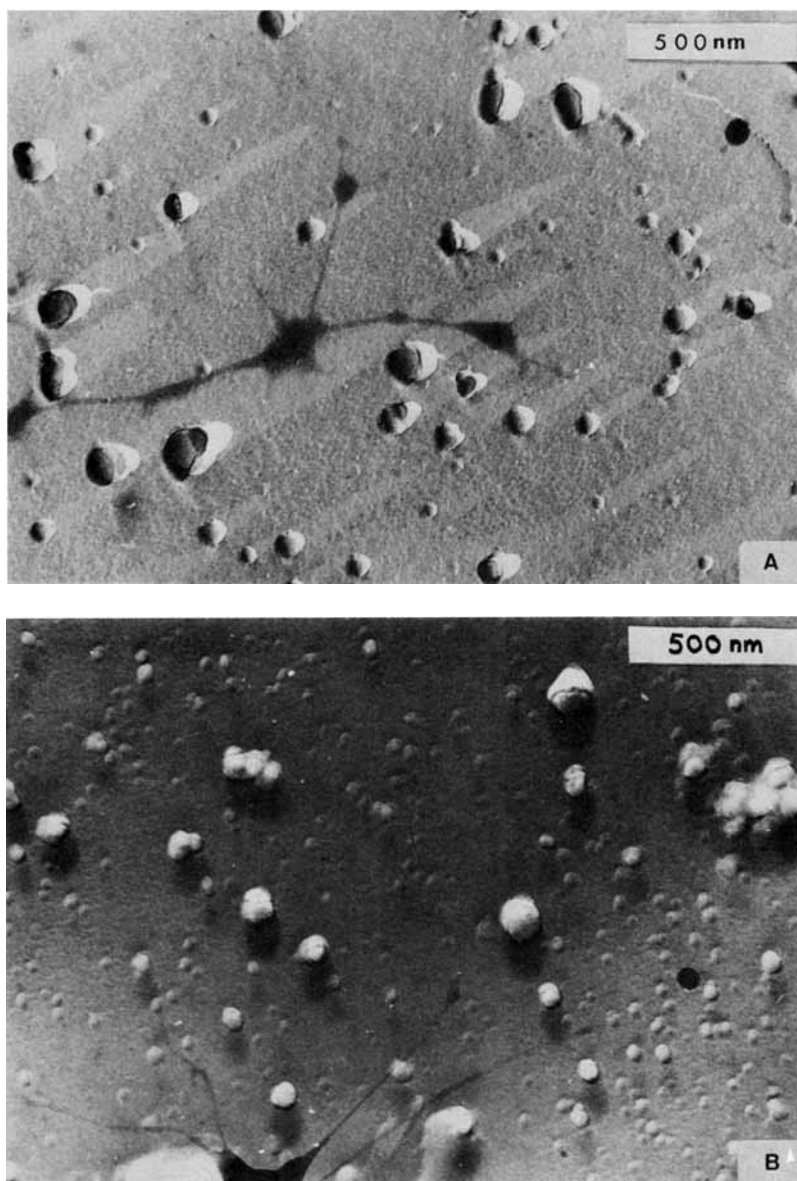
Figure 10 . Transmission electron micrographs of Am-MAA inverse
emulsions (30mole% MAA) before(A) and after polymeriza-
-tion(B)

MAA concentration.

TABLE IV

PARTICLE SIZE ANALYSIS OF Am-MAA COPOLYMER LATEXES
(LIGHT SCATTERING METHODS)

MONOMER FEED COMPOSITION (MOLE-% MAA)	0 (P-Am)	10	20	30	50	75	100 (P-MAA)
BASIC pH SERIES							
$\bar{D}_v$ (nm) INITIAL	250		300			280	240
$\bar{D}_v$ (nm) FINAL	100		90	100	92	83	540
ACIDIC pH SERIES							
$\bar{D}_v$ (nm) INITIAL		330	350		300		
$\bar{D}_v$ (nm) FINAL		80	145	1000	1000		
				VERY UNSTABLE			

      In Table IV are collected the particle size results of these copolymer latexes as obtained from dynamic light scattering. It appears that the average particle size ($\bar{D}_v$) of the initial monomer emulsions is in the range 240-300 nm for the basic pH series, and slighty larger for the acidic pH series. Particle size of final latexes prepared under basic conditions is relatively insensitive to MAA concentration, except at high concentration where the bad efficiency of the selected emulsifier blend and also the higher ionic charge density inside the particles can promote the destabilisation of the latex. Poor latex stability is characteristic of inverse copolymer latex prepared under acidic conditions. This is well reflected by the large particle size (> 1000 nm) when the MAA is higher than 30 mole-% in the comonomer mixture. This also confirms the bad stability imparted by the emulsifying system, based on C18 acrylamide-oligomers
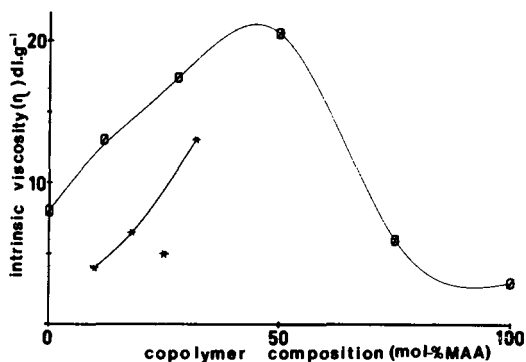
under acidic pH.

Figure 11 . Intrinsic viscosity variation versus the copolymer composition
of Am-MAA inverse latexes prepared at pH 10 (∅) or pH 4 (*)

Concerning the viscosity behavior of these copolymers, it is found
to depend upon the pH used during the synthesis of copolymers. In Figure
11 which gives the intrinsic viscosity variation versus the actual copo-
lymer composition, a higher $[\eta]$ is obtained in the case of the basic pH
series, with a maximum value at about 50 mole-% of MAA. Lower $[\eta]$ are shown
for the acidic pH copolymers but the variation against copolymer composi-
tion corresponds to a relatively narrow range since low conversion   copo-
lymers were obtained for this series. The results have to be correlated
first with the polymerization rate, a highest rate being obtained in the
former series, secondly with large differences in monomer sequence distri-
bution between the two types of copolymers (14).

These experimental results were found to provide valuable informa-
tions on the main mechanistic features in inverse emulsion copolymeriza-
tion. Concerning the initiation step, it was already proposed (13) that it
probably comes, essentially in the case of AIBN-initiated polymerization,
from the capture of radical produced either in the oil phase or in the
interfacial layer, which plays an important role because of the amount of
emulsifier. In the case of acidic pH inverse emulsion the contribution of
MAA-rich oligoradicals formed in toluene phase and diffusion towards the
particles has to be also taken into account.

Furthermore, it is obvious that the main polymerization loci are
the aqueous monomer droplets, even under acidic pH, the obtained reactivity
ratios being quite comparable to those determined under aqueous solutions
at similar pH. However, in the case of acidic pH inverse emulsion, the

polymerization mechanism is probably more complicated since it involves a diffusion process of the MAA molecules from the organic phase towards the aqueous droplet. These assumptions can be verified by simulation of the reactions, using models based on partition coefficients of monomers and actual reactivity ratios. More detailed results will be published (14).

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