

Semicontinuous Emulsion Polymerization of Methyl Methacrylate, Ethyl Acrylate, and Methacrylic Acid

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SYNOPSIS

By a semicontinuous emulsion polymerization method with a variable monomer feed rate, a terpolymeric latex of methyl methacrylate and ethyl acrylate functionalized with methacrylic acid was synthesized. Conversion and reactor temperature vs. time were followed during the reaction. Characterization of the latex system was performed by particle-size measurements, scanning electron microscopy, infrared spectroscopy, viscometric molecular weight, glass transition temperature measurement, and rheological behavior. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Acrylic emulsions are widely used in architectural and decorative coatings. The employment of water-based systems is growing rapidly and expanding vigorously. This must be attributed to government regulatory restrictions about solvent emissions and to ecological aspects. The measurement of solvent contents is made through the VOCs index (Volatile Organic Compounds Index) and the ideal product content should be zero VOC. For example, there is a proposal¹ that from 1996 onwards exterior waterborne coatings will have a fixed VOC limit of 200 g/L, and for interior waterborne coatings, 150 g/L. Latexes seem to be the ideal substitutes for traditional solvent-borne paints and coatings to achieve the target limits, because these materials are all based on water and have no organic solvent content, using only very small amounts to modify the final film properties or the paint flow and rheological properties.

Other aspects of paints and coating formulations are the optimal combinations of the additives' quality and quantity and the sequence of addition. Owing to the fact that the emulsion polymer is the most important component of a paint and that it deter-

mines properties like durability, elasticity, UV resistance, and early block, it is necessary to deal with a well-known system. The behavior after application is the definitive test of the paint. When using commercial latexes, so as to optimize a paint formulation, the results of tests are not always correlated to the latexes' properties, perhaps due to the inhomogeneity in different commercial batches or to unknown impurities or components present in the latexes. This fact suggests the need for syntheses of latexes with well-known properties and chemical composition. The latter are intended to correlate with the coatings' performance of a latex paint made from them.

Semicontinuous emulsion polymerization is the most common method of latex synthesis and it is known that any modification in the process can affect the characteristics of the polymer and, therefore, the latex paint quality. Up to the present, there has been little investigation on the influence of latex characteristics (in particular, the reaction pathway for the latex synthesis) and the performance of the latex paints. The present work is part of a research program on the study of properties of synthetic latexes and coatings made from them.

A description is made of the synthesis and characterization of a full acrylic latex (MMA/EA/MAA) using a variable feed rate addition technique, following a semicontinuous method proposed by Arzamendi et al.,²⁻⁴ to achieve a copolymer system with almost a constant composition.

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The gravimetric conversion and temperature were followed during the reaction. Particle size, surface tension, and rheological behavior studies (both prior and after neutralization) were performed. Polymer films from the latex were characterized by infrared spectroscopy and DSC techniques. The molecular weight of the polymer was estimated from intrinsic viscosity measurements.

EXPERIMENTAL

Acrylic monomers are generally stabilized by hydroquinone or hydroquinone methyl ether to prevent polymerization during shipping. The removal of inhibitors is associated with product losses and additional equipment, which costs time and money. However, with the availability of monomers containing low levels of inhibitors, it is common to override the inhibitors with a slight excess of initiators. The reaction begins after an induction period.⁵ Shoaf and Poehlein⁶ found that removal of the inhibitor is unnecessary for most runs since their only effect is the occurrence of an induction period at the beginning of the reaction. When the inhibitor is consumed, the reaction proceeds in a normal fashion. In the present case, the induction period was ca. 6 min.

Analytical-grade monomers (Fluka Chemika) were used in this research as received. Methyl methacrylate (MMA) contained 25 ppm of hydroquinone. Ethyl acrylate (EA) and methacrylic acid (MAA) contained hydroquinone monomethyl ether (100 and 250 ppm, respectively). The emulsifier sodium lauryl sulfate (SLS), the buffer, sodium bicarbonate (SBC), and the initiator, potassium persulfate (KPS), were of analytical grade and were also used without further purification. Doubly distilled water (DDW) from a KMnO_4 — NaOH solution in an all-Pyrex apparatus was used throughout the experimental work.

Polymerizations were carried out using a separable reactor composed of a conical-based cylindrical glass vessel (capacity 0.47 dm³) with a thermostatic jacket and sampling utility and a five-necked cap. The cap was fitted with a reflux condenser, a stirrer (two-blade propeller type of Teflon), an inlet for inert gas (nitrogen), a thermocouple, and a calibrated dropping funnel. The agitation speed was between 200 and 250 rpm. The list of components is given in Table 1, and the initial charge was calculated using the relation

$$\frac{dM_1}{dM_2} = \left[\frac{M_1 \cdot (r_1 M_1 + M_2)}{M_2 \cdot (r_2 M_2 + M_1)} \right] \quad (1)$$

Table I Components Used to Prepare the Latex (All Quantities in g)

Component	Initial Charge	Emulsion Feed
Ethyl acrylate (EA)	100.00	—
Methyl methacrylate (MMA)	46.36	81.54
$\text{K}_2\text{S}_2\text{O}_8$ (KPS)	0.58	—
Sodium lauryl sulfate (SLS)	0.73	0.43
NaHCO_3 (SBC)	0.19	—
Double-distilled water (DDW)	176.36	86.10
Methacrylic acid (MAA)	—	4.56

where (dM_1/dM_2) is the relation of monomers in the polymer at the beginning of reaction. M_1 and M_2 are the adequate concentrations of monomer 1 and 2, and r_1 and r_2 are the reactivity ratios. In this case, M_1 corresponds to MMA with $r_1 = 2.03$, and M_2 , to ethyl acrylate with $r_2 = 0.24$.⁷ The MAA was not considered in this stage because it was incorporated in the second part of the reactor feed.

Emulsions and MAA were separately freed from oxygen by bubbling "oxygen-free" nitrogen from which residual oxygen was removed by passage through an alkaline pyrogallol solution. A slow stream of nitrogen was maintained in the reactor during polymerization.

The initiator was dissolved in 30 mL of DDW, and the procedure for the emulsion polymerizations was as follows: The initial SLS and the SBC buffer were added to the initial water in the stirrer reactor. Then, all the EA (the less reactive monomer) and a fraction of the MMA (see Table I) were added with stirring and nitrogen was passed through the emulsion during 30 min while heating to 60°C. The aqueous solution of the initiator was then added. The emulsion was allowed to react for ca. 30 min, during which *in situ* seed particles formed, and then the feed was started at ca. 3 g of emulsion per minute. The flow rate of the emulsion was adjusted adequately. The nitrogen purge line was pulled to the top level of the emulsion after 30 min of reaction to prevent polymer coagulation. The monomer emulsion feed was prepared using an emulsification apparatus at 1500 rpm and placed in the dropping funnel and deaerated for 30 min. Total addition time was ca. 278 min.

Owing to the dependence of the decomposition of the persulfate on pH,⁸ it was checked periodically during the reaction. The initial value was 8 and it was constant during the reaction until MAA was added (at ca. 234 min of reaction), then it dropped to 5–6, and the final pH value in the cold latex was 5.

To complete the polymerization after monomer addition, the temperature was maintained at 60°C for ca. 60 min. The pH of the final latex was adjusted to 8–9 with ammonia.

The conversions were determined by taking at variable intervals a few grams of sample into a tared aluminum cup. The content of polymer for each sample was determined gravimetrically. The samples were quenched in an ice-water bath and dried under reduced pressure at 50°C. The weight of the residue (polymer) was used for the calculation of the conversions. No inhibitor hydroquinone was added because it was found⁹ that the addition to the samples before drying provided no additional inhibition effect.

The polymer necessary for characterization was coagulated by adding, drop by drop, isopropanol to the latex and shaking. The polymer was then filtered off, washed exhaustively with water, and dried to constant weight in a desiccator.

The mean latex particle size was measured by light scattering using a laser radiation of 632.8 nm and a refractive index of 1.5 at this wavelength. Samples were prepared by diluting the latex in DDW at concentrations ca. 10^{-5} g/cm³.

Scanning electron microscopy (SEM) observations were performed on a Phillips SEM-505 scanning electron microscope. Samples were prepared by adding the appropriate amounts of water and SLS to the original latex. A droplet of the highly dilute dispersion was placed onto a glass cover and dried in vacuum. The samples were sputter-coated with a thin layer of gold in an argon atmosphere.

The glass transition temperature (T_g) was determined on a DuPont 910 Instrument differential scanning calorimeter at a heating rate of 10°C/min, using between 5 and 10 mg of the purified polymer.

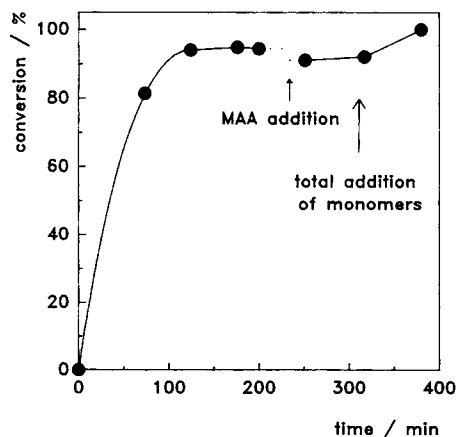


Figure 1 Time evolution of the conversion for the MMA/EA/MAA terpolymerization.

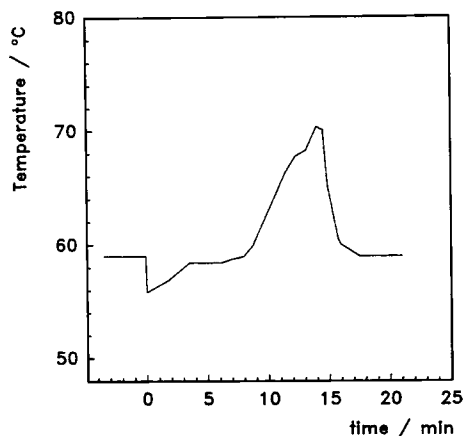


Figure 2 Time evolution of the reactor temperature in the MMA/EA/MAA terpolymerization in the first 20 min of reaction.

Minimum film formation temperature (MFT) was estimated using data reported in the literature for related systems.

The IR spectra was recorded on a Perkin-Elmer 580B spectrometer provided with an Infrared Data Station Model 3500. Samples were prepared dissolving a film of the latex or a fine purified powder in acetone or chloroform and letting the solvent evaporate putting on a CsI plate. Viscosity data of the latex, at a variable shear rate and different pH, were obtained with a Haake Rotovisco RV2.

The molecular weight was estimated from viscometric measurements using chloroform as a solvent at 25°C. The viscosity of the solutions was determined by means of a calibrated Ubbelohde-type viscometer. Data were analyzed with the usual Huggins' relationship:

$$\left(\frac{\eta_{sp}}{C}\right) = (\eta) + K \cdot (\eta)^2 \cdot C \quad (2)$$

where $\eta_{sp} = (\eta - \eta_0)/\eta_0$ is the specific viscosity; η and η_0 , the solution and solvent viscosities, respectively; (η) , the intrinsic viscosity; K , the Huggins coefficient; and C , the concentration of the polymer in grams per 100 mL. The surface tension of the latex was measured using a DuNoüy ring tensiometer at room temperature, after calibration with DDW.

RESULTS AND DISCUSSION

Time Evolution of Conversion and Reactor Temperature

Figure 1 presents the time evolution of the overall conversion during the emulsion polymerization, defined as follows:

Table II Latex Parameters

	Solids	D_p	pH	Density	γ
Acidic latex	47.7%	144 nm	5	1.08 g cm ⁻³	54 mN m ⁻¹
Basic latex	44.2%	158 nm	8	—	—

D_p : particle diameter (LS); γ : surface tension.

$$\frac{\% \text{ conversion}}{\text{total amount of polymer in the reactor}} = \frac{\text{total amount of monomers added in the reactor}}{\text{total amount of monomers added in the reactor}} \quad (3)$$

Calculations were corrected taking into account the previously extracted samples. The curve obtained until the MAA addition is similar to that reported previously.² It can be seen that total conversion is reached after 60 min of the total addition of the emulsion feed.

Figure 2 shows the time evolution of the temperature reactor, where it can be seen that after the initiator addition there is an induction time of about 6 min. If this moment is taken as the “zero” time, the maximum temperature (70°C) is reached at ca. 14 min. After this peak, the temperature drops to the thermostat value. It is interesting to note that the last part of the curve follows that of the time evolution of the free radicals in emulsion polymerization of MMA as determined by electronic spin resonance spectroscopy.¹⁰

It is well known that free-radical reactions are extremely rapid and highly exothermic. For this particular case, and taking into account the initial quantities of Table I, the heat of polymerization of monomers is 104.7 kJ and the heat capacity of the medium (water + monomers) is 1021 J/°C. Ignoring the small quantities of surfactant, buffer, and initiator, the calculated temperature increase on polymerization is 102°C, assuming that the reaction vessel is perfectly insulated and of zero heat capacity. However, the jump in temperature observed in the initial stage of the experiment was only 10°C. After this stage of polymerization was completed, the temperature dropped to the thermostat value and it was almost constant until the end of the synthesis.

Properties of the Latex

Table II presents parameters of both acidic and basic forms of latex. The scanning electron micrographs of diluted samples confirm the diameter of the latex particles determined by light scattering (LS) and show that the particles are narrowly dispersed (see Fig. 3).

Intrinsic Viscosity and Viscosity-average Molecular Weight

From the experimental flow times, the Huggins' equation was adjusted using least-squares regression analysis to give the following relation:

$$\left(\frac{\eta_{sp}}{C}\right) (\text{dL/g}) = 2.74 + 2.12 \cdot C \quad (r = 0.9994) \quad (4)$$

This relation and eq. (2) results in $(\eta) = 2.74 \text{ dL/g}$ and $K = 0.28$. The dependence of the intrinsic viscosity on the viscosity-average molecular weight of a polymer is given by the Mark-Houwink-Sakurada (MHS) equation, i.e.:

$$(\eta) = K' \cdot M^a \quad (5)$$

where K' and a are the empirical constants for the system studied. Unfortunately, these constants are not known for the investigated terpolymer. However, there are literature data for related systems, i.e., for poly(methyl methacrylate) (PMMA) and poly(ethyl acrylate) (PEA).¹¹ For the system MMA/EA, there is also available information between (η) values and the MMA/EA ratio.^{7,12} From this information, it is possible to estimate that the viscosity-average molecular weight of the MMA/EA/MAA system should be ca. 10^6 .

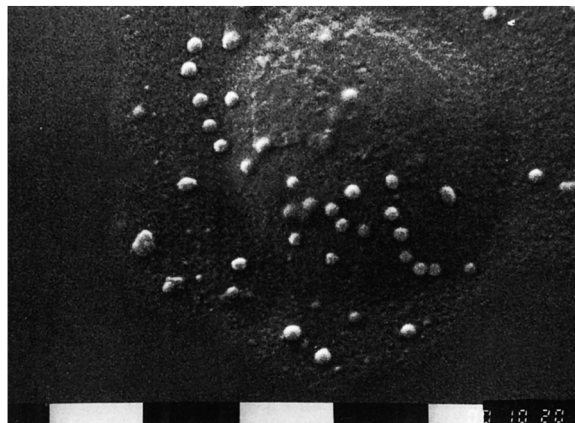


Figure 3 Scanning electron micrograph of the MMA/EA/MAA acidic latex. $\times 20K$. Bar equals 1 μm .

Infrared Spectra

A typical room temperature IR spectra in the 4000–200 cm^{-1} range of the latex film is shown in Figure 4. Wavenumbers of the IR absorption bands observed, as well as their tentative assignments and intensity, are reported in Table III. The IR spectra is similar to that reported in the literature for commercial “acrylic” latexes and for related systems.¹³

Some details of interest are the features observed at 1690 cm^{-1} as a shoulder (due to the low concentration) assigned to the stretching mode of the carbonyl bond of the carboxylic acid group, from the MAA contribution to the polymer. A fine structure is observed in the region between 815 and 750 cm^{-1} associated with the rocking mode of the $(-\text{CH}_2-)_n$ chains, with $n = 1, 2, 3$, etc.¹⁴

Glass Transition Temperature and Minimum Film Formation Temperature

The glass transition temperature (T_g) determined from the DSC curve is ca. 45°C. This temperature is comparable to the value of 47°C for the MMA/EA/AA (56/43/1) system.¹⁵

The minimum film formation temperature (MFT) of the latex could not be measured, but it can be estimated using data from the literature for the MMA/EA system,¹⁶ neglecting the MAA contribution to the T_g value. By fitting the reported data by a least-squares regression analysis, the following relation is obtained:

$$\text{MFT (}^\circ\text{C)} = 2.15 \cdot [\% \text{MMA}] - 84.0 \quad (r = 0.999) \quad (6)$$

Table III Wavenumbers, Assignments, and Intensity Observed in the IR Spectra of the MMA/EA/MAA Terpolymer Latex

Wavenumber (cm^{-1})	Assignment	Intensity
3442	$2\nu_{\text{C}=\text{O}}$	Weak
2985	ν_{aCH}	Strong
2952	ν_{sCH}	Strong
2880	ν_{CH}	Medium
2847	ν_{CH}	Medium
1735	$\nu_{\text{C}=\text{O}}$ (ester)	Very strong
1690	$\nu_{\text{C}=\text{O}}$ (acid)	Shoulder
1477	$\delta(\text{CH}_2) + \delta_{\alpha}(\alpha\text{-CH}_3)$	Shoulder
1450	$\delta(\text{CH}_2) + \delta_{\alpha}(\text{CH}_3\text{-O})$	Strong
1439	$\delta_{\text{s}}(\text{CH}_3\text{-O})$	Shoulder
1384	$\delta(\alpha\text{-CH}_3)$	Strong
1365	$\delta(\alpha\text{-CH}_3)$	Shoulder
1300	$\delta(\text{CH}_2)$	Shoulder
1266	$\delta_{\text{s}}(\alpha\text{-CH}_3)$	Shoulder
1243	$\nu_{\text{C}-\text{O}-\text{C}}$	Very strong
1178		Very strong
1160	$\nu_{\text{C}-\text{O}-\text{C}}$	Very strong
1100		Strong
1026		Medium
990	$\gamma_{\text{r}}(\text{CH}_3\text{-O})$	Shoulder
969	$\gamma_{\text{r}}(\alpha\text{-CH}_3)$	Weak
914		Weak
852		Weak
815	$\gamma_{\text{r}}(\text{CH}_2)$	Weak
780	$\gamma_{\text{r}}(\text{CH}_2)$	Shoulder
750	$\gamma_{\text{r}}(\text{CH}_2)$	Weak

where [%MMA] is the porcentual composition of MMA in the system. In the present case, its value is ca. 55–56% and the estimated MFT is ca. 34–

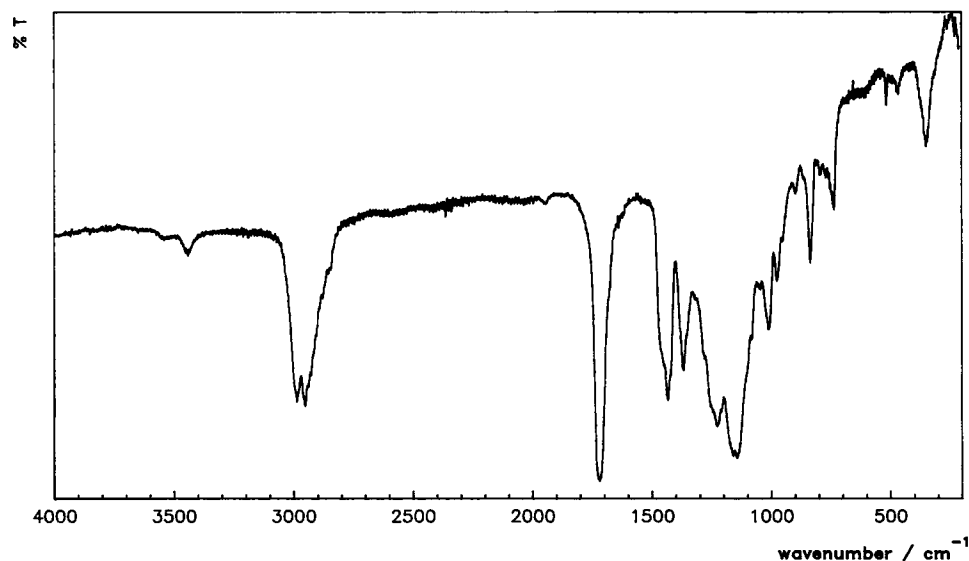


Figure 4 IR spectra of the film obtained from the latex MMA/EA/MAA.

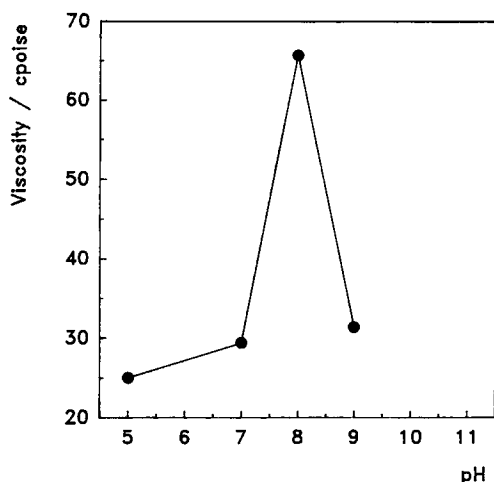


Figure 5 Viscosity dependence on pH for MMA/EA/MAA latex at $\dot{\gamma} = 300 \text{ s}^{-1}$.

36°C. Water and surfactant generally decrease the MFT, and by comparing with the MMA/EA/AA (56/43/1) system,¹⁵ a value of ca. 30°C is expected.

Latex Rheology

Latexes with a small amount of monomer containing a carboxylic group (known as "carboxylic latexes") significantly increase the viscosity upon neutralization with a base like ammonia.¹⁷ The addition of a few percent of an acid monomer (MAA in this case) during the synthesis improves the freeze-thaw and mechanical stability of the product.^{17,18} The presence of acid groups also enhances adhesion and increases the critical pigment volume concentration (CPVC) value.¹⁹

As the MAA is added in the latter stages of the process, acid moieties are on the surface of the latex particles. With the addition of ammonia, the acid moieties expand due to electrostatic repulsions, increasing the effective volume fraction of the latex and, therefore, the viscosity of the system. In this case, the MMA/EA/MAA latex displays a non-Newtonian, pseudoplastic flow (i.e., a decrease in viscosity with increasing shear rate).

Figure 5 shows the latex viscosity at different pH values. The viscosity passes through a maximum at about pH 8–9 as a result of the electroviscous effect and then decreases by dissolution of dispersion particles.¹⁷

CONCLUDING REMARKS

A semicontinuous emulsion terpolymerization of MMA, EA, and MAA with a variable monomer addition rate to achieve a homogeneous terpolymer has been carried out. Both kinetics and final properties

of the latex were considered. The method produces a stable high solid latex dispersion with a polymer with high molecular weight and a complete conversion at relatively low temperature. Works are in progress to compare the results obtained in this case (with the variable monomer rate addition) with those from copolymerization carried out under different conditions.

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