

Reaction calorimetry as a tool to determine diffusion of vegetable oil macromonomers in emulsion polymerization

Carolina Quintero, D. Delatte, K. Diamond, S.K. Mendon, J.W. Rawlins*, S.F. Thames

*The University of Southern Mississippi, School of Polymers and High Performance Materials,
118 College Drive #10037, Hattiesburg, MS 39406-0001, USA*

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Abstract

Reaction calorimetry proved to be a useful technique to determine unsaturated macromonomer incorporation in emulsion polymerization. Vegetable oil macromonomer (VOMM) incorporation into emulsion polymerization is complicated by diffusion issues through the aqueous phase. Special techniques such as high shear and miniemulsion polymerization assist incorporating VOMM into latexes, but the film performance resembles polymer blends rather than crosslinked systems. Fatty acid surfactants with different ethoxylate lengths were acrylated and used as model macromonomers for this study. Monomer diffusion through the water phase was investigated by monitoring particle size, residual monomer, and heat evolution during polymerization using dynamic laser light scattering, gas chromatography, and reaction calorimetry, respectively. Macromolecules of lower hydrophobicity incorporated better in conventional emulsion polymerization. No special technique was required to obtain coagulum-free latexes and glossy films. Specifically for acrylated fatty acids, an average ethoxylate chain of 10 units was sufficient to facilitate diffusion through the aqueous phase.

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1. Introduction

Coalescing agents are often required in waterborne coating to achieve good film formation. These coalescing agents are classified as volatile organic compounds (VOCs), and the search for “green” alternatives has been the focus of extensive research. Manipulation of particle morphologies such as core-shell polymers with hard cores and soft shells [1], core-shell polymers with a functionalized core (e.g., oil-modified polyester and urethane) [2], latex blends of hard and soft polymers [3,4], and acrylic hybrid latexes [5,6] have had some success, however, low temperature coalescence without the use of solvents remained elusive.

Vegetable oil macromonomers (VOMMs) incorporated into latex polymers are effective in reducing the volatile organic compounds in waterborne coatings. VOMMs possess multiple functionalities including acrylic, alkyl, and allylic moieties that result in unique kinetic, thermodynamic, and mechanical

properties. The acrylate group allows the VOMM to be copolymerized into the polymer backbone, the alkyl moieties impart internal plasticization during film formation, and the residual unsaturation provides a mechanism for oxidative curing post application. Thus, VOMMs are non-fugitive, oxygen-responsive plasticizers that crosslink after application, resulting in property development over time.

VOMMs by nature are highly hydrophobic, consequently, their incorporation into emulsion polymerization poses challenges since monomer transfer through the aqueous phase is essential for random copolymerization. Special techniques involving high shear preemulsion preparation and miniemulsion polymerization have been employed to copolymerize a variety of hydrophobic monomers including VOMMs [7,8]. However, the final properties of these early VOMM latexes resemble polymer blends rather than crosslinked systems. It is believed that VOMM hydrophobicity prevents its diffusion to the growing particles, and VOMMs remain concentrated in monomer droplets.

Given the system's complexity, determining whether a specific molecule has been incorporated through emulsion polymerization is very difficult. Molecular tags in combination

* Corresponding author. Tel.: +1 601 266 4781; fax: +1 601 266 5880.
E-mail address: james.rawlins@usm.edu (J.W. Rawlins).

with methods such as fluorescence microscopy and internal reflectance infrared (IRIR) spectroscopy have been used to study mechanistic details of emulsion polymerization [9–12]. However, the use of tags alters the hydrophobic–hydrophilic nature of the molecule, further complicating the investigation. Previous research in our labs established that unsaturated molecules participate in degradative chain transfer during polymerization [13]. This paper, using reaction calorimetry, exploits the chain transfer effect and uses it to monitor the incorporation of model compounds with varying hydrophilicity synthesized from unsaturated non-ionic surfactant molecules.

2. Experimental

2.1. Materials

Chemicals were purchased or acquired from several vendors throughout this research project and are organized predominantly by vendor name. All chemicals were used as received unless otherwise noted.

Sodium carbonate, ammonium persulfate, methyl methacrylate, butyl acrylate, *t*-dodecanethiol, and hexanediol diacrylate (HDDA) were purchased from Sigma–Aldrich. Rhodapex® CO-436 was purchased from Rhodia. Irgacure® 651 was purchased from Ciba.

2.2. Macromonomer synthesis

The chemicals used for macromonomer synthesis were obtained from Aldrich unless otherwise stated. Materials include oleic and stearic acid derived surfactants with average of 5 ethoxylate repeat units, termed EO-5 and ES-5, respectively, and 10 ethoxylate repeat units, termed EO-10 and ES-10, acryloyl chloride, triethylamine (TEA), and methylene chloride (Fisher). All chemicals were used as received.

Macromonomers EOA-5, EOA-10 (unsaturated via oleic acid basis) and ESA-5, ESA-10 (saturated via the stearic acid building block) were prepared via acrylation of hydroxyl functional groups with acryloyl chloride (Fig. 1). The reaction was performed in a 1000 mL three-necked, round-bottom flask equipped with a 500 mL addition funnel, a mechanical stirrer, and an ice bath. Non-ionic surfactant, TEA, and methylene chloride were added to the flask, and acryloyl chloride was introduced dropwise over a 2-h period and then set overnight. Methylene chloride was introduced as a solvent and triethylamine as an HCl scavenger. The methylene chloride and excess acryloyl chloride were removed under reduced pressure. The reaction mixture was transferred to a separatory funnel and washed with brine solution (NaCl, 2 M) in equal portions.

2.3. Emulsion polymerization for GC and particle size analysis

Semi-batch polymerization was conducted to follow monomer consumption and particle size analysis throughout the process. Water, surfactant (Rhodapex® CO-436), buffer, and macromonomer were charged into a 1 L glass kettle and heated to 80 °C under shear while purging with N₂. The preemulsion and initiator feed were added over 2 and 2.5 h, respectively. Magnetic agitation (low shear) was used to mix the preemulsion (water, surfactant, butyl acrylate, and methyl methacrylate). Samples were taken throughout the polymerization for GC and particle size analysis. Particle size and distribution were determined using dynamic light scattering on a Microtrac UPA 250.

2.4. Emulsion polymerization in Mettler Toledo's reaction calorimeter RC-1e™

Batch polymerization was implemented for kinetic analysis. The kettle contents were prepared by adding water, surfactant, buffer, butyl acrylate, methyl methacrylate, and macromonomer into a beaker and submitting it either to low shear (magnetic stirrer) or high shear (Lightnin® mixer at 18,000 rpm) for 5 min. The contents were added into the RC-1e for heating (70 °C) and calibration. The initiator solution was added via a syringe pump over 2 h.

2.5. Analytical techniques

2.5.1. ¹H NMR spectroscopy

Structural characterization of surfactants and acrylated macromonomers was performed via ¹H NMR using a Bruker 300 MHz NMR spectrometer. Deuterated acetone was used as the solvent. The ¹H spectra for both S-5 and S-10 have characteristic peaks at $\delta = 3.45$ ppm which is attributed to the RCH₂-OH proton, (no. 8 in Fig. 2a and c). This peak is absent from the macromonomer spectra (Fig. 2b and d), while peaks develop at $\delta = 4.2$ ppm and between $\delta = 5.8$ –6.4 ppm, each attributed to the CH₂CHCOOCH₂R proton (no. 10), and the vinylic protons of the acrylate group (nos. 11 and 12).

2.5.2. Radical reactivity screening using photo-differential scanning calorimetry (photo-DSC)

Photo-DSC was used to investigate bulk macromonomer copolymerization. Monomer blends with 1 wt% Irgacure® 651 (photoinitiator based upon 2,2-dimethoxy-1,2-diphenylethan-1-one) were prepared, 2 mg of blended raw materials were placed in a DSC pan and purged under N₂ for 5 min before exposing to ultraviolet (UV) light supplied by a medium pressure mercury lamp. The UV light was filtered to ensure that the sample

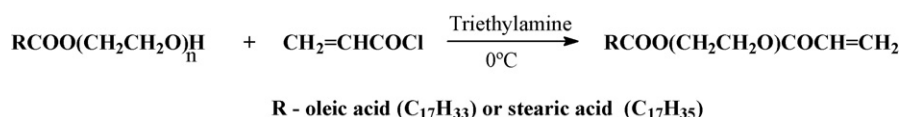


Fig. 1. Model structure for saturated and unsaturated compounds.

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