Characterization of the Initial Conditions in Emulsion Polymerization:
Loci for Particle Nucleation

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1 INTRODUCTION

Emulsion Polymerization is a process of considerable industrial importance used in the manufacture of a wide range of products including paint, toner, adhesives, coatings and other synthetic materials. Particle nucleation is the forcing function in emulsion polymerization processes and as such it plays a significant role in the development of most of the properties of the final latex[1]. Particle nucleation is not fully understood and as such it remains an area of active research[1,2]. The main locus for particle nucleation in emulsion polymerization is a subject of considerable controversy. Different theories advocate different loci[1,2]. The work reported herein focuses on the characterization of the reactor conditions in terms of the liquid-liquid emulsion existing prior the addition of the initiator. Because of its high-resolution capabilities a real time spectroscopy technique has been implemented to obtain the chemical composition, particle number and the particle size distribution of the liquid-liquid emulsions. The experimental results for a variety of initial conditions suggest the presence of at least two distinct populations within the initial emulsion: a previously unidentified nano-droplet population of size range 30 to 100nm, and a large-droplet population of the oil with mean sizes in the 1-10 μm range. The nano-droplet populations were also found to contain 18 to 70 % of the dispersed phase depending upon the emulsification conditions.

2. APPROACH

2.1 Model Emulsion Systems

Two emulsion systems have been investigated: liquid-liquid emulsions prepared with monomers, and oil-in-water emulsions prepared with non-reacting model systems. Model emulsion systems are comprised of linear hydrocarbons, which under emulsification conditions typical of emulsion polymerization processes show dispersion characteristics similar to those of monomers, but have the added advantage of transparency in the Uv-vis portion of the electromagnetic spectrum. The data reported herein is for the Decane-in-water model system. The physico-chemical properties used as criteria for the selection of model systems typically include solubility in water, viscosity, density, and vapor pressure. Transparency in the Uv-vis portion of the spectrum implies favorable conditions for the detection, location, and quantification of chromophoric molecules such as emulsifiers and initiators. The variables explored for the preparation of the emulsion include pH of the continuous medium, temperature of emulsification, and Surfactant to Oil ratio.

2.2 Emulsion Characterization Technique.

There are several techniques available for the characterization of the particle size distribution: Angular light scattering, dynamic light scattering, and transmission electron

microscopy are the most widely used. Unfortunately, these techniques do not provide direct estimates of the particle counts, and in some cases, extensive sample preparations (i.e., vacuum evaporation) are required when monomer-rich polymer particles are to be analyzed. This problem is compounded for liquid-liquid emulsions, and when the dispersed phase has a high vapor pressure. Due to its size resolution, electron microscopy is often used to characterize early stages of particle formation. Unfortunately the issues of representative sampling, and sample integrity limit the applicability of this technique.

Light scattering techniques, and in particular laser light scattering methods, are very powerful. However, in the presence of broad particle size distributions, or in the presence of large particles, the fraction of small particles tends to be underestimated. This is due to the fact that the smaller droplets scatter less light, and therefore their contribution to the total scattered light signal tends to be small, making it difficult to quantify them. Spectroscopy techniques do not suffer this limitation to the same extent. The reason being that smaller particles absorb more light than large particles and therefore compensate the total attenuation making it possible to differentiate large and small particle populations. Multiwavelength Uv-vis spectroscopy is ideally suited for the characterization of the emulsions for the following reasons:

1. Modern spectrometers equipped with diode array technology enable the acquisition of the Uv-vis spectrum over a broad range of wavelengths with excellent resolution.

2.   The short measurement times of modern spectrometers enable real-time continuous monitoring applications.

3. The resolution in terms of particle sizes is   proportional to the size parameter α, where
α =D/λ. Therefore spectroscopy measurements over a broad range of wavelengths result in a large dynamic range for particle analysis.

4. In addition to the dynamic range for scattering, the absorption component, due to the presence of naturally occurring chromophores and/or labeled molecules, provides quantitative information for the estimation of the concentration of the chromophoric groups.

Uv vis Spectroscopic techniques have been successfully implemented to characterize the particle size distribution of a large variety of particulate systems such as polymer lattices[3], protein aggregates[4], SiO_2 particles[5], whole blood- and blood components[6] and liquid-liquid emulsions[7]. The results from theses studies have been validated using Scanning Electron Microscopy (SEM)[7], Osmium tetra oxide [7], particle counters[8] , and other methods[9-13].

2.3 Spectroscopy Interpretation Model

The Turbidity equation relating the optical density to the normalized particle size distribution for the homogeneous particles at a particular wavelength as given by Kerker[9] was extended as shown in equation 1 for an emulsion containing M populations, such that each of the population can be characterized by its corresponding absorption and scattering components. The turbidity spectrum of an emulsion can be written in terms of M distinct populations[14,15]:

$$\tau(\lambda_0) = N_p \ell \left(\frac{\pi}{4}\right) \sum_{i=1}^{M} x_i \int_0^\infty Q_{ext,i}(m_i(\lambda_0), D) D^2 f_i(D) dD$$

(1)

Where ℓ is the pathlength, D represents the particle diameter, Q_{ext} corresponds to the Mie extinction efficiency, and N_p is the number of particles per unit volume. The total extinction efficiency, $Q_{ext}(m(\lambda_o),D)$ is a function of the optical properties of the particles and suspending medium through the complex refractive index, $m(\lambda_o)$[15].

$$m(\lambda_0) = \frac{n(\lambda_0) + i\kappa(\lambda_0)}{n_0(\lambda_0)}$$

(2)

where $n(\lambda_o)$ and $\kappa(\lambda_0)$ represent the real and imaginary components of the complex refractive index of the particles and $n_o(\lambda_o)$ represents the real refractive index of the suspending medium.

x_i (i = 1 → M) is the number fraction corresponding to each population such that,

$$\sum_{i=1}^{M} x_i = 1$$

(3)

The real and imaginary parts of the complex refractive index m are functions of the chemical composition and can be calculated as a weighted sum of the contributions from the chromophores within each population,

$$n_i = \sum_{j=1}^{N_i} \omega_{ij} n_{ij}$$

(4)

$$k_i = \sum_{j=1}^{N_i} \omega_{ij} k_{ij}$$

(5)

where ω_{ij} represents the mass fraction of jth chromophore contained in the ith population, n_i and k_i correspond to the real and imaginary refractive indices of each population, and N_i represents the total number of chromophoric groups in the ith population. It is important to note that the additivity of the optical properties applies only within each population. Adding the scattering contributions represented by equations (3-6) closes the total mass balance for each chromophoric group. Assuming volume additivity, the total concentration of any chromophoric group can be readily calculated in terms of the concentration of each population c_i:

$$c_{total} = \sum_{i=1}^{M} c_i$$

(6)

The optical properties of the continuous phase at the reaction conditions were estimated using the expression developed by P. Scheibener[16]. The optical properties of decane at different temperatures were estimated using the Sellimeir-Drude equation[7]. The procedures for calculating the optical properties of the continuous phase and decane are given in Shastry[16].

3 MATERIALS AND METHODS

3.1 Materials and Equipments

Phosphate buffer saline (PBS) used as the continuous phase was obtained from the Florida Blood Services. Spectral grade Decane, Sodium Dodecyl Benzene Sulfonate were obtained from Sigma Aldrich. HCl and NaOH were obtained from Fisher Scientific.
The emulsion was prepared in a 500 ml glass reactor. An electric temperature controller was used to adjust the heat to the jacket to maintain a desired constant temperature inside the reactor. Two baffles were introduced in the reactor for breaking the vortex due to agitation. The stirrer rod passed through the central opening of the reactor lid. A motor rotates the stirrer providing constant agitation at 500 RPM. The rate of rotation was verified with a stroboscope for each experiment. A sample slip-stream, drawn continuously from the reactor with the help of the sample pump was sent to an automatic sampling and dilution system dilution system[21] where it was diluted with the suspending medium. The temperature of the diluent was maintained the same as that of the emulsion. The flow rates of the diluent stream and the sample slip-stream were such that the transmission spectrum of the diluted emulsion always was within the linear range of the spectrometer. The spectrometer used was a HP8452A Uv-vis Hewlett Packard spectrometer with a resolution of 2nm and an acceptance angle smaller than 2^0. The sample cell holder of the spectrometer was also maintained at the desired temperature with an electrical temperature controller manufactured by Perkin Elmer (Model: C5700820). All hoses and tubes were insulated with glass fiber to minimize heat losses. The pH of the suspending medium and the diluent was monitored with a Fisher (Fisher accumet model: 610) pH meter. The two surface tensiometer probes, through which nitrogen was bubbled, were placed in the reactor to measure the interfacial tension of the emulsion.

3.2 Methods

The emulsions were prepared in Phosphate buffer saline buffer (PBS). The pH of the PBS buffer was adjusted using either HCl or NaOH. The emulsions were prepared by adding 150 ml of the suspending medium to the 500ml glass reactor placed in the temperature-controlled jacket. Additional 30 ml of the appropriate surfactant solution were added to the suspending medium. The surfactant solution was prepared at different surfactant concentrations. The contents in the reactor were heated until the desired temperature was reached. At this point, 160 ml of decane were added. The reactor contents were kept under continuous agitation at 500 RPM to form the emulsion. After verifying that the emulsion was stable, it was sampled for analytical purposes. A sample of the emulsion inside the reactor was pumped into the dilution-measurement system with a rotary peristaltic pump so that the transmission spectrum of the emulsions could be obtained within the linear range of the spectrometer. At the desired time intervals the spectra were recorded and saved for further analysis.

3.3 Experimental Conditions

Emulsions were prepared at different emulsification conditions of Surfactant to Oil ratio, pH of the continuous medium and Temperature. Designed experiments were performed with the lower and upper limits of the surfactant to oil ratio as 0.0154 to 0.046. The pH of the continuous medium was varied from 2 to 10 and the temperature was varied from 22, 50 to 60 Deg C. The Decane to PBS ratio was maintained constant at 0.71 by weight.

4 RESULTS AND DISCUSSION

The measured spectra of the emulsions, and therefore the relative populations of nano-droplets and large droplets change dramatically as a result from the differences in emulsification conditions due to temperature, surfactant concentration and pH of the suspending medium. Figure 1 shows a sample of typical spectra recorded as function of the emulsifier concentration at neutral pH and constant temperature. Figures 2 and 3 show typical comparisons between measured and calculated spectra of Decane-in-Water emulsions at the two extremes of the selected experimental conditions. The excellent agreement found further justifies the presence of at least two distinct droplet populations. Notice the changes in the amplitude of the contribution of the small particle population to the total spectrum. These changes in amplitude reflect changes in the relative concentration of large to small particles.

Emulsifier concentration, temperature, and pH are known to affect the distribution of emulsifier between the oil and the water phase. Therefore it is of interest to explore the effect of these variables on the relative concentrations of the two populations identified. The ratio of surfactant/oil has a considerable effect on the size and concentration of the nano-droplet population. As the surfactant to oil ratio is increased, the size of the nano-droplets varies from approximately 30-110 nm. The mean diameter of the small particle populations at the high surfactant to oil ratio was around 30 nm in diameter whereas at low surfactant to oil ratio, it was measured to be 100 to 110 nm. Similarly, at low surfactant to oil ratios only 18% of the dispersed phase is present in the small particles while the emulsion recipes with a higher surfactant to oil ratio, it was about 70 to 80%. Over the range of the variables investigated, pH and temperature have small to negligible effects. Clearly, most of the effects caused by the distribution of the emulsifier between the two populations are due to the relative concentration of the emulsifier.
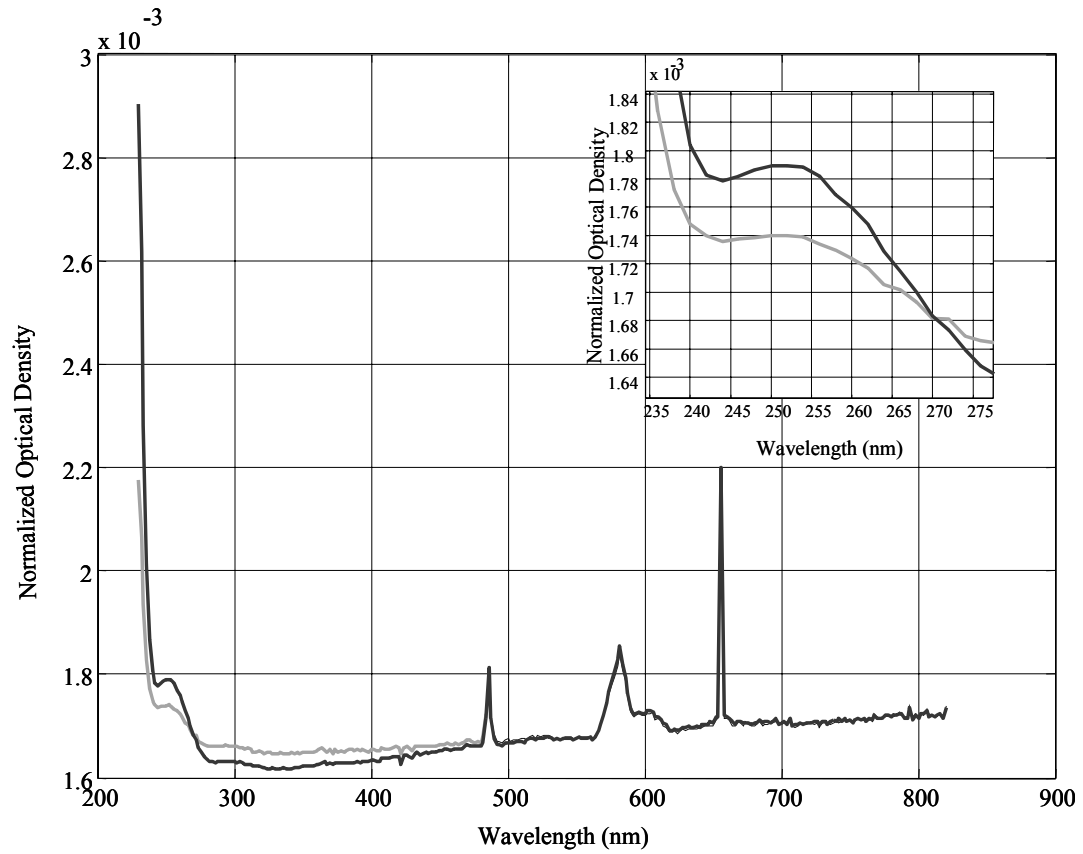
Figure1. Comparison of the Transmission Spectra of the Emulsions prepared with different emulsifier concentrations. The difference in the spectral features of the emulsions due to the difference in the emulsifier concentration is highlighted in the insert.
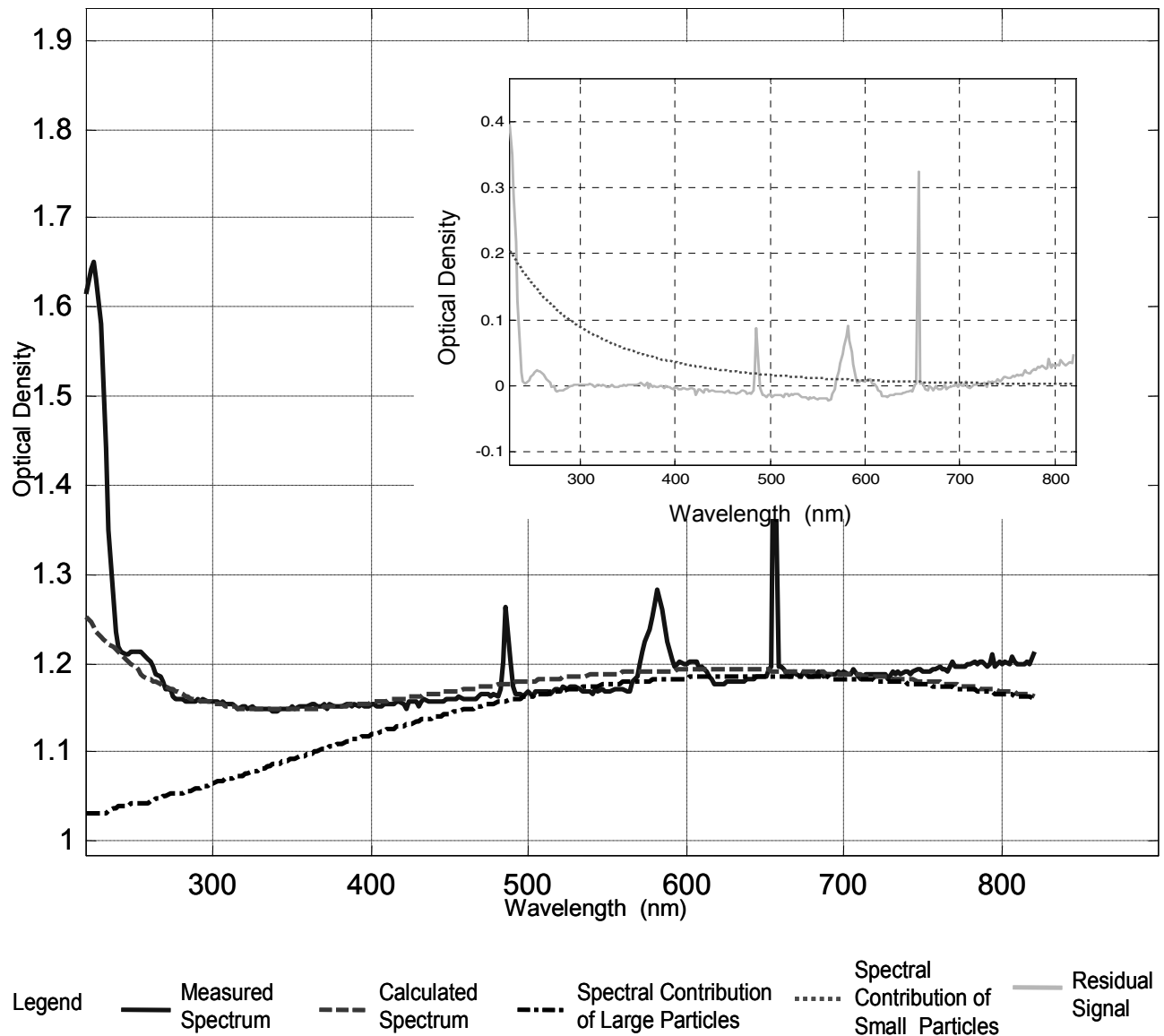
Figure 2 Comparison of the Measured Transmission Uv vis Spectrum with the Estimated Spectrum for the Decane in PBS Emulsion prepared at the Emulsification Conditions such that (S/O = 0.0154 T = 50 Deg C and pH =2). The contribution to the spectral signal by the small particles and the residual signal is shown in the insert. The Estimated Spectral Contributions of the Large and the Small Droplet Population add up to the Estimated Spectrum. The Residual Spectral features show the presence of Surfactant.
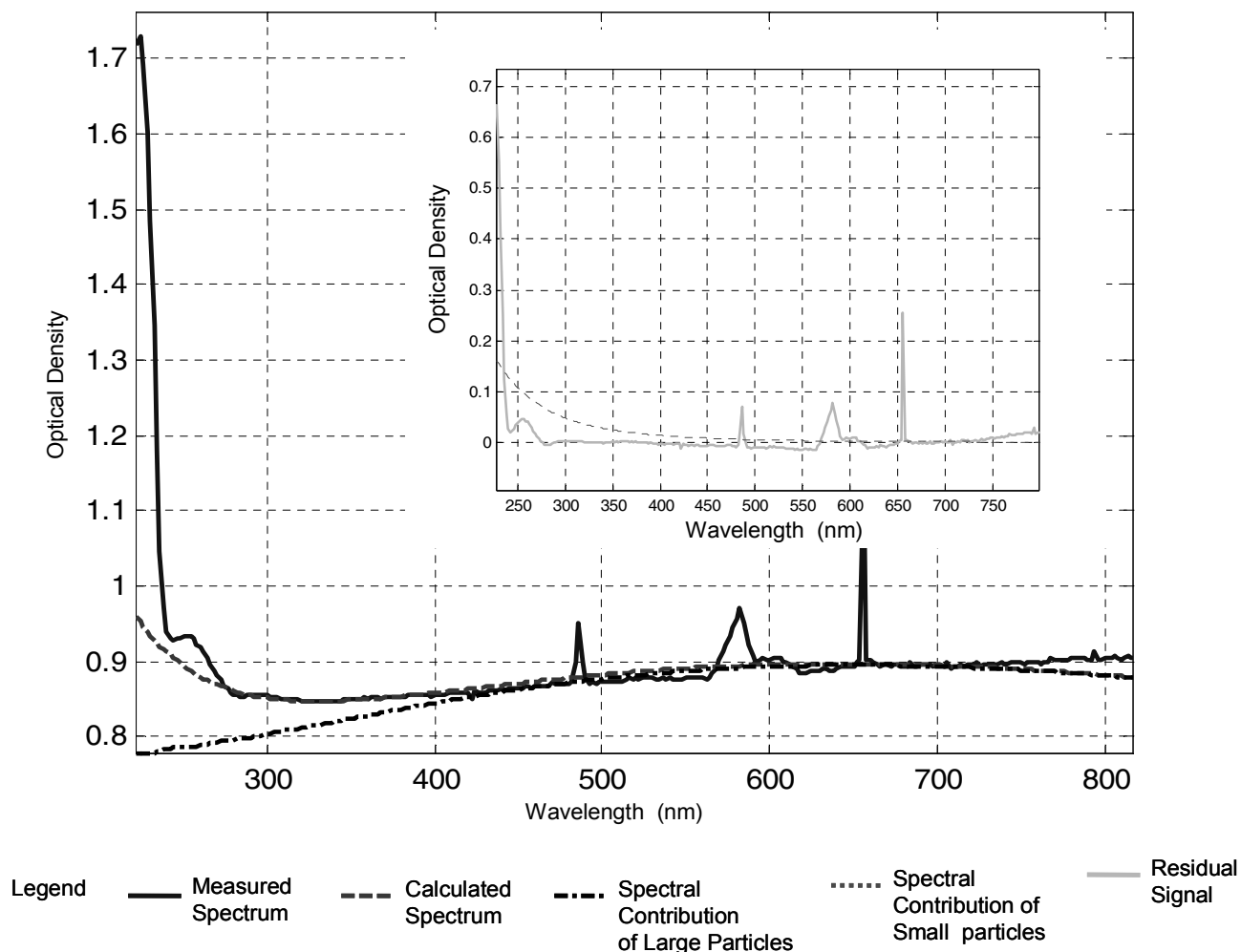
Figure 3. Comparison of the Measured Transmission Uv vis Spectrum with the Estimated Spectrum for the Decane in PBS Emulsion prepared at the Emulsification Conditions such that (S/O = 0.046 T = 60 Deg C and pH =10). The contribution to the spectral signal by the small particles and the residual signal is shown in the insert. The Estimated Spectral Contributions of the Large and the Small Droplet Population add up to the Estimated Spectrum. The Residual Spectral features show the presence of Surfactant.

5 CONCLUSIONS

Nano-droplet population with mean droplet size between 30 to 100 nm containing large fractions of the oil phase has been identified for the first time. Both, the small size with a concomitant large surface area and the high proportion of the oil phase present in the nano-droplet population make the nano-droplet population a strong candidate for being the main nucleation locus in emulsion polymerization processes. Clearly, better control in the formation of the of the initial emulsion will enable better control and design of polymerization reactions.

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