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Photopolymerization of butyl acrylate-in-water microemulsions: Polymer molecular weight and end-groups

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Abstract

Solubilization of butyl acrylate in water using sodium dodecyl sulfate (SDS) and 1-pentanol produced transparent oil-in-water microemulsions stable at room temperature. These microemulsions were polymerized using a two-component water-soluble initiator system comprising of Rose Bengal (RB) and methyldiethanolamine (MDEA). These compounds undergo photo-induced electron transfer upon absorption of visible light to produce amine radicals active in free radical polymerization. Analysis of the NMR spectra of polymers revealed only monomer peaks and amine fragments which were incorporated as the polymer ends. Effect of initiator composition on polymer length was also investigated using GPC. When RB concentration was increased with constant concentration of excess MDEA, the average chain length decreased up to a specific concentration where after the polymer length reached an asymptotic value. Experiments were performed to identify this asymptotic value and it was observed that as the MDEA concentration was increased, the asymptotic values of number average degree of polymerization decreased.
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1. Introduction

Microemulsions are thermodynamically stable, optically clear dispersions of organic and aqueous medium which may form spontaneously with an appropriate combination of surfactants and cosurfactants (typically short-chain alcohols) [1]. The role of these surfactant/cosurfactant mixtures is to lower the interfacial tension between the two immiscible liquids to ultra-low values (as low as 0.001 dyn/cm) that allow very small droplets (typically in the 10–100 nm range) of the dispersed domain to form [2]. Microemulsions exhibit low viscosity, and the small droplet size maintains efficient heat transfer from the droplets to the continuous domain [3]. It is widely known that microemulsions may form different phase structures, most notably, oil-in-water (o/w); bicontinuous; and water-in-oil (w/o) (for excellent description of microemulsion phase structures and their potential applications), see Refs. [1,2,4–8]. It is important to distinguish between microemulsions and the more common type of emulsions that have been used in polymerization for decades. In contrast to microemulsions, the emulsions are turbid or opaque, and contain relatively large droplets (whose diameters fall in the range of 0.2–10 μm [9]), and therefore may require mechanical agitation to prevent agglomeration.

The unique properties exhibited by microemulsions make them attractive for a variety of applications, including polymerizations. In addition to previously mentioned properties (efficient heat transfer, low viscosity, etc.), microemulsions possess an extraordinarily large interfacial area (on the order of 100 m^2/g) [10], and therefore active centers and other reactive species can efficiently react interfacially with the organic monomer. These properties and attributes of the microemulsion polymerizations are significantly different from either solution polymerization or conventional emulsion polymerization. Over the past two decades, a number of authors have reported the use of thermally-initiated microemulsion polymerizations to achieve high reaction rates and high molecular weight polymers. The first systematic studies of microemulsion polymerizations were reported in 1981 by Atik and Thomas who carried out polymerizations of styrene-in-water microemulsions initiated with oil-soluble initiators [11]. Subsequent research by a number of authors, including Kaler and collaborators [12,13], Capek et al. [3,14–17], Co and collaborators [18], and Pokhriyal et al. [19], has focused

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mainly upon characterizing the kinetics in microemulsion polymerization systems, and has identified the significant variables that control the reaction kinetics, including the initiator type (water-soluble/oil-soluble), surfactant type and formulation, the nature and concentration of additives and other constituents in the microemulsion [12,15,19,20]. In addition, detailed kinetic models that describe the reaction mechanism and predict the rate of polymerization (and therefore the monomer conversion) as a function of initiator concentration and time have been reported for some microemulsion polymerization systems [12,20,21].

Photopolymerizations are reactions in which the initiating free radical active centers are generated using light, rather than heat, resulting in rapid and energy-efficient initiation of the polymerizations. Light-induced initiation is typically achieved by the addition of small amounts of a photoinitiator that produces active centers upon absorption of a photon of the appropriate wavelength. Use of light to produce active centers provides both spatial and temporal control of initiation since light can be directed to locations of interest and can be shuttered at will [22,23]. It is notable that since the initiating energy is provided by light rather than heat, the rate of active center production is independent of temperature. This is significant for microemulsion polymerizations since the phase behavior of microemulsions can greatly depend upon temperature.

The fact that microemulsions are optically clear makes them attractive for photoinitiated polymerizations. As described above, the vast majority of the papers on microemulsion polymerizations focus primarily on thermally-initiated polymerizations, however there have been a few reports available on photoinitiated microemulsion polymerizations, most notably by Capek et al. [24–26]. This group of investigators has reported studies on photopolymerizations through direct photolysis of butyl acrylate monomer in o/w microemulsions. These authors have used UV light to initiate reactions and have investigated the effect of reaction conditions and presence of additives on the rate of polymerization, particle size and final conversion. In addition, Kuo et al. have provided an extensive characterization of the photoinitiated polymerization of styrene in microemulsions using oil-soluble initiators and UV light [27]. These authors have investigated polymerization kinetics and have developed empirical relationships relating the degree of polymerization and the rate of polymerization to the initiator concentration and light intensity. More recently, David et al. have reported studies of photopolymerization of methacrylates in microemulsions using UV light [28]. These investigators have produced latexes of copolymers of methacrylates and acetylethylenimines and have presented methods to incorporate macromers in the polymer chains.

In this contribution, we present the free radical microemulsion photopolymerizations of butyl acrylate as a proof-of-concept example of a potentially simple and cost-effective route to vinyl addition polymers with controlled molecular architecture. In particular, we are focusing on methods to provide controlled molecular weight while imparting specific reactive end-group functionality (hydroxyl groups in this case). We believe this class of architecturally controlled polymers may have significant utility in a variety of important technological applications, including high performance, low-VOC acrylic thermoset coatings. Butyl acrylate was selected as the model monomer because it is a relatively non-volatile water-insoluble monomer that undergoes free radical polymerization and termination almost exclusively by combination. The water soluble two-component initiator system of Rose Bengal (RB) and methyldiethanolamine (MDEA) was selected because the components provide the desired hydroxyl end-functionality, and because the effective initiating wavelengths are in the visible region of the spectrum, which minimizes the deleterious effects of light scattering and prevents absorption of the initiating light by the monomer. Microemulsion polymerization was selected because (1) it provides an environmentally friendly, water-based and low cost polymerization medium, and (2) high interfacial area is available to facilitate interfacial transport of hydrophilic initiating species (with polar functional groups) to react with hydrophobic monomers.

We have investigated the effect of the initiator concentration on the resulting polymer molecular weight, and have characterized the polymer end-groups to determine the active initiating radical. The formation of the butyl acrylate-in-water microemulsions and the characterization of the resulting polymers are described below.

2. Experimental

2.1. Materials

Reagent-grade sodium dodecyl sulfate (SDS), 1-pentanol, Rose Bengal (RB) and methyldiethanolamine (MDEA), all obtained from Aldrich, were used as received. Rose Bengal is a xanthenic water-soluble dye that exhibits a prominent absorption peak in the visible region (~549 nm). In addition to the presence of hydroxyl functionalities, MDEA was selected as the electron donor because electron transfer from the MDEA to the excited state of RB is thermodynamically feasible. The monomer *n*-butyl acrylate was obtained from Aldrich and treated with dehibitor (DeHibit 200, obtained from Polysciences, Inc.) before use. Polystyrene standards for GPC studies were obtained from Polysciences, Inc. Double distilled and deionized water was used for preparation of all microemulsions.

2.2. Microemulsion preparation and characterization

Microemulsions used in polymerization studies contained 0.09 g/(mL water) of butyl acrylate, 0.2 g/(mL water) of SDS, and 0.6 g/(mL water) of 1-pentanol at 22 °C temperature. The undiluted microemulsions were characterized by using dynamic light scattering (DLS) to determine the approximate droplet size distribution. The experiments have been conducted using an ALV-NIBS/HPPS instrument equipped with a helium–neon laser with output at 632.8 nm and an ALV-5000/E multiple tau digital correlator.

2.3. Polymerization technique

Batch polymerizations were carried out at 22 °C using visible light obtained from a 200 W mercury–xenon lamp. A two-component initiator system consisting of Rose Bengal and methyldiethanolamine had been selected for polymerizations. The initiator concentration was varied as indicated later. All polymerization experiments were performed in 25 mL glass vials and the reaction mixture was continuously stirred during polymerization to ensure uniform exposure to light. A 380 nm long pass filter was used in all the experiments to block UV light to ensure that only Rose Bengal absorbed photons. The system was bubbled with nitrogen for 180 s prior to polymerization. All the polymerizations were carried out for 5 h. For all experiments, the microemulsions were initially transparent with a red hue, and became light yellow and opaque (due to light scattering indicative of the polymerization reaction) upon illumination with the initiating light.

2.4. Polymer separation and characterization

After the polymerization, the mixture spontaneously separated into a viscous opaque gel-like polymer phase and an aqueous phase.

This polymerized mixture was dialyzed in a regenerate cellulose Spectra/Por6 dialysis wet membrane (Fisher Scientific). A regenerate cellulose membrane is efficient for samples containing high percentage of organic solvents. This membrane was effectively able to retain the polymer as the remaining components passed through. The mixture was suspended inside the membrane for 24 h for complete separation of polymer. The separated polymer was subsequently successively washed three times with methanol and water to remove traces of SDS, pentanol, unreacted monomer, and any other reaction species. The polymer was then characterized using nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). NMR spectroscopy was performed using a Bruker Avance, DRX-400, operating at ^{1}H frequency of 400.13 MHz. The NMR spectra of the individual microemulsion components (in deuterated chloroform) were obtained to facilitate the NMR peak assignments.

A PLgel Mixed D 300×7.5 mm column from Polymer Labs was used for the GPC studies. The analytical instrument assembly obtained from Shimadzu consisted of a differential refractomeric detector, RID-10A, a solvent delivery pump, LC-10AT*VP*, and a system controller SCL-10A*VP*. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 cm^3/min and polymer concentrations of approximately 1.0 mg/cm^3 were used. Narrow range polystyrene standards (eight standards, molecular weights between 4×10^3 and 1×10^6) were used for construction of the universal calibration curve. The Mark–Houwink parameters used to compute the molecular weight distribution were $k/\text{dL g}^{-1}=11.4\times10^{-5}$ and $a=0.716$ for polystyrene standards and $k/\text{dL g}^{-1}=12.2\times10^{-5}$ and $a=0.700$ for poly butyl acrylate [29].

3. Results and discussion

3.1. Investigation of surfactant systems

A series of studies were performed to determine surfactant/cosurfactant formulations that were effective for producing microemulsions. A variety of nonionic surfactants were investigated in a series of screening studies, including, tritons (a family of surfactants based upon octyl phenoxy poly(ethoxy) ethanol); neodol (alcohols and ethoxylates); tergitol (manufactured through the reaction of propylene oxide with ethylene oxide); in combination with a variety of cosurfactants (propanol, butanol, pentanol, hexanol, heptanol) at various temperatures and concentrations. These studies revealed that nonionic surfactants resulted in microemulsions having a three-phase system with a bicontinuous microemulsion as the middle phase. These microemulsions solubilized very low quantity of monomer in water and produced highly temperature-sensitive microemulsions.

Systems of butyl acrylate using anionic surfactant, SDS, and 1-pentanol spontaneously produced optically clear, single phase o/w microemulsions. These microemulsions were prepared with 0.09 g/(mL water) of butyl acrylate, 0.2 g/(mL water) of SDS, and 0.6 g/(mL water) of 1-pentanol at 22 °C temperature. It should be noted here that these systems were not optimized for surfactant level. Significantly lower surfactant levels would be required and surfactant content would have to be rigorously minimized in order to produce a commercially useful process. Strategies for this will include use of efficient surfactant packages as well as multiphase microemulsion systems. However, we consider the current systems to be sufficiently robust to demonstrate the concepts and in the future will be extended to real world polymerization formulations and processes. To determine the size of the microemulsion droplets, dynamic light scattering experiments were conducted. These experiments revealed a narrow distribution of the droplets with an average hydrodynamic diameter of ∼19 nm, which was typical of a microemulsion droplet diameter (10–100 nm). Therefore, this microemulsion system was used for all of the polymerization reactions.

3.2. Photoinitiation mechanism

The generally accepted reaction mechanism by which the two-component initiator system produced active centers is shown in Fig. 1. Upon illumination, Rose Bengal (RB) absorbs light to produce excited-state RB molecule, which accepts an electron from the MDEA, followed by a proton transfer resulting in the formation of diethanolamine radical and a neutral Rose Bengal radical. The radicals generated from MDEA have been reported to be active in initiation, while the RB radical has been reported to be inactive for initiation [22,23]. Control experiments performed using microemulsion systems that contained only one of the initiator components, confirmed that no polymerization was observed for systems containing only RB or MDEA, consistent with the mechanism shown in Fig. 1.

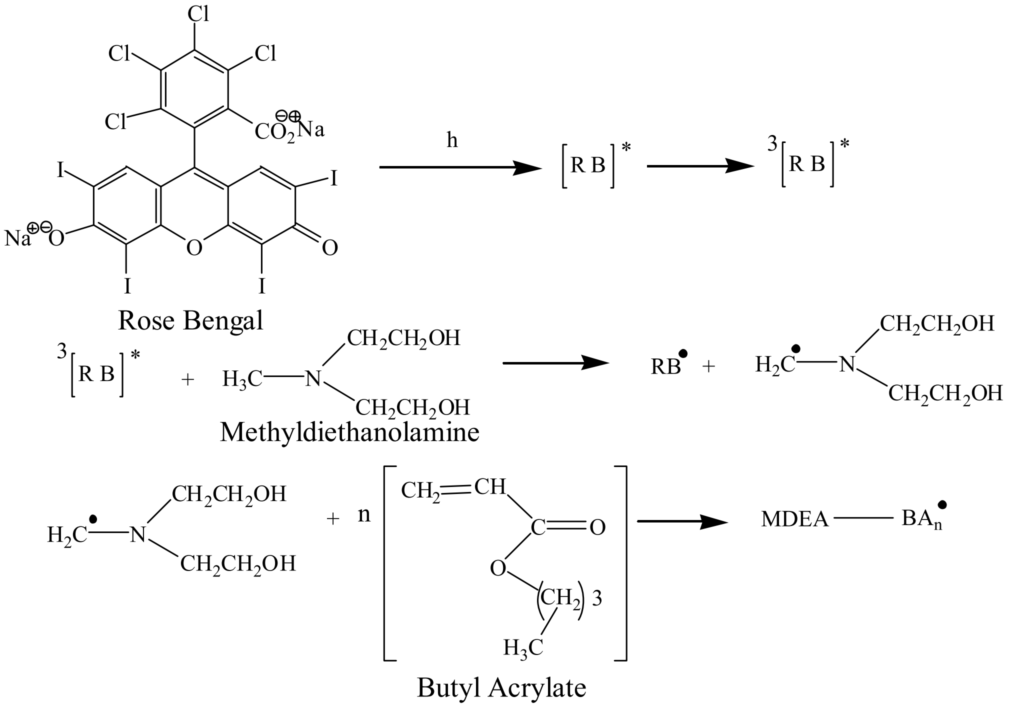

Fig. 1. Reaction mechanism of a two-component initiator system. The Rose Bengal (RB) absorbs a photon in the visible region of light. The excited dye extracts an electron from methyldiethanolamine (MDEA) followed by a proton transfer from the amine resulting in the formation of an active MDEA initiating radical which starts the chain polymerization reaction by attacking the double bond of butyl acrylate monomer (BA).

3.3. Polymer end-group analysis using nuclear magnetic resonance spectroscopy

Analysis of the NMR spectra of the unpurified system before and after reaction revealed that the polymerization had proceeded to a conversion of approximately 85%. Typical yields of the polymer were 70% (mass of the polymer collected divided by the total mass of the initial monomer). NMR spectra of the purified polymer indicated that the separation process described in Section 2 effectively removed the unreacted monomer, surfactant, cosurfactant, and RB since no NMR peaks corresponding to these components were observed. NMR peaks corresponding to the poly(butyl acrylate) repeat unit were observed at 0.9 ppm (acrylate methyl); 1.4 and 1.6 ppm (acrylate CH_2 in the butyl chain); 1.9 ppm (acrylate methylene); 2.3 ppm (acrylate methine); and 4.1 ppm (acrylate CH_2 adjacent to carbonyl). These peaks were broadened in a manner characteristic of ^{1}H NMR spectra of polymers. In addition, a well-resolved broad peak at 3.6 ppm was observed in all samples and was attributed to the methylene groups (two per molecule) adjacent to the alcohol moieties on MDEA. This result indicates that the MDEA fragments are indeed incorporated as the polymer chain ends. Peaks from the other methylene groups on the MDEA were too broad to be reliably interpreted.

3.4. Effect of initiator composition on the resulting polymer molecular weight

A series of experiments were performed to determine the effect of the Rose Bengal and methyldiethanolamine concentrations on the resulting polymer molecular weights. The molecular weights of the polymers were characterized using gel permeation chromatography (GPC) by the procedure described in the experimental section. It is anticipated that the concentrations of the initiator components should have an effect on the molecular weight of the polymers produced in the microemulsion polymerizations since they determine the concentration of the active centers in the aqueous phase. However the relationships between the initiator component concentrations and the polymer molecular weight are difficult to determine theoretically due to the complexity of the photo-induced, multi-phase reaction system. Many steps in the process are limited by diffusion (including the electron transfer step from the MDEA to the excited RB, the partitioning of the active centers from the aqueous phase to the organic phase, etc.). The situation is further complicated by the limited lifetime of the excited RB triplet state (for electron transfer to occur, the molecule must encounter MDEA during this lifetime). Therefore an empirical approach was used to determine the effect of the initiator component concentrations on the resulting polymer molecular weight.

Table 1 shows the compositions of the initiator systems that were examined in this study. The concentrations to be investigated were selected due to the following considerations. First of all, since Rose Bengal is the light-absorbing molecule, its concentration was selected based upon light absorption considerations for the experimental system. Rose Bengal has a molar extinction coefficient of 90,400 M^{-1}/cm^{-1} at 559 nm and its triplet state lifetime (in an oxygen-saturated aqueous environment) is 2.5 μs [30]. Therefore, to generate active

Table 1
Compositions of initiator systems investigated for microemulsion studies (concentrations based upon total monomer volume)

	RB (mM)	MDEA (M)
Series 1	0.177–8.844 in increments of 0.884	0.05
Series 2	0.177–8.844 in increments of 0.884	1.68
Series 3	8.844	0.20–5.20 in increments of ∼0.4

The microemulsions contained 0.09 g/(mL water) of butyl acrylate, 0.2 g/(mL water) of SDS, and 0.6 g/(mL water) of 1-pentanol in addition to the two-component initiator system.

MDEA centers and initiate polymerization, RB excited state must be quenched by MDEA within that time period. As the concentration of MDEA in the system is increased, the probability of excited-state RB encountering an MDEA molecule also increases, thereby leading to a higher number of successful electron transfer steps (and thereby a higher concentration of MDEA active fragments). The higher concentration of MDEA-based active centers in the aqueous phase results in a decrease in the time interval between entry of two successive MDEA fragments into the microemulsion droplets. Since this time interval corresponds to the time at which the active center propagates inside the monomer droplet, the higher MDEA concentration ultimately leads to the production of shorter polymer chains.

As indicated in Table 1, experiments in series 1 and 2 were carried out by varying RB concentration in polymerization systems containing excess MDEA. MDEA concentration was held constant with either an average of 10 times or 400 times in excess to RB. High MDEA concentrations increase the likelihood that an excited state RB molecule will encounter MDEA during its lifetime (and they could undergo the electron transfer reaction). In the Series 3 experiments, the RB concentration was kept constant in all of the reactions and polymerizations were carried out with varying MDEA concentrations.

Fig. 2 contains plot of the number average degree of polymerization in microemulsion polymerizations of systems containing 50 mM and 1.68 M MDEA, respectively, and varying RB concentrations. The polydispersity index (PDI) observed in these systems was on the order of 1.6 for systems containing 50 mM MDEA and 1.7 for systems containing 1.68 M MDEA. The degree of polymerizations observed is this microemulsion photopolymerization are at least an order of magnitude shorter than generally obtained for a standard bulk polymerization or a dispersed polymerization system in which the droplet size is much larger. For example, in an experiment in which 0.5 mL of butyl acrylate was dispersed in 5 mL of water using strong agitation (in the absence of SDS and 1-pentanol), photopolymerization yielded polymers with a degree of polymerization in excess of 10,000. The figure shows that for both MDEA concentrations, if the Rose Bengal concentration is below 1.8 mM, the average polymer chain length decreases with increase in RB concentration. This trend may be attributed to the fact that the aqueous-phase concentration of photo-induced active centers increases as the RB concentration is increased (RB is the light-absorbing molecule). For a given monomer droplet, the time interval between the entry of successive active centers decreases as the aqueous-phase active center concentration is increased. Since the droplet size is very small, we postulate that only one active center will propagate at a given time, and that termination will occur immediately upon the entry of a second active center into the same droplet. Therefore, the propagation time (and the polymer degree of polymerization) is determined by the time interval between the entry of successive active centers into the droplet.

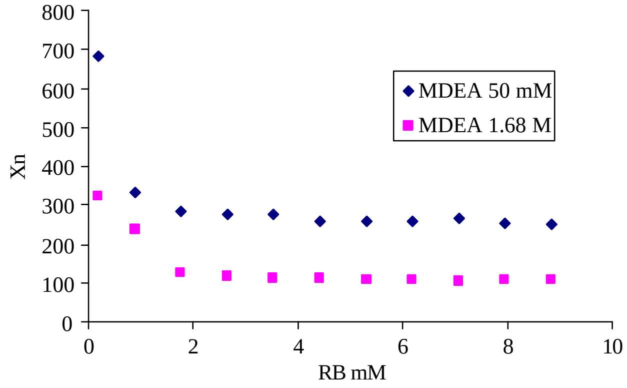

Fig. 2. Number average degree of polymerization (X_n) as a function of RB concentration for photopolymerizations of butyl acrylate-in-water microemulsions. Microemulsions were polymerized using variable quantities of the RB and 50 mM and 1.68 M (with respect to the monomer) of MDEA.

Fig. 2 also indicates that the asymptotic value of the polymer chain length (the value that is approached as the RB is increased) depends upon the MDEA concentration, and decreases as the MDEA concentration is increased (for 50 mM and 1.68 M, the asymptotic values are approximately 260 and 110, respectively). This trend may be attributed to the fact that the concentration of free radical active centers in the aqueous phase generally increases as the MDEA concentration is increased since the probability that an excited state Rose Bengal encounters an MDEA electron donor is enhanced. Therefore, the RB dye is more effectively used to create active centers (by photo-induced electron transfer with MDEA) as the MDEA concentration is increased. The fact that an asymptotic value is observed in these systems could arise from self-quenching of RB at higher concentrations that limit the concentration of RB in the triplet state available for electron transfer with MDEA.

To identify the asymptotic value of number average degree of polymerization as a function of MDEA concentration, a third series of experiments was performed with constant Rose Bengal concentration and variable MDEA concentration. To ensure that the reaction system would correspond to the asymptotic region of the curve, a relatively high RB concentration was chosen for these experiments (8.844 mM with respect to the monomer). The amine concentration in all tests was always in excess to the RB concentration in the system. Fig. 3 shows the number average degree of polymerization of the polymers produced by this method. The results in this figure show that as the MDEA concentration is increased, the asymptotic values of number average degree of polymerizations decreases. As observed from the trend in

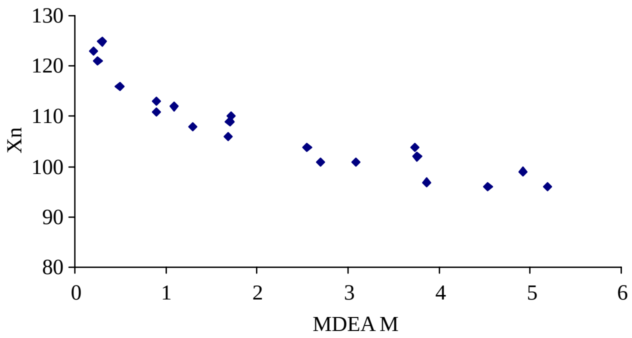

Fig. 3. Number average degree of polymerization (X_n) as an inverse function of the MDEA concentration for photopolymerizations of butyl acrylate-in-water microemulsions. Microemulsions were polymerized using variable quantities of the MDEA and 8.844 mM (with respect to the monomer) of Rose Bengal.

this figure, the number of monomer units in each polymer chain decreased monotonically with the increase in the initiator concentration, from a value of approximately 125 repeat units per chain for 0.202 M MDEA, to slightly less than 100 repeat units per chain for 5.193 M MDEA. The average value of PDI for these systems was 1.7.

4. Summary and conclusion

Solubilization of butyl acrylate in water using SDS surfactant and 1-pentanol cosurfactant produced transparent oil-in-water microemulsions which were stable at room temperature and were relatively insensitive to the variation in temperatures. A series of butyl acrylate-in-water microemulsions were polymerized using a two-component initiator system comprised of Rose Bengal (RB) and methyldiethanolamine (MDEA) dissolved in the aqueous domain. These compounds undergo photo-induced electron transfer upon absorption of ~550 nm light to produce amine radicals which are active in free radical polymerization. The purified polymer was analyzed using NMR and GPC. Analysis of the NMR spectra revealed only monomer and amine peaks and that the MDEA fragments were incorporated as the polymer chain ends.

A series of experiments were performed to investigate the effect of the initiator composition on the polymer chain length and polydispersity. It was observed that when Rose Bengal concentration was varied with constant concentration of excess MDEA, the average polymer chain length decreased with increase RB concentration up to a specific concentration where after the polymer chain length reached an asymptotic value. Further experiments were performed to identify this asymptotic value and it was observed that as the MDEA concentration was increased, the asymptotic values of number average degree of polymerizations decreased.

This research shows the promise of microemulsion photopolymerization using water-soluble initiators for the production of polymers with specified end-groups. While MDEA was used as the electron and proton donor in this study (thereby imparting diol end-groups), nearly any tertiary amine could be used, as well as many others alcohols, thiols, etc. Therefore a variety of functional end-groups could be imparted using this general approach. By imparting reactive end-groups it is possible to simply and inexpensively construct polymers that may be used as precursors in a second reaction step. For example, acrylates with alcohol end-groups could be reacted with isocyanates to yield urethane/acrylate block copolymers. We believe this class of architecturally controlled polymers may have significant utility in a variety of important technological applications, including high performance, low-VOC acrylic thermoset coatings.

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