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ORIGINAL CONTRIBUTION

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Polymerization of brightly colored emulsions in a glycerol suspension medium

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Abstract Upon emulsification of a mixture of methyl methacrylate or methacrylic acid monomer, along with divinylbenzene crosslinker and octane porogen into a glycerol suspension medium, brightly colored emulsions form. The bright colors of the emulsion originate from an exact matching of the refractive index of the emulsion droplets with that of the glycerol medium only at certain wavelengths of light – other wavelengths of light scatter. Polymerization of the brightly colored emulsions yields three different latex morphologies depending upon the polymerization temperature and the type of emulsifier, monomer, initiator, or hydrocarbon applied. The latex morphologies obtained range from large porous latex (1–10 μm in size) to medium-sized porous latex (0.1–1 μm in size) to small latex (up to 0.1 μm in size).

Keywords Emulsion polymerization · Porous latex · Glycerol

Introduction

Water, the most common suspension medium for emulsion, dispersion, and suspension polymerizations, offers many benefits; however, in certain situations other solvents provide advantages. Emulsification of water-soluble monomers into a non-polar suspension medium yields droplets (''inverse'' emulsions) and polymerization of these emulsions creates small latex particles of acrylic acid and acrylamide [1, 2]. Emulsification and polymerization of monomer droplets dispersed into an alcohol or ketone suspension medium facilitates, for example, the creation of latex with narrow particle size distributions [3, 4]. However, one potentially interesting suspension solvent, pure glycerol, remains little studied in the literature on polymer latex formation.

Like water, glycerol provides some hydrogen bonding capabilities; however, glycerol is less polar than water and much more viscous. As a suspension medium, the high viscosity of glycerol offers advantages and disadvantages: emulsification into glycerol requires high energy input to overcome viscous resistance to droplet breakup, but after the droplets form the high viscosity of glycerol slows the coalescence and settling of droplets [5]. As a polymerization medium, many questions remain open as to the influence of glycerol on reaction kinetics: the high viscosity may hinder diffusion of monomers between droplets, and the polarity of glycerol may change the solubility and partitioning of monomers between droplets and the continuum. In addition, an open question revolves around the presence or absence of micelles in glycerol, and the possibility for micelle catalyzed polymerizations.

Formation of latex in a glycerol medium might also provide important advantages in controlling the surface chemistry of the latex. One particular technique, ''molecular imprinting'', exploits strong hydrogen bonds formed between monomers and template molecules to ''imprint'' chemical environments on polymer surfaces. Such chemical environments enhance the adsorption of molecules similar in chemical structure to the template molecule, and thus facilitate chromatographic and catalytic reaction processes [6, 7]. However, water will interfere with molecular imprinting by breaking the

template-monomer hydrogen bond. Glycerol has less hydrogen bonding capability than water, and indeed the same porous and high surface area latex described in this report have been successfully molecularly imprinted and applied in chromatographic separations [8].

The work reported here examines the influence of emulsion composition, type of initiator, and the polymerization conditions on the morphology of the polymer obtained from emulsions of monomers plus oil dispersed in a glycerol suspension medium. Remarkably, the emulsions examined here also exhibit bright colors. As concluded from a detailed analysis of the optical properties of the emulsions described in another publication [9], the bright colors result from the exact matching of the refractive index of the droplets with that of the glycerol medium only at certain wavelengths of light. As highlighted here, polymerization of these brightly colored emulsions yields three different latex morphologies, some of them highly porous, in addition to a non-latex morphology.

Experimental

Ingredients. Glycerol and sodium dodecyl sulfate (SDS) were from Sigma Chemicals and 99% pure. Octane (>96%), decane (98%), hexadecane (98%), cyclohexane (99%), toluene (99%), divinylbenzene (DVB, 80%), and the initiator 2,2′-azobis-isobutyl nitrile (AIBN, 98%) were from Fluka Chemicals. The surfactant sorbitan monooleate (unknown purity) and the monomers methacrylic acid (MAA, 99%) and methyl methacrylate (MMA, 99%) were from Aldrich Chemicals and were used as received. The initiator 2,2′-azobis-2,4-dimethyl valeronitrile (ADVN, 98%) was from Wako Chemicals.

Preparation of emulsions. For the standard recipe, 9 ml of glycerol was mixed with 100 mg SDS surfactant, 200 µl MMA, 400 µl DVB, and 400 µl octane by stirring to generate a turbid coarse emulsion with roughly 10 vol.% (7.6 wt%) dispersed phase and 0.8 wt% surfactant overall. Ultrasonication of the coarse emulsion (Model UP 200S from Dr. Hielscher GMBH) for 1 min at 70% power yielded a transparent emulsion. Due to energy dissipation during ultrasonication, the temperature of the emulsion rose to about 60 °C.

Polymerization. The polymerization reaction was initiated upon addition of either AIBN or ADVN. Since AIBN is soluble in glycerol, 50 mg was dissolved in the emulsion after ultrasonication. Since ADVN is more hydrophobic than AIBN, 50 mg ADVN was dissolved in the monomer and oil mixture prior to emulsification in glycerol. The emulsion plus initiator was charged to a 20-ml reactor under rapid stirring, equilibrated at 60 °C and purged with nitrogen. Initially the emulsion was transparent and opalescent; however, within 1 h, the mixture had turned white due to polymer formation. After 2 h of reaction time the reactor was cooled to room temperature. After diluting the suspension with water, vacuum filtering the dispersion through filter paper, and rinsing the resulting solids with water, acetone, and methanol to remove residual glycerol and oil, the polymer solids were dried in an oven at 45 °C for 6 h.

Characterization. The refractive index (white light) of the emulsion ingredients was measured with a thermostated Zeiss refractometer. The color spectra of the emulsions were measured with UV-visible spectroscopy (Uvikon Model 943) using 10 mm path length quartz cells. The droplet size of the emulsions was measured using a static and dynamic light scattering apparatus (ALV). The morphology of the solids obtained after polymerization were examined with Hitachi S-4000 Field-Emission Scanning Electron Microscope (SEM), and the specific surface area of the polymer latex measured by a BET analysis of the adsorption of nitrogen (Micromeritics).

Results

Transparent colored emulsions

Ultrasonication of the standard emulsion recipe (9 ml glycerol, 100 mg SDS, 200 µl MMA, 400 µl DVB, 400 µl octane) yields a transparent and brightly colored emulsion (Fig. 1). At room temperature, illumination of the emulsion by a strong beam of white light reveals the transmission of reddish colored light (at 0°), and the scattering of bluish light (at 90°, Fig. 1a). Static light scattering measurements show that the intensity of the scattered light increases strongly as the detector is moved to smaller angles. The high viscosity of the medium makes quantification of the droplet diameters difficult; however, the static and dynamic light scattering

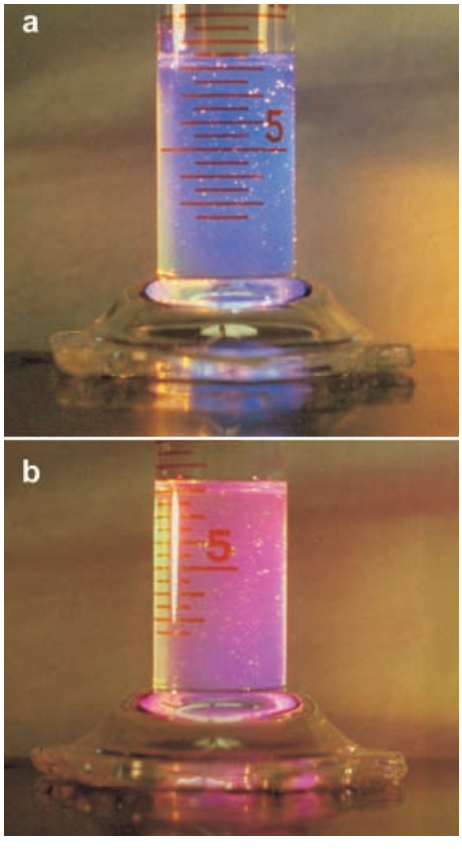

Fig. 1a,b Photograph of graduated cylinder filled with transparent and colored emulsion, illuminated with white light from side (90° to camera): **a** T = 25 °C; **b** T = 60 °C

results suggest the emulsion contains polydisperse emulsion droplets of roughly 1 μm mean diameter.

The light absorption spectra of the emulsions indicate that the absorption is essentially zero (the emulsions are transparent) over a narrow range of wavelengths (Fig. 2). Upon increasing the temperature, the absorption minimum shifts to shorter wavelengths (Fig. 2). Visual observations confirm that the color of the transmitted light shifts from reddish to blue-green, and the color of the scattered light (the combination of the absorption bands on either side of the absorption minimum) shifts from blue at low temperatures (Fig. 1a) to violet at higher temperatures (Fig. 1b). A thorough analysis published elsewhere [9] shows that the same shift in color observed upon increasing the temperature also occurs at fixed temperature upon systematically varying the emulsion composition by changing the oil type, MMA concentration, surfactant concentration, etc. As discussed in the publication [9] the emulsion becomes transparent due to the exact matching of the refractive index of the continuous phase (glycerol) with that of the droplet phase (monomers plus oil) only at certain wavelengths. At other wavelengths, light scatters from the dispersed droplets. Since refractive index depends sensitively upon wavelength, temperature and the composition of the emulsion, so do the wavelengths of light at which exact matching occurs (Fig. 2) [9].

Polymer latex

As polymerization proceeds and solid polymer appears, the colored emulsions become turbid. After recovery of the polymer solids by washing and filtration, SEM images indicate four different morphologies occur depending upon the emulsion recipe and polymerization conditions: (I) spherical latex particles of 0.1–1 μm diameter, (II) mostly spherical latex less than 0.1 μm in diameter, (III) spherical latex up to 10 μm in diameter, and (IV) small irregularly shaped particles, often fused together into larger units.

Upon polymerization of the standard formulation (9 ml glycerol, 100 mg SDS, 200 μl MMA, 400 μl DVB, 400 μl octane) at 60 °C with AIBN as initiator, latex particles 0.1–1 μm in diameter form, denoted as morphology I (Fig. 3). The largest latex particles exhibit rough surfaces and appear to be composed of smaller units fused together. Examination at higher magnifications reveals that the smaller latex particles also exhibit surface roughness, albeit on a smaller scale (Fig. 4). BET analysis of the adsorption of nitrogen yields a specific surface area of 335 m^2/g, which suggest that the particles are highly porous.

Polymerization of the standard emulsion recipe using the more hydrophobic ADVN initiator instead of AIBN also yields spherical latex in the 0.1–1 μm size range (Fig. 5). However, the latex formed with ADVN exhibit substantially smoother surfaces (Fig. 5) than those found with AIBN (Fig. 3). A few very small particles dot the surfaces of the latex (Fig. 5). Specific surface area remains high at 300 m^2/g.

With AIBN as polymerization initiator, substitution of sorbitan monooleate for the SDS surfactant used in the standard recipe results in substantially smaller latex particles, less than 0.1 μm (100 nm) in diameter, denoted as morphology II (Fig. 6). The particles appear somewhat non-spherical, uniform in size, and the images suggests the particles are relatively non-porous. The specific surface area of the particles is 270 m^2/g.

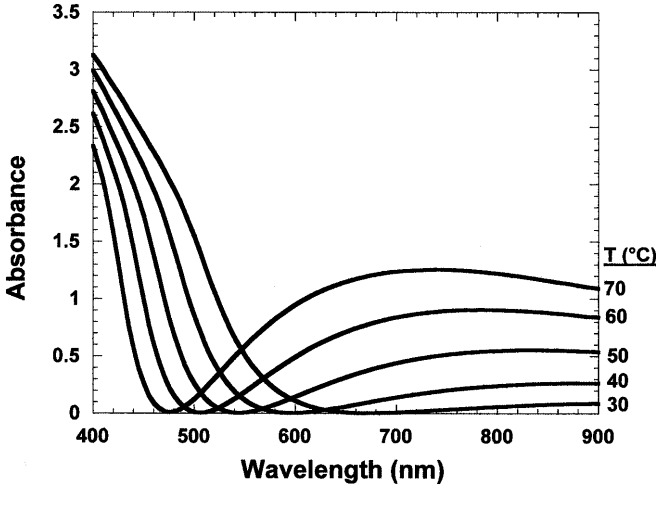

Fig. 2 Light absorption spectra as a function of the wavelength of light (nm) and temperature for the standard emulsion formulation

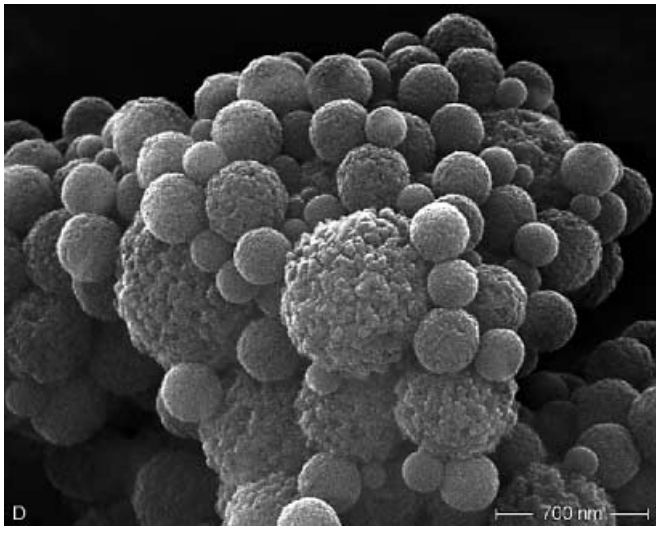

Fig. 3 Scanning electron micrograph of latex (morphology I) obtained upon polymerization of the standard emulsion formulation (AIBN initiator, T = 60 °C)

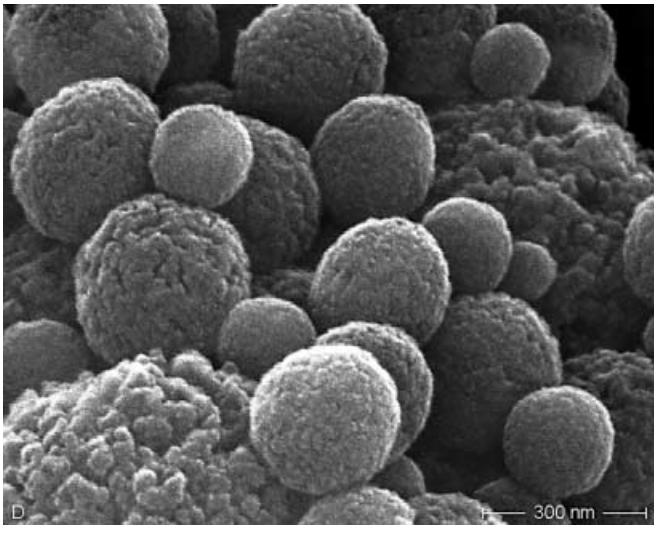

Fig. 4 Higher magnification scanning electron micrograph of latex (morphology I) obtained upon polymerization of the standard emulsion formulation (AIBN initiator, T = 60 °C)

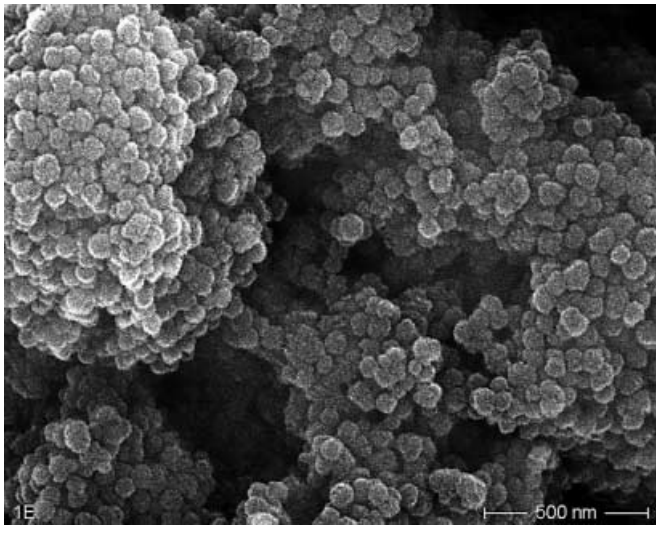

Fig. 6 Scanning electron micrograph of latex (morphology II) obtained upon polymerization of an emulsion with sorbitan monooleate as surfactant (AIBN initiator, T = 60 °C)

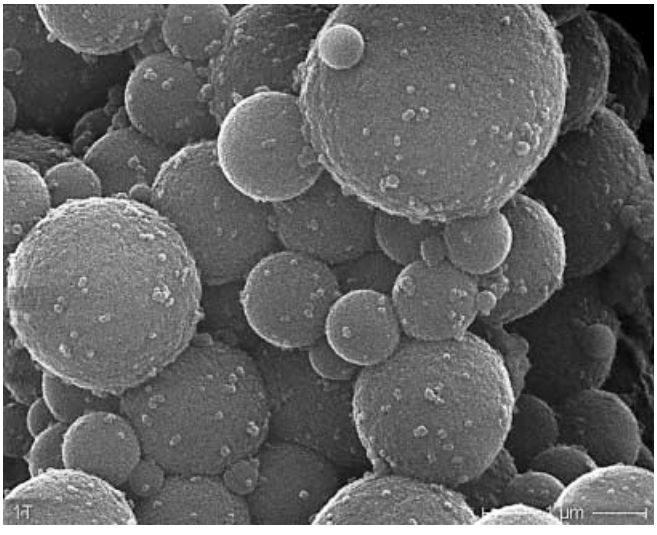

Fig. 5 Scanning electron micrograph of latex (morphology I) obtained upon polymerization of the standard emulsion formulation (ADVN initiator, T = 60 °C)

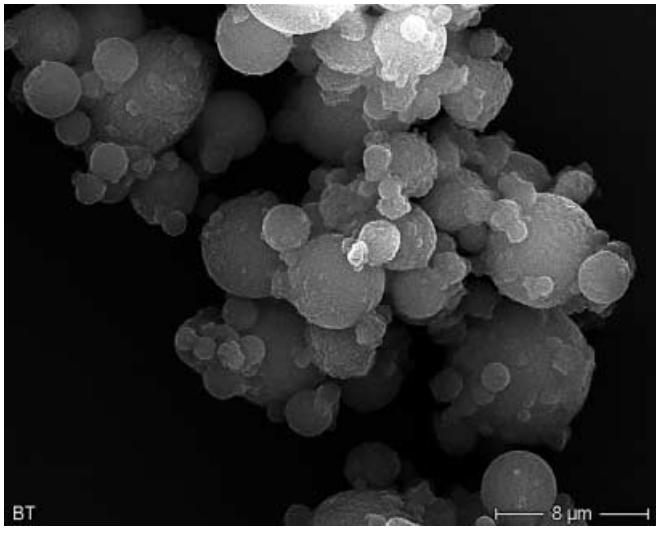

Fig. 7 Scanning electron micrograph of latex (morphology III) obtained upon polymerization of an emulsion with methacrylic acid (MAA) as monomer (AIBN initiator, T = 60 °C)

Variation of the MMA monomer concentration from 50% to 200% of the concentration found in the standard formulation yields no change in latex size or morphology. However, upon substitution of the more polar monomer methacrylic acid (MAA) for methyl methacrylate (MMA), substantially larger latex form, up to 10 mm in diameter, denoted as morphology III (Fig. 7). The polydisperse latex, with a minority amount of small irregular shaped particles present, appears porous and has a specific surface area of 350 m^2/g.

However, under other polymerization conditions or with other ingredients, or with other ingredient concentrations, non-latex morphologies appear. These small irregularly shaped particles, often fused together into larger units (denoted as morphology IV), sometimes appear alone or in combination with spherical latex particles. For example, upon substitution of decane for octane, and upon raising the polymerization temperature from 60 to 70 °C, morphology IV appears (Fig. 8). In general terms, upon raising the polymerization temperature, increasing the chain length of

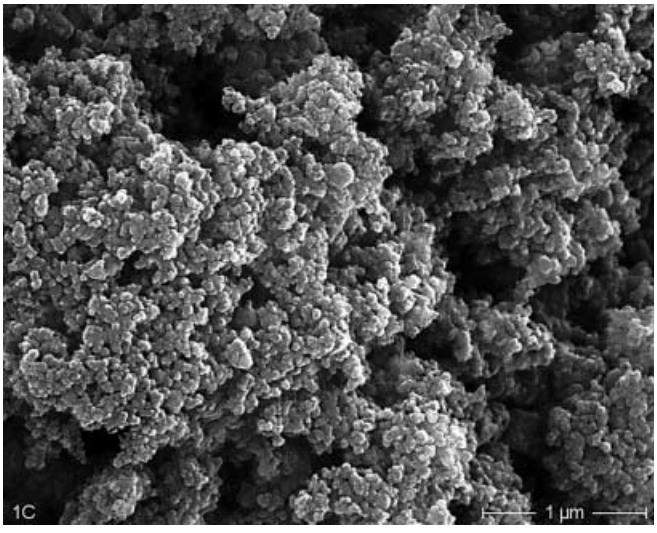

Fig. 8 Scanning electron micrograph of polymer solids (morphology IV) obtained upon polymerization of an emulsion with decane as oil (AIBN initiator, T = 70 °C)

the hydrocarbon oil (decane, hexadecane), increasing the octane concentration, substitution of aromatic oils for the hydrocarbon oils, or increasing the SDS concentration, morphology IV becomes a larger fraction of the sample.

Discussion

The partitioning of the emulsion ingredients between the droplet and continuous phases, along with the kinetics of the polymerization reaction, determine the morphology of the resulting polymer. In simplified terms, droplet polymerizations proceed via two types of mechanisms. In "emulsion polymerizations", monomer-filled droplets coated with surfactant float in a continuum containing surfactant micelles. Monomers diffuse from the droplets to the micelles, and the micelles "catalyze" the polymerization [10]. In "suspension polymerizations", all of the surfactant coats the monomer droplets, the continuum contains no micelles, and polymerization proceeds primarily within the emulsion droplets [11, 12]. As argued in the following discussion, since glycerol is less polar and more viscous than water, polymerization appears to proceed more along the path of a suspension polymerization rather than a micelle-catalyzed emulsion polymerization.

MMA monomer exhibits low solubility in water but appears quite miscible with glycerol (all of the 200 µl MMA charged in the standard formulation dissolves completely in 9 ml of glycerol). On the other hand, DVB and octane are of low polarity and appear effectively immiscible with glycerol. Upon mixing MMA, DVB, octane, and glycerol together at the ratios of the standard recipe *without surfactant present*, two phases form. Refractive index measurements (at 60 °C) indicate that the bottom phase ($n_D = 1.4623$) is essentially composed of glycerol ($n_D = 1.4625$). The top phase ($n_D = 1.4520$) appears essentially composed of MMA, DVB, and octane, since a mixture of MMA, DVB, and octane (mixed at the composition ratios found in the standard emulsion recipe) has $n_D = 1.4512$. This partitioning experiment suggests that MMA prefers to partition into the DVB and octane-rich droplet phase, even though MMA is significantly soluble in glycerol.

After emulsification of the monomers and oil in the presence of SDS surfactant, any SDS not associated with the droplets likely resides in the glycerol-rich continuum. To our knowledge, the critical micelle concentration (CMC) of SDS in glycerol remains unmeasured. However, glycerol is less polar than water, so monomeric SDS may be more soluble in glycerol than in water, and micelle formation might be suppressed compared to that in water.

The low probability for SDS micelle formation in glycerol, along with the apparent preferential partitioning of the MMA monomer into the droplet phase, in combination with the inhibited diffusion of MMA and SDS through the continuous glycerol-rich phase due to the high viscosity of glycerol (88 mPa·s) at the polymerization temperature (60 °C), all suggest an increase in the probability of a "suspension polymerization" mechanism. In addition, the high viscosity of glycerol should inhibit droplet coalescence during polymerization.

Indeed, the simplest explanation for the porous latex morphology (I) obtained with the standard emulsion formulation is that the emulsion proceeds similarly to a suspension polymerization. The polymer latex obtained with the standard formulation (Fig. 3) exhibits particle diameters roughly similar in size to the estimated size of the emulsion droplets (1 µm). The high specific surface area and the rough surfaces of the particles indicate that the particles are highly porous. Such particles could be obtained if the gel-point of the polymerization occurs in the droplet phase, and the polymer entraps significant amounts of the porogen octane. On the other hand, the AIBN initiator and the MMA monomer are soluble in glycerol, so the polymerization could proceed to some extent within the glycerol phase before reacting with the crosslinker DVB in the droplets.

The three other morphologies observed (II, III, and IV) likely result from differences in the partitioning of the ingredients, but might also result from changes in the ability of the surfactant to stabilize the resulting polymer as polymerization proceeds. Substitution of the more oil-soluble ADVN initiator for AIBN results in smoother particles (Fig. 5) perhaps because the polymerization both starts and proceeds in the droplet phase. Substitution of sorbitan monooleate for the SDS surfactant results in small latex (Fig. 6) perhaps because the

polymerization proceeds along the path of a emulsion polymerization rather than a suspension polymerization. Substitution of the more polar methacrylic acid (MAA) monomer for methyl methacrylate (MMA) monomer results in larger latex (Fig. 7), perhaps because of the likely higher solubility of MAA in glycerol compared to MMA, or perhaps because the starting droplets are larger due to Ostwald ripening (caused by monomer diffusion through the continuum). In the cases where the non-latex morphology IV forms, the surfactant appears unable to stabilize the solid polymer into a spherical latex morphology as polymerization proceeds, and the particles crosslink into larger entities (Fig. 8). Morphology IV might be a consequence of polymerizations that proceed to a significant extent within the glycerol continuum rather than within the droplet phase.

Conclusions

The results presented here clearly show the formation of porous polymer latex upon polymerization of optically transparent and brightly colored emulsions dispersed in a glycerol medium. The bright colors of the emulsion originate from an exact matching of the refractive index of the emulsion droplets with that of the glycerol medium at certain wavelengths of light. Polymerization of the emulsions yields three different latex morphologies depending upon the surfactant emulsifier, the monomer (methyl methacrylate or methacrylic acid), the initiator, the hydrocarbon porogen, or the polymerization temperature. The morphologies range from large porous latex (1–10 μm in size) to medium-sized porous latex (0.1–1 μm in size) to small latex (0.1 μm in size). The results suggest that a suspension rather than a micelle-catalyzed polymerization occurs; however, clear elucidation of the polymerization mechanism requires further experimentation.

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References

1. Vanderhoff JW, Branford EB, Tarkowski HL, Schaffer JB (1962) Adv Chem Ser 34:32
2. Renken A, Hunkeler D (1999) Polymer 40:3545
3. Sugimoto T (2000) Fine particles: synthesis, characterization and mechanisms of growth. Marcel Dekker, New York
4. Asua JM (1997) Polymeric dispersions: principles and applications. Kluwer Academic, Dordrecht Boston
5. Bibette J, Leal Calderon F, Poulin P (1999) Rep Prog Phys 62:969
6. Mosbach K, Ramström O (1996) Bio/Technology 14:163
7. Brüggemann O, Haupt K, Ye L, Yilmaz E, Mosbach K (2000) J Chromatogr A 889:15
8. Brüggemann O, Herzhoff M, Wormuth K (2002) In preparation
9. Wormuth K, Brüggemann O, Strey R (2002) In preparation
10. Lovell PA, El-Aasser MS (1997) Emulsion polymerization and emulsion polymers. Wiley, New York
11. Arshady R (1992) Colloid Polym Sci 270:717
12. Arshady R (1999) Colloids Surfaces A Physiochem Eng Aspects 153:325