Polymer 114 (2017) 54–63

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Multi-lobed composite polymer nanoparticles prepared by conventional emulsion polymerization

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ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form
24 February 2017
Accepted 26 February 2017
Available online 27 February 2017

Keywords:
Asymmetric
Polymer particles
Formation mechanism
Reactive processing

ABSTRACT

The vast majority of latex particles, including those made from multiple polymers, are spherical in shape. This is a result of the minimization of the combined interfacial free energies at the polymer particle–water interface and the polymer–polymer interfaces within the particle. Yet there are special situations in which latex particles containing two, incompatible polymer phases can form asymmetric, multi-lobed particles during conventional, two stage emulsion polymerizations. Here we report on a variety of situations used to produce these interesting polymer particles and discuss the mechanism by which they are formed. The key condition is that the reaction process be carried out in a manner in which the second stage oligoradicals in the water are not allowed to significantly penetrate the first stage latex particle during the reaction. Then, the important variables are the relative differences between the interfacial tensions at the water-polymer interface for the two polymers in question, and the second stage polymer chain diffusivity on the surface of the first stage particles. By extension, the same fundamental parameters of interfacial tensions and polymer chain surface diffusion apply to the morphology possibilities when inorganic first stage particles are used to create inorganic-organic composite latices.

1. Introduction

It is most often observed that latex particles produced via conventional emulsion polymerization techniques are spherical in nature. This includes those produced via mini-emulsion techniques and even those that consist of multiple polymer phases (composites). Indeed, it is seldom that one reads about the possibility of producing non-spherical particles in the many literature reports involving emulsion polymers. However in the 1980's, Okubo's group published a series of articles describing “anomalous” composite latex particles including “raspberrylike” [1], “voids” [2] and “confetti-like” [3] structures. Shortly thereafter they reported that the mechanical and optical properties of films based on poly(ethyl acrylate)/polystyrene composite particles changed dramatically upon thermal annealing and suggested that this was due to phase separation of the polymers within the film [4]. Min et al. [5] reported that “dumbellshaped” particles were formed after the aging of poly(butyl acrylate)/polystyrene composite latex particles. All of these articles were cited in a US patent [6] issued to Rohm and Haas for “multilobals” – this patent specifically claims the preparation of multi-lobed polymer particles and the techniques by which they can be manufactured. Many interesting examples of composite latex recipes and processes are described in this patent and it is to be noted that the first stage (or seed) latex contains some level of divinyl monomer. Such industrial products typically find use as viscosity enhancers in latex coating formulations (i.e. the “effective volume” of the multilobe > true volume of the particles). Two related journal articles were published by Chou et al. [7] and Strauss [8]; all authors were employees of Rohm and Haas. Sheu et al. [9,10] reported the synthesis of non-spherical, homopolymer (polystyrene, PSty) particles (in the micron size range) in aqueous dispersions by using divinyl monomers in the one or more stages of a multi-staged polymerization process. They reported achieving non-symmetrical, hemispherical particles and even “ice cream cone”, or three piece, particles by choosing to use different levels of divinyl benzene (DVB) in one or more of the stages of the overall polymerization process. They always started by making a first stage particle with the highest DVB content, then swelling those particles with the same monomer at room temperature but with a lower (or no) DVB level. They then conducted the subsequent polymerization(s) at normal polymerization temperatures. Scanning electron microscope images clearly displayed the non-spherical nature of

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http://dx.doi.org/10.1016/j.polymer.2017.02.080
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the particles. They concluded that the reason for the non-spherical nature of the particles was that upon heating the swollen polymer particles (crosslinked polymer + swelling monomer), the monomer was exuded in part from the first stage, crosslinked polymer particle and then polymerized as spherical cap. Light microscope images supported this sequence of events. Mock et al. [11] used the same sequential technique to produce hemispherical particles of PSty at particle sizes < 0.5 μm and expanded upon the monomer exudation mechanism suggested by Sheu [9,10]. Lastly, Weitz and colleagues [12,13] further expanded on the use of the crosslinked, monomer swollen, seed particle technique to produce "triple rod", "triangular", "cone" (much as reported by Sheu [9,10]) and "diamond" PSty particles in the 10 μm size range.

As part of our own program in studying the morphology of composite latex particles, we too have noticed that upon occasion composite particles are not completely smooth and spherical, even when using *no crosslinking monomer* in any of the process steps. This led us to return to the Okubo articles [1–4] and then conduct a new series of experiments aimed at developing data to provide a mechanistic understanding of the events leading to the production of non-spherical, or multi-lobed, particles in the sub-300 nm particle size range via standard emulsion polymerization processing. We sought to answer the following questions: 1.) Why do lobes form on some particles and not on others?; 2.) When does this happen during the polymerization?; 3.) How can this effect be enhanced or diminished if desired?

2. Experimental

It was already quite clear from the literature that for non-crosslinked, first stage latex particles, the polymer should be relatively to greatly more polar than the second stage monomers. Thus the vast majority of our experiments were conducted under those conditions. In addition, our early work taught us that the glass transition temperature, T_g, of the first stage polymer (i.e. the seed polymer) relative to the reaction temperature is a key variable in producing multi-lobed particles during the polymerization (i.e. without the effect of post-polymerization thermal annealing). The T_g's of the second stage polymers were varied to be either below or above the reaction temperature while maintaining a non-polar polymer characteristic. These T_g – polarity characteristics were achieved by using copolymer pairs for the seed polymer based on methyl methacrylate (MMA) and methyl acrylate (MA), and for the second stage polymer based on styrene (Sty) and hexyl methacrylate (HMA). Both pairs allowed us to vary the T_g greatly while maintaining the relative polarity differences between the first and second stage polymers. The particle size of the seed particles was controlled to be ~180 nm and we varied the ratio of second stage monomer to seed polymer (referred to as "stage ratio", or SR). Most experiments were carried out at SR = 1.0.

2.1. Latex preparation

The seed latices were prepared by forming P(MMA-co-MA) particles in an *ab initio* batch reaction (forming a "pre-seed latex") and then growing the particles to the desired size by feeding the MMA/MA monomer over an extended period of time (usually 4 h). The second stage reactions all utilized a seeded, semi-batch reaction strategy so as to control the free monomer level in the particles during polymerization. All of the polymerizations were conducted with potassium persulfate (KPS - Acros) initiator and latex stability was achieved through the use of sodium dodecyl sulfate (SDS – 99+% - Acros). The latices were buffered with $NaHCO_3$ – Acros). Small amounts of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) were used in some second stage experiments. All monomers were sourced from Acros and were of research grade purity. The monomers were cleaned of inhibitors by passing them through a column filled with Alumina (Acros). The recipe and process conditions for our experiments are described in Table 1 below. All polymerization reactions were conducted at 70 °C and most of the reactions were carried out under "starve fed" conditions where the instantaneous level of second stage monomer in the particles was at or below 1.0 M (>90% instantaneous conversion).

2.1.1. Reaction process conditions

The first stage (seed) latex reactions were conducted in two stages, both at 70 °C. As noted above, in the first stage we created a "pre-seed latex" at about 85 nm via a batch reaction. Additional monomer was added to this latex over a 4 h period to grow the particles to their desired ~180 nm size with narrow size distribution. Second stage reactions were conducted at the same temperature and the hydrophobic comonomers were added evenly as a neat solution over a 2 h period. The very early portions (<5% conversion) of the second stage reactions experienced variable monomer concentrations in the latex particles as the monomer levels build up from zero to the steady, monomer starved levels. Latex samples were withdrawn periodically (~every 20 min) in order to assess the level of conversion of the second stage monomer to polymer. In all cases the "instantaneous conversion" levels were greater than 90%, assuring starve feed conditions.

2.2. Latex characterization

2.2.1. Latex particle size

All of the particle size measurements were made on a capillary hydrodynamic fractionation chromatograph (Matec CHDF 2000). The calibration curve was created from latex standards (Thermo Scientific) over the 40–240 nm range.

2.2.2. Scanning electron microscopy (SEM)

Very dilute latex samples were spread onto graphite grids and dried. These grids were then sputter coated with platinum prior to observation in the SEM (Amray 3300FE field emission).

2.2.3. Transmission electron microscopy (TEM)

Latex samples were prepared for TEM observation by embedding dried polymer powders in epoxy resin (Z-poxy™, Pacer Technologies) and curing at 60 °C, microtoming at room

Table 1
Latex recipes.

Component	Seed Latex	Second Stage Latex
Pre-seed latex[a] (~85 nm),g	240	N/A
Water, g	583	N/A
SDS, g	1.02	N/A
KPS, g	0.50	N/A
$NaHCO_3$	0.47	N/A
MMA, g	92–134	N/A
MA, g	0–42	N/A
Seed latex[b] (~180 nm),g	N/A	99.8
Water, g	N/A	80.0
KPS, g	N/A	0.062
SDS, g	N/A	0.084
$NaHCO_3$	N/A	0.051
Sty, g, for SR = 1	N/A	10.6–20
HMA, g, for SR = 1	N/A	0–9.4
MAA, g	N/A	Variable - see text below
EGDMA, g	N/A	Variable – see text below

[a] 5% solids content.
[b] 20% solids content.