Progress in Organic Coatings 77 (2014) 305–314

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

A feasible method of preparation of block copolymer latex films with stable microphase separation structures

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ARTICLE INFO

Article history:
Received 17 February 2013
Received in revised form 13 October 2013
Accepted 16 October 2013
Available online 7 November 2013

Keywords:
RAFT polymerization
Miniemulsion polymerization
Structured latex
Nanostructured latex film
Mechanical properties

ABSTRACT

RAFT (reversible addition–fragmentation chain transfer) miniemulsion polymerization was engaged to engineer latex particle morphology. With this approach, a macromolecular amphiphilic RAFT agent with epoxy groups was synthesized that assembled onto the surface of monomer mini-droplets. It caused the polymer chains to grow inwards gradually in particles as polymerization proceeded. The batch polymerization of *n*-butyl acrylate (BA) followed by addition of styrene (St) led to the formation of PBA-*b*-PSt diblock copolymer shell–core latex, where epoxy groups were enriched on the particle surface. The shell–core ratio was varied feasibly by changing the mass of St. When the structured latexes were dried, epoxy groups underwent efficient curing reactions triggered by a thermal-latent curing agent (dicyandiamide) in a controlled manner, leading to the formation of bonded PBA blocks connecting the PSt blocks in adjacent particles. Mechanical tests show that the films behaved like ductile materials, whose modulus and elongation at break were functions of copolymer compositions. Furthermore, curing reaction was a very robust method of preserving film morphology which correlated well with that observed for the latex particles. The results demonstrated a feasible method of preparation of latex films with stable microphase separation structures and thus improved mechanical properties.

1. Introduction

Over the past thirty years, being driven by the regulations to reduce the amount of volatile organic compounds (VOCs) in coatings, there has been a substantial effort to develop new approaches to replace traditional solvent-based coating compositions with waterborne alternatives. While the aqueous latex coatings bring health and safety benefits, their compositions must meet or exceed the performance standards expected from solvent-based compositions [1,2].

The aqueous latex film formation process can be divided into three stages [3–6]. It is in the final stage that the polymer molecule diffusion provides a latex film with mechanical strength. In this manner, film full tensile strength depends on the formation of entanglement by the polymer chains that span the initial interface between adjacent particles [4–6]. Theoretical and experimental evidences indicate that polymer diffusion coefficient varies significantly with several important parameters such as: chain length [7,8]; spatial distribution and location of chain ends at the interface [9]; especially annealing temperature at which whether the polymer is above or below its glass transition temperature (T_g) [10]. Traditionally, polymers with low T_gs have much higher diffusion coefficient values than those with high T_gs. From a practical view, these low-T_g polymer-based latexes have good film-forming abilities while the films are poor with respect to the mechanical strength [11].

Several approaches have been explored to offer a compromise between latexes that have good mechanical properties and that are good film formers. One way to enhance the soft latex film mechanical properties is using physical blends of hard and soft latex particles both with homogeneous morphology [12–16]. Another way is to make films from structured latexes, for instance, with hard-core/soft-shell morphology [17,18]. In these two cases, when latexes are dried, the polymers in soft latex particles or constituting the soft shell are able to coalesce, whilst the high-T_g polymers remain dispersed. It leads to biphasic films where the latter one is dispersed in a matrix of the low-T_g polymers, and improves the film

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Abbreviations: DICY, dicyandiamide; TTCA-4, S-1-butyl-S′-(α-methyl-α′-acetic acid) trithiocarbonate.

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http://dx.doi.org/10.1016/j.porgcoat.2013.10.004

strength. In comparison to the latex blend film, film prepared from core–shell structured latexes exhibits superior mechanical properties at medium and high drawing ratios during the tensile tests [17]. It is ascribed to debounding between the hard particles and the soft polymer matrix happening to the latex blend films [19].

Structured latex particles are usually prepared by multistage emulsion polymerizations [20–22]. When the monomer postadded to seed latex particles is polymerized, a two-phase structure will normally be observed within the particles because of the incompatible nature of most monomer pairs. The basic understanding of the mechanism controlling phase separation and latex morphology has been extensively reviewed by Sundberg et al. [22]. However, contradictory results are often found in the literature because latex particle morphology is complicatedly influenced by an interplay of thermodynamic as well as kinetic parameters during the polymerization process [20–22]. On the other hand, upon film formation, the uncertainty of particle morphology results in an uncertain phase distribution in the films. The adjustment of the morphology of phase separation in films and therefore the film mechanical properties are often arbitrary and based on trial-and-error.

Block copolymers contain of two or more chemically distinct polymer chains being covalently linked to form a single molecule. They have drawn much attention due to self-assembly into nanometer-sized morphology such as lamellae, cylinders, spheres, and gyroids [23–26]. At first, block copolymers were successfully synthesized by living anionic polymerization [27–29]. Due to its requirement for the extremely strict reaction conditions (i.e., very low temperature, exhausting removal of moisture, rigorous purification of reagents.), the use of anionic polymerization techniques is mainly restrained in organic solution, and attempt to synthesize block copolymer latex remains a great challenge [27–29]. In the last twenty years, controlled/living radical polymerizations (CLRP) have attracted great attentions due to their abilities to prepare well-defined polymers with precisely designed molecular architectures under mild conditions [30,31]. Three major CLRP methods are nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT) polymerization [32–37]. More recently, the implement of CLRP in (mini)emulsion achieved great success. It allows for the possibilities of controlling over the macromolecular architecture and particle morphology simultaneously [38–42]. By now, block copolymer particles with three main types of morphology have been fabricated: the core–shell morphology [38], the 'onion-like' morphology [39–41] and 'inclusion particle' morphology [42], but to our knowledge, few investigations on their latex film performances have been reported.

In this paper, an amphiphilic macro-RAFT agent was prepared, which was poly(*N*,*N*-dimethylacrylamide)-*b*-poly(*n*-butyl acrylate-*co*-glycidyl methacrylate) block copolymer with a trithiocarbonate group. As shown in Fig. 1, the RAFT agent was used to mediate two-step miniemulsion polymerizations. A variety of poly(*n*-butyl acrylate)-*b*-polystyrene (PBA-*b*-PSt) diblock copolymer shell–core latexes with varied shell–core ratios were prepared, whose interface was enriched with epoxy groups. On the basis, we studied the morphology and mechanical properties of their latex films.

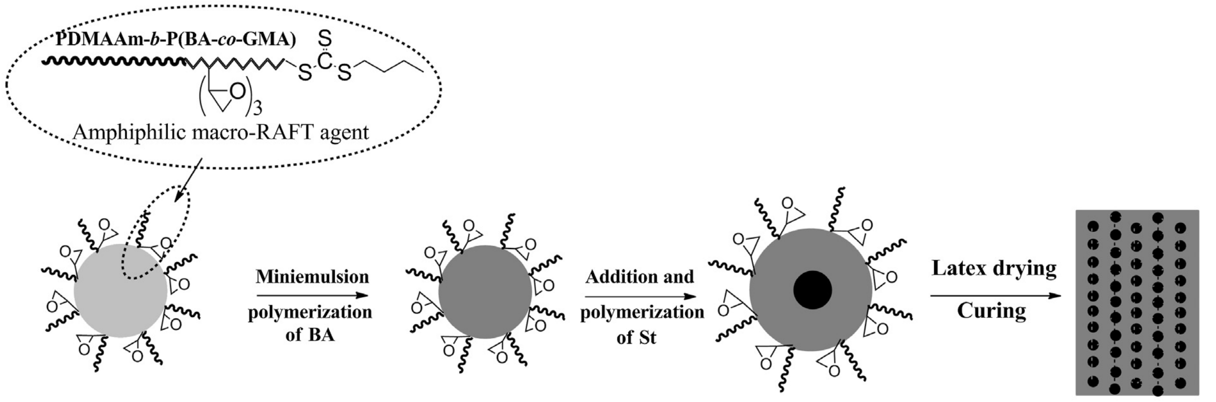
2. Materials and methods

2.1. Materials

De-ionized water (conductivity < 4 μS cm^{-1}) was used as received. Styrene (St), *n*-butyl acrylate (BA), glycidyl methacrylate (GMA), *N*,*N*-dimethylacrylamide (DMAAm) was purified by vacuum distillation. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) was re-crystallized twice from methanol. Potassium persulfate (KPS, >99%), sodium dodecyl sulfate (SDS, surfactant), *n*-hexadecane (HD, co-stabilizer, from Aldrich), 1,4-dioxane, ethylenediamine, and DICY were used without further purification. Small RAFT agent TTCA-4 was synthesized and purified according to the literature [43].

2.2. Synthesis of poly(N,N-dimethylacrylamide)-b-poly(n-butyl acrylate-co-glycidyl methacrylate) trithiocarbonate amphiphilic macro-RAFT agent

The macro-RAFT agent was synthesized by a two-step solution polymerization process under nitrogen atmosphere at 70 °C. During the first step, a solution containing 9.03 g (90 mmol) of DMAAm, 0.719 g (3 mmol) of TTCA-4, 0.016 g (0.1 mmol) of AIBN, and 18 g (200 mmol) of 1,4-dioxane was transferred into a flask. The reaction proceeded for 4 h. DMAAm conversion exceeded 95% from the GC analysis result (Gas chromatograph, Shimadzu GC-2010 High-Performance Capillary Gas Chromatograph with FID detector.) using 1,4-dioxane as the internal standard. Then, another solution containing 0.98 g (7.6 mmol) of BA, 1.63 g (11.5 mmol) of GMA, 0.03 g (0.2 mmol) of AIBN and 15 g (170 mmol) of 1,4-dioxane was deoxygenated and introduced to the reactor. The second step reaction lasted for 1.5 h. BA and GMA conversion were both 80%. The product (amphiphilic macro-RAFT agent) was collected by precipitation of the mixture in cyclohexane. The macro-RAFT agent was dried under reduced pressure at 50 °C. Fig. 2 shows the structure



macro-RAFT agent self-assembly onto the BA mini-droplet

PBA-*b*-PSt shell-core particles prepared by two-step miniemulsion polymerization

Ductile latex films with stable PSt spherical microphases

Fig. 1. Illustration of preparation of structured latex particles and films with microphase separation structures.