Polymer 50 (2009) 5892–5900

Contents lists available at ScienceDirect

Polymer

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

Post-polymerization of waterborne alkyd/acrylics. Effect on polymer architecture and particle morphology

Roque J. Minari, Monika Goikoetxea, Itxaso Beristain, María Paulis, María J. Barandiaran, José M. Asua*

Institute for Polymer Materials, POLYMAT, Departamento de Química Aplicada, The University of the Basque Country, Centro Joxe Mari Korta, Avenida Tolosa 72, 20018 Donostia-San Sebastián, Spain

ARTICLE INFO

Article history:
Received 29 June 2009
Received in revised form
13 October 2009
Accepted 17 October 2009
Available online 24 October 2009

Keywords:
Miniemulsion polymerization
Alkyds/acrylics
Post-polymerization

ABSTRACT

The limiting conversion commonly attained in the synthesis of waterborne alkyd/acrylic hybrid latexes hinders their industrialization. In this work, the mechanisms causing the limiting conversion were studied and post-polymerization conditions to efficiently remove the residual monomer determined. Further, it was observed that both the polymer architecture and the particle morphology were modified during post-polymerization. The mechanisms involved in the modification were investigated.

1. Introduction

Waterborne alkyd/acrylic coatings are interesting materials as they combine the positive properties of the alkyd resins (e.g. autoxidative curing, high gloss and penetration in wood) with the fast drying and color retention of acrylic latexes. It is expected that properties will improve with the intimate contact between the components of the hybrid system. Miniemulsion polymerization offers the possibility to achieve this intimate contact using a solution of the alkyd resin in the acrylic monomer as disperse phase [1]. Unfortunately, miniemulsion polymerization of monomer/resin system often shows a limiting monomer conversion which results in an unacceptable high concentration of residual monomer [1–3]. This is a serious problem that hinders the commercialization of these products.

Although several hypotheses have been proposed to explain the limiting conversion in waterborne polymer–polymer latexes (impurities within the resin [1,4], retardative chain transfer [1,5], retardative addition [6] and segregation of the resin within the polymer particle [5]), the actual reason is still an open question. (Meth)acrylate radicals may either abstract a hydrogen from the resin or propagate with the vinyl group of the resin. In the case of reaction with alkyds, it has been postulated that, due to steric features, methacrylate groups were more prone to abstract allylic hydrogens from the resin yielding a quite stable (and inactive) alkyd radical by conjugation with the adjacent double bond [5]. According to this hypothesis, these stable radicals would cause the limiting conversion. On the other hand, it has been postulated that addition to a resin double bond was favored for acrylates. As this alkyd radical is more reactive than the one produced by hydrogen abstraction, this mechanism was not considered as the main cause of limiting conversion in acrylate-based latexes [5]. Furthermore, it has been proposed that segregation results in alkyd-rich regions where the radicals cannot enter, either because of the hard shell, as in the methyl methacrylate (MMA)/alkyd system or because the high viscosity of the particle-phase, as in butyl acrylate (BA)/alkyd system [5]. Hence the monomer solubilized in those alkyd-rich domains cannot be polymerized. Tsavalas et al. [5] suggested that both mechanism, retardative chain transfer and segregation could be applied. But their simulation studies showed that the retardative chain transfer was not capable of producing the limiting conversion for the MMA/alkyd system, and that phase segregation was the most likely cause of the limiting conversion [7]. However, it was reported that complete conversion was achieved during polymerization of acrylic monomer-alkyd dispersions in the presence of preformed acrylic latex [8]. This seems to challenge the segregation model because it shows that monomer may diffuse not only out of the segregated resin but also through the aqueous phase to the alkyd-free particles.

The use of redox initiators during the synthesis of the hybrid alkyd–acrylic latex can improve monomer conversion, but still the concentration of residual monomer is unacceptable [9]. The

---

* Corresponding author. Tel.: +34 943 01 8181; fax: +34 943 01 7065.
E-mail address: jm.asua@ehu.es (J.M. Asua).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.10.042

residual monomer contained by the latex at the end of the polymerization is usually removed by devolatilization and/or post-polymerization [10–12]. Devolatilization is a unit operation in which the latex is stripped under vacuum conditions using either steam or inert gas, until acceptable low concentrations of residual monomer are reached. For this particular case, devolatilization is not adequate because the amount of residual monomer is high and because, due to the low water solubility of the (meth)acrylic monomers used and their low vapour pressure, the efficiency of devolatilization is limited and the complete elimination of the residual monomer could hardly be achieved [12].

Post-polymerization consists of adding, after the end of the main polymerization process, fresh radical generating initiators to polymerize the residual monomer. Water-soluble redox systems yielding hydrophobic radicals were found to be advantageous in either acrylic or vinylic latexes, because they yield a higher flux of radicals, in particular under mild conditions, having easy access to the place where the monomer is located (i.e., polymer particles) [13]. However, in polymer–polymer hybrid latexes post-polymerization can be a challenging matter, because the presence of the resin can severely reduce the efficiency of the radical [5,6]. On the other hand, Ilundain et al. [14] showed that post-polymerization using an initiator system producing highly reactive *tert*-butoxyl radical was able to modify the polymer structure of either vinylic or acrylic latexes. In VAc-rich copolymers, the *tert*-butyl radicals led to a decrease of the molecular weight, while in BA-rich copolymers, an increase of the gel content was observed. If a similar mechanism is operative for acrylic/alkyd systems, this is both a threat because the properties achieved during the synthesis of the latex may be modified during post-polymerization and an opportunity to extend the range of properties achievable. In order to turn the threat into an opportunity it is necessary to understand the mechanisms involved in the changes in polymer structure and particle morphology during post-polymerization of acrylic/alkyd hybrid latexes.

In this work, the performance of post-polymerization for removing the residual monomer in high solids alkyd/acrylic hybrid latexes was studied aiming at producing hybrid latexes with residual monomer lower than <100 ppm, to fulfill the requirements of commercial latexes. Also, the evolution of molecular architecture and particle morphology during post-polymerization was investigated. Two hybrid latexes with different acrylic monomers were considered: BA-based monomer system (BA/MMA/AA: 49.5/49.5/1 wt%) and BMA-based monomer system (BMA/MMA/AA: 49.5/49.5/1 wt%). Because of the reactivity ratios, in the first case, the residual monomer is mainly butyl acrylate while in the second case both methacrylates can be present. The different nature of the residual monomer could affect the grafting mechanism and in consequence the final architecture of the polymer.

2. Experimental

2.1. Materials

Technical grade monomers, methyl methacrylate (MMA) and butyl acrylate (BA), supplied by Quimidroga, and acrylic acid (AA) and butyl methacrylate (BMA) supplied by Aldrich were used without purification. The alkyd resin (SETAL 293, acid value 11 mg KOH/g) was supplied by Nuplex Resins. Potassium persulfate (KPS, Panreac), 2,2-azobis(2-methylbutyronitrile) (V59, Wako Chemicals); *tert*-butyl hydroperoxide (TBHP, Panreac), ammonium persulfate (APS, Panreac), H_2O_2 (Aldrich); ascorbic acid (AsAc, Panreac), and sodium metabisulfite (SMB, Fluka) were used as initiators. GPC grade tetrahydrofuran (THF, Scharlau) and diethyl ether (Sigma Aldrich) were used as received. Distilled water was used throughout the work.

2.2. Synthesis of the latexes

Table 1 summarizes the latexes used in this work. All latexes had a 50% of solids content and 50 wt% (based on organic phase) of alkyd resin. In the upper part of Table 1, the latexes employing the BA-based monomer system (BA/MMA/AA 49.5/49.5/1 wt%) are presented, while the bottom part shows the latexes produced with the BMA-based monomer system (BMA/MMA/AA 49.5/49.5/1 wt%). The latexes were synthesized in batch by miniemulsion polymerization at 70 °C. Polymerizations were carried out in a 1 L glass reactor equipped with a reflux condenser, stirrer, sampling device, nitrogen inlet, and two feed inlet tubes. The thermal initiator KPS was injected as a shot at the beginning of the process. When V59 was used, it was dissolved in the organic phase before miniemulsification. The reaction was allowed to react for 4 h. When the redox initiator system was used, APS and SMB were fed separately during 4 h, and then the system was allowed to react in batch for 1 more hour. The particle diameter (d_p) and the monomer conversion (x) achieved after the polymerization are also indicated in Table 1. Notice that latexes 2A and 2B, as well as 4A and 4B have been produced under the same conditions but in different batches. Details about the kinetics of most of those latexes can be found elsewhere [9].

2.3. Post-polymerization

Two different redox initiators were used in the post-polymerization: TBHP/AsAc, and H_2O_2/AsAc. Post-polymerizations were carried out in the same reactor used for synthesis of the latex, at 70 °C. The aqueous solutions of the oxidant and the reductant were separately fed into the reactor. Two different feeding times were used (30 min and 90 min), and they are specified in the description of the corresponding experiment. After the feeding of the initiator system was completed, the reactor temperature was held at 70 °C for 30 min.

2.4. Characterization

Residual monomers were measured by headspace gas chromatography using the full evaporation technique. The analysis was performed with a Hewlett–Packard HP 7694E Headspace Sampler interfaced to a Hewlett–Packard HP 6890 GC system with electronic pneumatic control and a flame-ionization detector. Pentanol was used as the internal standard.

Polymer architecture was characterized in terms of the fraction of gel content, sol molecular weight, the fraction of acrylic polymer that contained grafted alkyd (acrylic degree of grafting, ADG), the fraction of the alkyd resin that is grafted to the acrylic (resin degree of grafting, RDG), and the fraction of reacted double bonds (RDB).

The sol fraction of the latex was separated from the gel fraction using soxhlet extraction with THF. The filter containing the samples was dried under vacuum (<10 kPa) and then the sol fraction was extracted using THF under reflux during 24 h. The non-soluble part

Table 1
Summary of employed latexes.

Latex	Monomers	Initiator	d_p (nm)	x (%)
1	BA/MMA/AA	V59	134	66
2A	BA/MMA/AA	KPS	117	78
2B	BA/MMA/AA	KPS	126	83
3	BA/MMA/AA	APS/SMB	123	95
4A	BMA/MMA/AA	V59	140	73
4B	BMA/MMA/AA	V59	129	68
5	BMA/MMA/AA	KPS	125	98