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Abstract—The novel cross-linking (butyl acrylate-co-isobornyl methacrylate) colloids are prepared via semi-continuous seeded emulsion polymerization of butyl acrylate, isobornyl methacrylate and N-methylol acrylamide in aqueous phase using mixture of polyethylene glycol mono(octylphenyl) ether and sodium dodecyl sulphate as emulsifier and potassium persulphate as initiator. The optimal composition for preparing the novel cross-linking colloid was determined, and the structure of the as-prepared colloid was confirmed with FTIR spectrum. The formation of colloidal polymer was also corroborated by a difference between glass transition temperatures of colloid film and corresponding homopolymers. Calorimetry measurements showed that the colloid is composed of random copolymer. The particle size distribution exhibits unimodal character, suggesting a high stability of the colloid polymer.

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1. INTRODUCTION

Isobornyl methacrylate (IBOMA) is a relatively new monomer, which has many particular merits such as nonirritant property, transparency, low volatility and small polymerization shrinkage. However, the homopolymer of IBOMA has many drawbacks such as poor mechanical properties and brittleness.

The active bond along with the isobornyl alkoxy group in the IBOMA molecule makes it prone to free radical copolymerization with other monomers giving a polymer with advantageous properties. Qu et al. prepared novel crosslinked poly(IBOMA-co-BA) copolymers by free-radical copolymerization from IBOMA and butyl acrylate (BA), using 4,4'-isopropylidenediphenol dimethacrylate (BD) as crosslinking agent and 2,2'-azobisisobutyronitrile (AIBN) as thermal initiator [1]. Kurt et al. synthesized a copolymer of 4-methoxybenzyl methacrylate (MBMA) and IBOMA by atom transfer radical polymerization using methyl-2-bromopropionate as an initiator and pentamethyldiethylenetriamine/CuBr as catalyst under nitrogen atmosphere [2].

However, the preparation of the cross-linking polymer colloids by copolymerizing IBOMA and BA remains poorly explored. Herein, the novel cross-linking colloid is prepared via semi-continuous seeded emulsion polymerization of IBOMA, BA and cross-linking monomer (see Scheme 1). The goal of this study is to add cross-linking ability to colloid films by incorporating functional moieties, which are capable of chemical cross-linking after synthesis during film formation (see Scheme 2, which illustrates possible reactions of pendant N-methylol acrylamide (NMA) units [5, 6]). We report on the preparation and characterization of novel cross-linking colloids obtained through these routes.

1 The article is published in the original.
SYNTHESIS AND CHARACTERIZATION

2. EXPERIMENTAL

2.1. Materials

BA was obtained from Shanghai Chemical Reagents Supply Procurement of Five Chemical Plants (China). IBOMA was supplied with Wuxi Acryl Technology Co., Ltd. (China). IBOMA and BA were distilled under reduced pressure prior to polymerization. NMA was obtained from Shanghai Chuangxin Chemical Co., Ltd. Potassium persulfate (KPS) was obtained from the Second Chemical Reagent Factory in Yixin (China). Sodium bicarbonate (NaHCO\textsubscript{3}) was purchased from Shanghai Hongguang Chemical Plant Co., Ltd. (China). Sodium dodecyl sulfate (SDS) was obtained from Shanghai Yingpeng Chemical Reagent Co., Ltd. (China). Polyethylene glycol mono(octylphenyl) ether (OP-10) was obtained from Shanghai Minchen Chemical Co., Ltd. (China).

The water used in this work was distilled and then deionized.

2.2. Preparation of Novel Cross-linking Colloids

All runs were performed as seeded semi-continuous emulsion polymerizations in three stages. The first stage was a batch seed production step, the second one was a continuous stage involving feeding a monomer mixture and initiator stock solution, and the third stage was a batch finishing to increase the monomer conversion to completion.

The monomer mixture contained 20.00 g of BA and 10.00 g of IBOMA. A homogeneous aqueous solution containing 40.00 g of de-ionized water, 0.60 g of NaHCO\textsubscript{3} and mixed emulsifier composed of 1.00 g of OP-10 and 0.50 g of SDS was placed into a 250 mL four-neck flask equipped with a reflux condenser, a mechanical stirrer, and two dropping funnels and heated with the water bath. The stirring speed was maintained at 200 rpm throughout the runs. The reaction temperature was increased to 80°C within 30 min. An initiator solution was composed of 0.60 g of KPS, 1.00 g of NMA and 20.00 g of de-ionized water. 10% of initiator solution and 10% of mixed monomers were added to the reactor to produce the seed latex within 15 min. The seeded polymerization was continued for an additional 15 min. Then the rest of mixed monomers and the initiator solution were added slowly to the reactor using two separate dropping funnels within 3.0 h.

After the feed was completed, the temperature was raised to 90°C and maintained for another 60 min to increase monomer conversion rate. The colloids were then cooled to about 40°C, and NH\textsubscript{4}OH (25 wt %) was added to increase the pH to about 8.0. Finally, the mixture in the flask was cooled and filtered.

2.3. Characterizations

Fourier transform infrared (FTIR) spectroscopy (Avatar 370 spectrometer, Thermo Nicolet, USA) was used to confirm the structure of the novel cross-linking poly(BA-IBOMA) colloids. The IR spectra were obtained on a Nicolet Avatar 370 FTIR spectrometer using KBr pellets.

![Scheme 1](https://example.com/scheme1.png)


![Scheme 2](https://example.com/scheme2.png)

Scheme 2. Potential cross-linking reactions for NMA (R\textsubscript{f1} and R\textsubscript{f2} stand for different chain segments in the novel colloids).