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Effect of polymerization time on monomer conversion in a semi-batch emulsion polymerization of styrene and butyl acrylate

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Introduction

Styrene-acrylic copolymers, as an important product of emulsion polymerization, have various applications such as paint, coating, ink and adhesive industries, owing to their good film forming, durability, adhesion and low cost [1]. One of the most important drawbacks of styrene and butyl acrylate emulsion copolymerization is remaining unreacted monomers in the product latexes that leads to a low monomer conversion and air pollution [2]. This problem, mainly, comes back to steric hindrance of benzene ring and n-butyl group in the monomers structure. One of techniques to overcome this challenge is increasing the final batch time (the time after completion addition of monomers) in the semi-batch emulsion polymerization process. In the present work, the influence of polymerization time on monomer conversion in a semi-batch emulsion polymerization was investigated using gravimetric method.

Experimental

Materials

Butyl acrylate (BA) and acrylic acid (AA) were purchased from Petro Chem Co, Dubai, UAE. Styrene(St) was attained from Shazand Petrochemical Co, Arak, Iran. Ammonium persulfate (APS, Aldrich, Lancaster, UK), dioctyl sulfosuccinate (DOSS, Sigma Aldrich, Saint Louis, USA), nonylphenol ethoxylate (K20, Kimiagaran Emrooz Chemical Industries Co, Arak Iran) and sodium hydrogen carbonate ($NaHCO_3$, Merck, Germany), used as initiator, anionic surfactant, nonionic surfactant and buffer, respectively.

Synthesis of St-BA-AA copolymers

Emulsion polymerization process was carried out in a four-necked glass reactor equipped with mechanical stirrer, reflux condenser, thermometer and dropping funnel. Chemicals such as water, emulsifier and buffer were transferred to the reactor as initial charge and agitated for 30 minutes. Then, about 5% of the monomer mixture was added to the reactor and agitation continued for another 30 minutes. As temperature reached to 70 °C a portion of initiator solution was fed and 15 minutes after that, the remaining monomers mixture added dropwise within 3.5 h with about constant rate. When addition of monomer was completed, temperature was increased to 80 °C and reaction continued for a determinate time. The emulsion polymerization recipe is presented in Table 1.

Table 1. Emulsion polymerization recipe

Materials	St	BA	AA	APS	water	DOSS	K20	$NaHCO_3$
Reactor charge (g)	7.5	5.5	0.25	0.25	300	4.5	8	0.6
Feeding (g)	130	107	4.75	0.55	10	–	–	–

Result and Discussion

Solid content calculation

To determine solid content of the synthesized latexes, about 0.5-1 g of the latex was poured to a special pan and placed in an oven at 60 °C for 2 h. The residue was weighted and solid content was calculated using equation (1) [4]:

$$Solid\ content = \frac{m_3 - m_1}{m_2} \times 100 \qquad (1)$$

Where, m_1, m_2 and m_3 are weight of pan, wet latex and residue, respectively.

Monomer conversion determination

To calculation of monomer conversion, equation (2) was used [4]:

$$Monomer\ conversion = \frac{(solid\ content - A)}{B} \times 100 \qquad (2)$$

Where, A and B are weight percentage of all nonvolatile materials before polymerization and whole monomers weight percentage, respectively.

Some monomers, such as St and BA due to steric hindrance of bulky groups in their structures, have low tendency to undergo copolymerization [3]. To overcome this problem, one of the simplest, and also effective strategies is increasing the polymerization time. As shown in Fig. 1 and Table 2, increasing the final batch time from 40 to 70 min. led to an increase in monomer conversion from 93.0% to 99.7%.

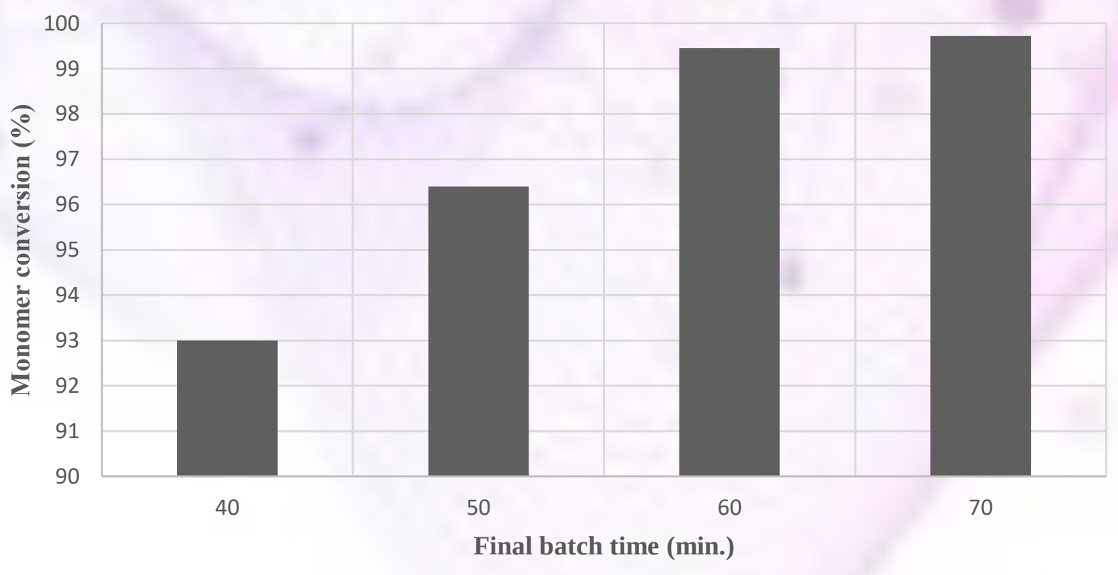

Fig. 1. Effect of the final batch time on monomer conversion.

Table 2. Monomer conversion and final batch time relationship.

Final batch time (min.)	Monomer conversion (%)
40	93.0
50	96.4
60	99.4
70	99.7

Conclusion

In a semi-batch emulsion polymerization of St and BA as main monomers and AA as functional monomer, influence of the final batch time on monomer conversion was investigated. It is concluded that monomer conversion dramatically increases with increasing time after monomer feeding completion (from 93.0% to 99.7%).

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