

OBTAINING A COPOLYMER OF STYRENE AND α -METHYLSTYRENE USING VARIOUS ANIONIC AND NON-IONIC EMULSIFIERS

¹Haydarov Bekzod, ²Asamov Javlon, ³Abdurimov Akbar, ⁴Elmurodov Doston, ⁵Muzaffarov Tolibjon

^{1,2} Assistant teachers of the Yangiyer branch of the Tashkent Institute of Chemical Technology

³ Trainee-teacher of the Yangiyer branch of the Tashkent Institute of Chemical Technology

^{4,5} Students of the Yangiyer branch of the Tashkent

Institute of Chemical Technology

<https://doi.org/10.5281/zenodo.7764299>

Abstract. A copolymer of styrene and α -methylstyrene was obtained by the method of emulsion copolymerization in the presence of an ammonium persulfate initiator and various emulsifiers at a mass ratio of the initial monomers of 70 : 30. The emulsifiers were used as ionic (sodium oleate, potassium oleate, potassium stearate, a mixture of oleate and potassium stearate), and non-ionic emulsifiers (OS-25 and OS-50). The yields of the copolymer in the case of using ionic emulsifiers were 74–85%, and the maximum yield was observed only when using a mixture of potassium oleate and stearate (1 : 1). When using nonionic emulsifiers OS-25 and OS-50, the yields of the copolymer were 75–90%, the highest yield was obtained when using emulsifier OS-50. The molar ratio of styrene and α -methylstyrene units, determined by ¹H NMR spectroscopy, was 8 : 3. It was found by IR spectroscopy that the copolymer of styrene and α -methylstyrene obtained using potassium stearate has minimal residual amounts of emulsifier due to its low adsorption by the resulting copolymer. In the case of using sodium or potassium oleates and their mixtures, very weak characteristic frequency bands appear, which are characteristic of the carboxyl group of emulsifier molecules, which indicates their inclusion in the synthesized polymer chains as comonomers. In the case of using nonionic emulsifiers OS-25 and OS-50, the copolymer cannot be washed away from them, despite the fact that the emulsifier molecules are not covalently bonded to the copolymer. The good adsorption of emulsifier molecules on the hydrophobic surface of the copolymer is associated with the presence of hydrophobic alkyl and ethylene fragments in the structures of the molecules of these emulsifiers and the inability to ionize the terminal OH groups under normal conditions.

Keywords: emulsion copolymerization, styrene, α -methylstyrene, anionic emulsifiers, nonionic emulsifiers, copolymer.

Introduction

It is known that at present copolymers of styrene and α -methylstyrene (SAM, SAM ED) are widely used in industry [1]. These copolymers belong to a group of polymers that increase the adhesion of synthetic rubbers. Copolymers of styrene and α -methylstyrene can be used as components of hot melt coatings and adhesives. Adhesives, mastics and sealants based on these copolymers are very sensitive to pressure. Their main application is to impart adhesion in elastomeric block copolymers of styrene, isoprene and polychloroprene - elastomers for the production of adhesives. Some, but not all, copolymers are as effective as hot-melt and hot-melt

formulations, where they exhibit good compatibility and low cloud point mixing. Copolymers can also be used as additives to paints and chemical coatings [2].

The purpose of this work is to study the effect of the nature of emulsifiers on the yield of the obtained copolymer of styrene and α -methylstyrene and on the presence of residues of emulsifiers used in its synthesis.

Experimental part

The starting monomers, styrene and α -methylstyrene, were distilled in a vacuum to free them from the main part of the inhibitor; then, immediately before the synthesis of the copolymer, the resulting distillates of the monomers were washed from the remnants of the inhibitor three times with 5% NaOH solution and then with distilled water until neutral in a separating funnel.

The infrared spectra of the synthesized copolymer samples were recorded on a Perkin Elmer Spectrum 100 IR Fourier spectrometer (USA) with an ATR attachment. ¹H NMR spectra were recorded on a Jeol JNM ECX-400 instrument (operating frequency 400.13 MHz) (Jeol, Japan).

Emulsion copolymerization of styrene and α -methylstyrene in the presence of potassium stearate emulsifier.

40 ml of distilled boiled water and 0.06 g (1 mmol) of KOH are placed in a four-necked flask with a volume of 250 ml. After dissolving the alkali, 0.24 g (0.84 mmol) of stearic acid is added. The contents of the flask are stirred in a water bath at 40–45°C for 20 min, then the pH of the resulting solution is checked using universal indicator paper, the value of the medium should correspond to 9. Then the resulting solution of potassium stearate is purged with a slow current of argon for 5 min, and then the mixture for the remainder of the copolymer synthesis time. A mixture of 7.7 ml (0.074 mmol) of styrene and 3.3 ml (0.027 mmol) of α -methylstyrene is added from a dropping funnel to the resulting solution of potassium stearate and vigorously stirred until an emulsion is formed. A solution of 0.05 g (0.2 mmol) of ammonium persulfate in 5 ml of distilled water is introduced into the resulting mixture.

Next, instead of a dropping funnel, a thermometer is inserted and the reaction mixture is gradually heated for 30 min to 60°C and the temperature is maintained for 3 h. The resulting latex is poured into a beaker and destroyed with 25% aqueous potassium chloride solution (10 ml) at 50°C.

The copolymer precipitate is filtered off on a Buchner funnel, washed several times with hot water until there is no reaction to chloride ion (sample with a solution of silver nitrate) and a minimum amount of residual emulsifier (no foam from potassium stearate). The copolymer is dried in a thermostat for 48 h to constant weight at a temperature of 65°C. The yield of the copolymer is 74% in terms of the initial monomers [3].

Emulsion copolymerization of styrene and α -methylstyrene in the presence of sodium oleate emulsifier.

20 ml of distilled boiled water and 0.166 g (4.15 mmol) of NaOH are placed in a four-necked flask with a volume of 250 ml. After the alkali is dissolved, 0.66 g (2.34 mmol) of oleic acid is added. The contents of the flask are stirred in a water bath at 40–45°C for 20 min, then the pH of the resulting solution is checked using universal indicator paper, the pH of the medium should correspond to 9. Then, the resulting sodium oleate solution is purged with a slow current of argon for 5 min, and the reaction mixture during the remaining time of the synthesis of the copolymer. A mixture of 7.7 ml (0.074 mmol) of styrene and 3.3 ml (0.027 mmol) of α -

methylstyrene is added from a dropping funnel to the resulting sodium oleate solution and vigorously stirred until an emulsion is formed. A solution of 0.05 g (0.2 mmol) of ammonium persulfate in 5 ml of distilled water is introduced into the resulting mixture.

Next, a thermometer is inserted into one neck of the flask instead of a dropping funnel and the reaction mixture is gradually heated for 30 min to 60°C and the temperature is maintained for 3 h. The resulting latex is poured into a beaker and destroyed with 10% aqueous sodium chloride solution (10 ml) at 60° C.

The precipitate of the copolymer is filtered off on a Buchner funnel, washed several times with hot water until there is no reaction to the chloride ion (sample with a solution of silver nitrate) and the minimum amount of residual emulsifier (no foam from sodium oleate).

The copolymer is dried in a thermostat for 48 h to constant weight at a temperature of 65°C. The yield of the copolymer is 80% in terms of the initial monomers [3].

Emulsion copolymerization of styrene and α -methylstyrene in the presence of potassium oleate emulsifier.

40 ml of distilled boiled water and 0.060 g (1 mmol) of KOH are placed in a flask. After the alkali is dissolved, 0.24 g (0.85 mmol) of oleic acid is added. The contents of the flask are stirred in a water bath at 40–45°C for 20 min, then the pH of the resulting solution is checked using universal indicator paper, the pH of the medium should be equal to 9. Then the resulting potassium oleate solution is purged with a slow flow of argon for 5 min, and then the reaction mixture for the remainder of the copolymer synthesis time. A mixture of 7.7 ml (0.074 mmol) of styrene and 3.3 ml (0.027 mmol) of α -methylstyrene is added from a dropping funnel to the resulting solution of potassium oleate and vigorously stirred until an emulsion is formed. A solution of 0.05 g (0.2 mmol) of ammonium persulfate in 5 ml of distilled water is introduced into the resulting mixture.

Next, a thermometer is inserted into the flask instead of a dropping funnel and the reaction mixture is gradually heated for 30 min to 60°C and maintained for 3 h. The resulting latex is poured into a beaker and destroyed with 25% potassium chloride solution (10 ml) at 50°C.

The copolymer precipitate is filtered off on a Buchner funnel, washed several times with hot water until there is no reaction to chloride ion (sample with silver nitrate solution) and a minimum amount of residual emulsifier (no foam from potassium oleate). The copolymer is dried in air to constant weight at 65°C. The yield of the copolymer is 77% in terms of the initial monomers.

Emulsion copolymerization of styrene and α -methylstyrene in the presence of a mixture of potassium oleate and potassium stearate emulsifiers.

40 ml of distilled boiled water and 0.06 g (1 mmol) of KOH are placed in a four-necked flask with a volume of 250 ml. After dissolving the alkali, a mixture of 0.24 g (0.84 mmol) of stearic acid and 0.24 g (0.85 mmol) of oleic acid is added. The contents of the flask are stirred in a water bath at 40–45°C for 20 min, then the pH of the resulting solution is checked using universal indicator paper, the pH of the medium should correspond to 9. Then the resulting solution of a mixture of potassium oleate and potassium stearate is purged with a slow stream of argon for 5 min, and then the reaction mixture for the entire remaining time of copolymer synthesis. To the resulting sodium oleate solution, a mixture of 7.7 ml (0.074 mmol) of styrene and 3.3 ml (0.027 mmol) of α methylstyrene is added and vigorously stirred until an emulsion is formed. A solution

of 0.05 g (0.2 mmol) of ammonium persulfate in 5 ml of distilled water is introduced into the resulting mixture.

Next, a thermometer is inserted into one neck of the flask instead of a dropping funnel and the reaction mixture is gradually heated for 30 min to 60 °C and the temperature is maintained for 3 h. The resulting latex is poured into a beaker and destroyed with 25% aqueous sodium chloride solution (10 ml) at 50 °C.

The copolymer precipitate is filtered off on a Buchner funnel, washed several times with hot water until there is no reaction to chloride ion (sample with a solution of silver nitrate) and a minimum amount of residual emulsifier (no foam from a mixture of potassium oleate and potassium stearate). The copolymer is dried in air to constant weight at a temperature not exceeding 65°C. The yield of the copolymer is 85% in terms of the initial monomers [3].

Emulsion copolymerization of styrene and α -methylstyrene in the presence of nonionic emulsifier OS-25.

90 ml of 0.1 n. sodium carbonate solution and add 1.8 g of OS-25. The contents of the flask were stirred in a water bath at 40–45°C for 20 min. Then, the resulting OS-25 solution is purged with a slow flow of argon for 5 min, and then the reaction mixture is purged for the entire remaining time of the copolymer synthesis. A mixture of 7.7 ml (0.074 mmol) of styrene and 3.3 ml (0.027 mmol) of α methylstyrene is added to the resulting OS-25 solution through a dropping funnel and vigorously stirred until an emulsion is formed. A solution of 0.05 g (0.2 mmol) of ammonium persulfate in 5 ml of distilled water is introduced into the resulting mixture.

Next, a thermometer is inserted into the flask instead of a dropping funnel and the reaction mixture is gradually heated for 30 min to 70°C and maintained for 5 h. and wash the precipitate of the copolymer on a Buchner funnel repeatedly with hot water at a temperature of 75°C to a minimum amount of residual emulsifier OS-25 (minimum or no foam in the wash water). Полимер высушивают на воздухе до постоянного веса. Выход сополимера – 75% в пересчете на исходные мономеры.

Emulsion copolymerization of styrene and α -methylstyrene in the presence of nonionic emulsifier OS-50.

90 ml of 0.1 n. sodium carbonate solution and add 1.8 g of OS-50. The contents of the flask were stirred in a water bath at 40–45°C for 20 min. Then, the resulting OS-50 solution is purged with a slow current of argon for 5 min, and then the reaction mixture is purged for the entire remaining time of copolymer synthesis. A mixture of 7.7 ml (0.074 mmol) of styrene and 3.3 ml (0.027 mmol) of α -methylstyrene is added to the resulting OS-50 solution through a dropping funnel and vigorously stirred until an emulsion is formed. A solution of 0.05 g (0.2 mmol) of ammonium persulfate in 5 ml of distilled water is introduced into the resulting mixture.

Next, a thermometer is inserted into the flask instead of a dropping funnel and the reaction mixture is gradually heated for 30 min to 70°C and maintained for 5 h. in a mortar and wash the precipitate of the copolymer on a Buchner funnel repeatedly with hot water at a temperature of 75°C to a minimum amount of residual emulsifier OS-50 (minimum or no foam in the wash water).

The copolymer is dried in air to constant weight. The yield of the copolymer is 90% in terms of the initial monomers.

Results and its discussion

In all the obtained samples of the copolymer of styrene and α -methylstyrene, according to IR spectroscopy data, the following absorption bands were determined, cm⁻¹: 3024– C–H (Ar);

2923–2926 (vas), 2844–2847 (vs) CH_3 (α -methylstyrene) and CH_2 ; 1599, 1491-1493 - (Ar); 1452 - CH_2 (δ sciss.); 1027–1029 - $\nu(\text{C-HAr})$; 756, 695–696 - $\delta(\text{C-HAr})$.

When using sodium or potassium oleates as emulsifiers, as well as a mixture of potassium oleate and potassium stearate, the IR spectrum of the obtained copolymer samples has a weak absorption band in the region of 1560 cm^{-1} , which is characteristic of the stretching vibrations of the carbonyl group in the carboxylate ion, which indicates copolymerization oleate ion together with styrene and α -methylstyrene [3]. In this regard, the use of such a copolymer of styrene and α -methylstyrene is excluded in cases where it is necessary to ensure high dielectric characteristics of the obtained copolymer, despite the highest yield of the copolymer from the initial monomers. It is necessary to use emulsifiers based on the stearate ion or other anions of higher aliphatic carboxylic acids that do not have $\text{C}=\text{C}$ double bonds in their structure and therefore do not participate in copolymerization processes.

In the case of using nonionic emulsifiers OS-25 or OS-50, according to IR spectroscopy, noticeable residual amounts of these substances are observed in the synthesized copolymer samples (peak 1104 cm^{-1} for the C-O-C fragment), which are not removed from the resulting copolymer by repeated washing hot water. In all likelihood, this is due to the good adsorption of these nonionic emulsifiers on the hydrophobic surface of the obtained copolymer due to the presence of hydrophobic alkyl and ethylene fragments in the structures of the molecules of these emulsifiers.

The obtained ^1H NMR spectra of samples of the copolymer of styrene and α -methylstyrene (70 : 30 wt %) showed that all samples are almost identical in terms of chemical shifts of protons and areas of the corresponding peaks. The ratio of monomeric units in the copolymer can be determined from the ratio of the signals of methine protons in the polymer chain (for styrene fragments) and α -methyl protons (for α -methylstyrene fragments). α -methylstrol has 3 units, the signal of methyl groups of which creates 9 conditional protons, styrene - 8 units, the signal of which creates 8 conditional methine protons. Peak 1.40 ppm refers to methyl protons; peak 6.57 ppm refers to methine protons. The ratio of signal intensities of methyl and methine protons is 9 : 8, which confirms the ratio of 8 : 3 for monomer units of styrene and α -methylstyrene in the copolymer obtained (see Diagram 1).

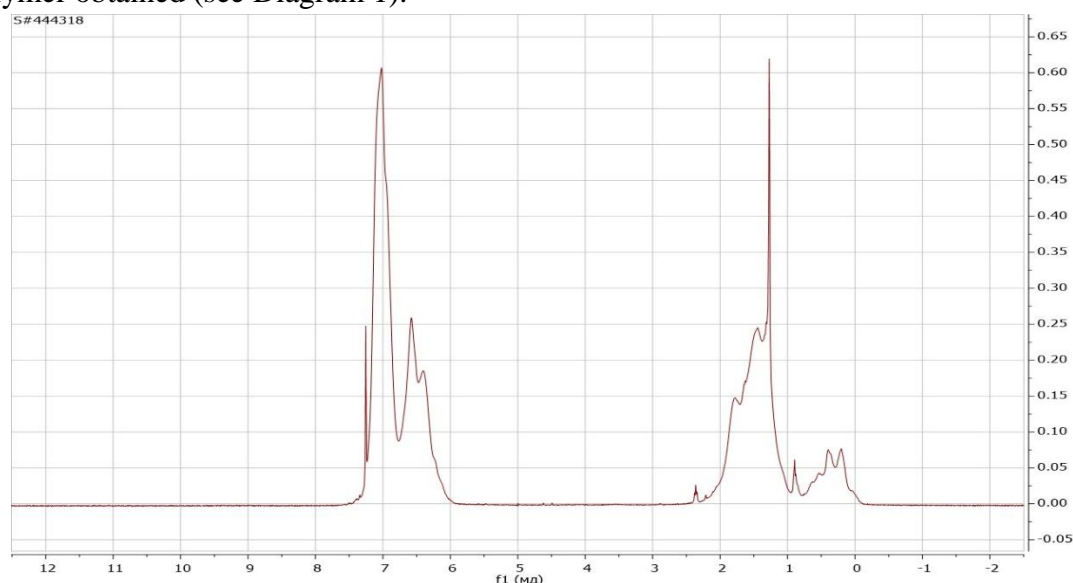


Diagram 1. ^1H NMR spectrum of the synthesized sample of the copolymer of styrene and α -methylstyrene

Conclusion

A copolymer of styrene and α -methylstyrene was obtained by emulsion copolymerization in the presence of an ammonium persulfate initiator and various emulsifiers at a mass ratio of the initial monomers of 70 : 30. The emulsifiers were used as ionic (sodium oleate, potassium oleate, potassium stearate, a mixture of oleate and potassium stearate), and non-ionic emulsifiers (OS-25 and OS-50). The most promising emulsifier is the use of potassium stearate, since the stearate ion, due to the absence of a double bond in the structure, is not included in the macromolecular chains of the copolymer. The use of nonionic emulsifiers does not make it possible to obtain a copolymer of styrene and α -methylstyrene with the lowest possible residual content of these emulsifiers due to their good adsorption on the hydrophobic surface of the obtained copolymer.

REFERENCES

1. Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers. Edited by John Scheirs and Duane B. Priddy. *John Wiley & Sons, Ltd.* **2003**. 744p.
2. Paul D., Newman S. Polymer mixture / per s English. Pod editor D. Pola, S. Newmena. T.1. M.: Mir. 1981. 541p. Султанова Г.И., Сайфетдинова Г.А.,
3. Rakhmatullina A.P., Akhmedyanova R.A., Liakumovich A.G. Effect of potassium salt on stearic acid and oleic acid on emulsion copolymerization of styrene and alpha-methylstyrene. *Vestnik Kazan Technological University*. 2006. #2. P. 67-71.