

Synthesis and characterization on hydrophobic monomer 4-butyl styrene

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4-butyl styrene has a good copolymerization activity with acrylamide. Benzene can improve rigidity of copolymer molecular and meanwhile benzene which is hydrophobic group, can not only enhance the thermal resistance and salt tolerance, but also produce hydrophobic association for copolymer. This paper describes how to prepare hydrophobic monomer 4-butyl styrene from butylbenzene by Friedel-Crafts Acylation Reaction, hydrogen transfer reduction, dehydration of the alcohol to alkene. Product is studied as 4-butyl styrene with high purity through IR, ¹HNMR.

(Received December 18, 2014; accepted April 5, 2016)

Keywords: 4-butyl styrene, Hydrophobic monomer, Micellar copolymerization, Temperature sensitive polymer

1. Introduction

In recent years, to meet the stringent demand of high-temperature and high-salinity reservoir for temperature and salt-resistant copolymer of acrylamide used for EOR, domestic and foreign researchers have developed temperature and salt-resistant copolymer, amphoteric polyacrylamide, hydrophobic associating polymer, comb polyacrylamide. Such performance of thermal resistance and salt tolerance is based on modification that polyacrylamide is the main chain where hydrophobic monomer is introduced into the side groups through an ester bond or an ether bond which is easy to hydrolysis on high temperature [1-10], and removes the hydrophobic groups in the external environment stimulation and so that loses the hydrophobic association effect. The alkyl styrene can preferably keep the hydrophobic association effect because the bonds are too strong to remove the hydrophobic groups under the stimulation of the external environment [11-20].

In this paper, 4-butyl styrene (nBS) was synthesized and was used for synthesis of polyacrylamide copolymer. 4-butyl styrene has a good copolymerization activity with acrylamide. Benzene could improve rigidity of copolymer molecular so that the molecular chain of copolymer aqueous solution became more stretch and adhesive ability was improved, and benzene which is hydrophobic group could produce hydrophobic association that was enhanced by n-butyl.

2. Experimental

2.1 Materials

Butylbenzene was purchased from Beijing J&K Scientific. Acetic anhydride, p-toluenesulfonic acid monohydrate, aluminum chloride, Sodium borohydride and dichloromethane were all purchased from Tianjin Fuchen Chemical Reagents Factory. All the purchased reagents were in analytical grade. FT-IR Spectrometer (colet 560) was purchased from TA Instruments Corporation. Super-conducting Fourier Digital NMR spectrometer (AVANCE AV 400) was purchased from Bruker Corporation.

2.2 Synthetic Route

4-butyl styrene was synthesized by Friedel-Crafts acylation reaction, carbonyl reduction reaction and alcohol dehydration reaction, which has a good hydrophobic effect due to the incorporation of the vinyl group into butylbenzene. The synthetic route is also applicable to synthesis other alkyl styrene with different carbon chain. The preparation method comprises the following steps:

2.2.1 Friedel-Crafts acylation reaction at the para position of n-butylbenzene

The n-butyl acetophenone was synthesized by Friedel-Crafts acylation of n-butylbenzene, with the aluminum chloride as catalysis and the maleic anhydride as acylation. The reaction equation was shown in Fig. 1.

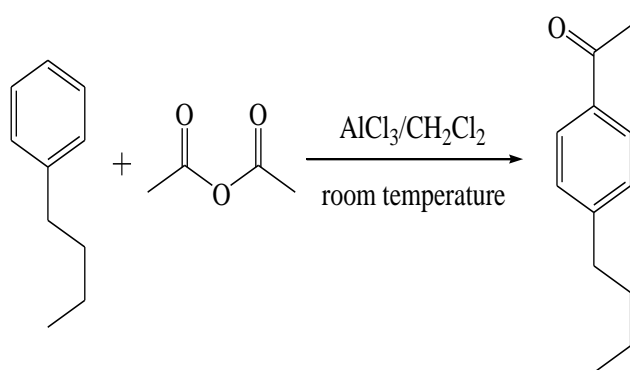


Fig. 1. Friedel-Crafts Acylation Reaction

2.2.2 Carbonyl reduction reaction

With the reductant of sodium borohydride, the second product 1-methyl butyl benzyl alcohol was synthesized through the carbonyl reduction reaction. the reaction equation was shown in Fig. 2.

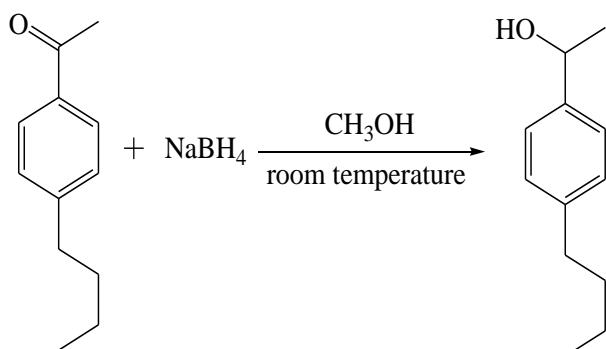


Fig. 2. Carbonyl reduction reaction

2.2.3 4-butyl styrene synthetic reaction

With the catalysis of toluenesulfonic acid monohydrate, the main product was synthesized when it reacts the elimination reaction in the molecule of 1-methyl butyl benzyl alcohol. The reaction equation was shown in Fig 3.

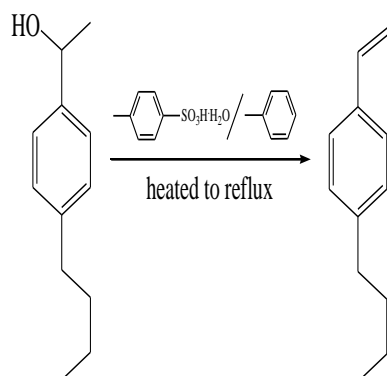


Fig. 3. Synthesis on 4-butyl styrene

2.3 Preparation

2.3.1 Preparation of 4-n-butyl acetophenone

In 500 mL three-necked flask with magnetic stirring, 56.75 g aluminum chloride was dissolved in 200 mL dichloromethane at 0°C for 30 min, in which 22.45 g acetic anhydride solution dissolved in 25 mL dichloromethane was slowly added, and stirred for 15 min at 0°C , followed by slowly dropwise addition 13.4g n-butyl benzene dissolved in 25 mL dichloromethane for 30 min. The reaction was lasted for 5 h at room temperature. After completion of the reaction, the mixture was cooled to 0°C , and then washed twice successively with 125 mL 10 wt% hydrochloric acid solution, 125 mL saturated sodium carbonate solution and 125ml saturated sodium chloride solution. 4-n-butyl acetophenone was synthesized from the resulting solution with anhydrous magnesium sulfate and vacuum rotary evaporation acetophenone.

2.3.2 Preparation of 1-methyl-n-butyl benzyl alcohol

In 500 mL three-necked flask with magnetic stirring, 13.2 g 4-n-butyl acetophenone was added to 250mL methanol at 0°C , which was gradually added 0.85 g sodium borohydride into decile. In the end, the temperature was raised to 60°C for 12 h. After completion of the reaction, the mixture with rotary evaporation to remove methanol was dissolved in 250 mL hexane and then washed twice with 125 mL 10wt% hydrochloric acid solution, 125 mL saturated sodium chloride solution. 1-methyl-n-butyl benzyl alcohol was synthesized from the resulting solution which was evaporated to remove hexane.

2.3.3 Preparation of 4-butyl styrene

In 500 mL Single neck flask with magnetic stirring and manifold, 350 mL methylbenzene, 6.489 g 1-methyl-n-butyl and 0.2077 g p-Methylbenzene sulfonic acid were added in order and was heated to 160°C for reflux condensation 2 h. After completion of the reaction, the mixture was cooled to room temperature, and then washed with 340 mL distilled water. Finally, the product, colorless, 4-butyl styrene was synthesized from the resulting solution which was evaporated to remove methylbenzene by means of silica gelcolumn chromatography separation and purification.

3. Results and discussion

3.1 IR spectrum of 4-butyl styrene

Each step product was studied through IR for 32 times scans, resolution of 4 cm^{-1} , scan range $4000 \sim 400\text{ cm}^{-1}$ on Nicolet 560 FTIR.

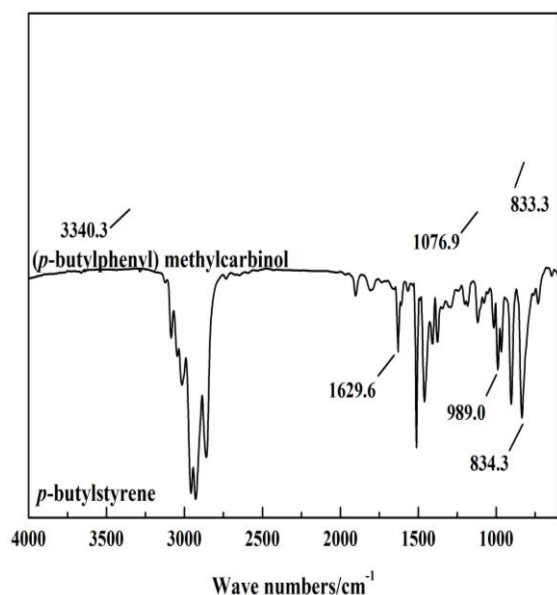


Fig. 4. IR spectrum of 4-butyl styrene

FTIR Spectroscopy results for the samples are shown in Fig. 4. The characterization peaks of benzene on 4-butyl styrene show at 835 cm^{-1} and double bond on 4-butyl styrene stretching at 989 cm^{-1} . The FT-IR spectrum of 4-butyl styrene exhibit the adsorption peaks at 1609, 1566 and 1512 cm^{-1} respectively. The discernible spectra preliminary proved that the major adsorption peaks are from 4-butyl styrene.

3.2 ^1H NMR spectrum of 4-butyl styrene

Deuterated chloroform as a solvent, product was studied through Bruker AV II-400 MHz NMR spectrometer for 90° pulse angle, 3 seconds sustained-release, 48 times scans.

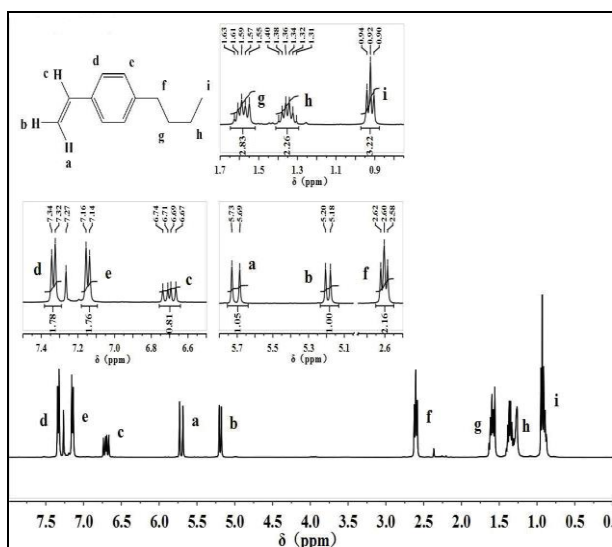


Fig. 5. ^1H NMR spectrum of 4-butyl styrene

FTIR Spectroscopy results for the samples are shown in Fig. 5, in which chemical shift and peak area of absorption peak have been marked and assigned. Chemical shift at 5.69 and 5.73 is double absorption peak of double bond hydrogen a, chemical shift at 5.18 and 5.20 exhibits another double bond hydrogen b. Four re-absorption peak of double bond hydrogen c shows at 6.67, 6.69, 6.71 and 6.74. chemical shift 7.32 and 7.34 is the absorption peak of hydrogen d close to benzene and chemical shift 7.14 and 7.16 is the absorption peak of hydrogen e close to n-butyl. Triplet absorption peak of methylene hydrogen f show at 2.58, 2.60 and 2.62. Five absorption peaks of methylene hydrogen g show at 1.55, 1.57, 1.59, 1.61 and 1.63. Six re-absorption peak of methylene hydrogen h show at 1.31, 1.32, 1.34, 1.36, 1.38 and 1.40. Triplet absorption peak of n-butyl methyl hydrogen i show at 0.90, 0.92 and 0.94. H NMR solvent peak of deuterated chloroform show at 7.27. The two discernible spectra revealed that the major adsorption peaks are from 4-butyl styrene, confirming the covalent modification, and the synthesized hydrophobic monomer can be got in high purity through purification.

4. Conclusions

4-butyl styrene, which can be synthesized through Friedel-Crafts acylation, carbonyl reduction reaction and dehydration of alcohol to alkene from n-butylbenzene, has a good copolymerization activity with acrylamide. The hydrophobic monomer has the characteristic of thermal resistance and salt tolerance resulting from rigidity of molecular and hydrophobic associating effect from hydrophobic groups.

Studied through IR, ^1H NMR, 4-butyl styrene 4-butyl styrene in high purity can be synthesized by three steps.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgements

Project is supported by the National Natural Science Foundation of China (Grant No. 51404036) and PetroChina Innovation Foundation — (Grant No. 2013D-5006-0207).

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