



Effect of ultrasound in the free radical polymerization of acrylonitrile under a new multi-site phase-transfer catalyst – A kinetic study



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ABSTRACT

The kinetics of polymerization of acrylonitrile (AN) was carried out under heterogeneous condition using a new multi-site phase-transfer catalyst (MPTC), viz., N,N'-dihexyl-4,4'-bipyridinium dibromide in the presence of water soluble initiator, potassium peroxydisulphate (PDS) under chlorobenzene/water two phase system assisted by ultrasound irradiation at constant temperature 60 ± 1 °C under nitrogen atmosphere. The rate of polymerization increases with an increasing the concentrations of AN, MPTC and PDS. The order with respect to [AN], [MPTC], and [PDS] were found to be 1.01, 1.03 and 0.52, respectively. Based on the observed results a suitable mechanism has been proposed to account for the experimental observations followed by a discussion on its significance.

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1. Introduction

The reaction between mutually immiscible reactants are usually difficult to conduct efficiently, even under severe operating conditions. Such problems as low reaction rate, low conversion of reactants and low yield of products can be overcome through multi-site phase-transfer catalysis (MPTC). The phase-transfer catalysts, usually quaternary onium salts, crown ethers, cryptands, etc., can be applied to give a high conversion and a high selectivity under very mild reaction conditions. Nowadays, the phase-transfer catalysis is found to be a useful tool for increasing efficiency, improving safety, and reducing environmental impact. Thousands of papers published and patents granted have expanded the use of MPTC in organic synthesis and is widely used for manufacturing pharmaceuticals, agricultural chemicals, perfumes, flavors, dyes, polymers and other important chemicals via substitution, displacement, condensation, polymerization, reduction and oxidation [1–14]. The primary purpose in adopting phase transfer catalysis in combination with ultrasound irradiation is to search for a more effective condition to enhance the reaction [15–20].

Many studies have carried out and it is well documented that the advantageous of ultrasound procedures are good yields, short reaction time and mild conditions [21–23]. Ultrasonic energy produces an alternating adiabatic compression and rarefaction of the liquid

medium being irradiated. As no direct interaction is possible between ultrasound and matter, an indirect phenomenon, i.e., cavitation phenomena is used to explain the enhanced reaction rate. Hence, ultrasound irradiation method [24–28] is now recognized as a viable and an environmentally benign alternative [25–31]. Although sonication methods have been initially applied to homogeneous reactions in a variety of solvents, this approach has now evolved into a useful technique in heterogeneous reactions [24,32–36].

In the recent past, the ultrasound irradiations have been employed in various chemical reactions due to its effective role for enhancement of chemical reaction rates and selectivity. Recently reported studies reveals that the ultrasonic technique combined with MPTC are proved to be an effective one in organic transformations [25,37–39]. However, from the literature survey, it is found that the combination of MPTC with and without ultrasonic technique for radical polymerization of acrylonitrile (AN) have not been reported under heterogeneous condition. In view of this background, in this study, the radical polymerization of acrylonitrile (AN) under heterogeneous conditions using a MPTC assisted with ultrasound irradiation is reported.

2. Experimental

2.1. Chemicals and equipments

Acrylonitrile (AN) (Aldrich – USA) was washed with 2% NaOH solution to remove inhibitor (HCl) and again washed with double

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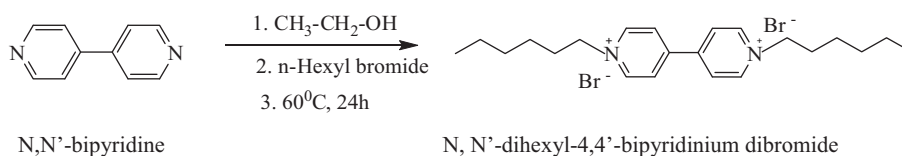
distilled water to remove the basic impurities. All other reagents potassium peroxydisulphate (PDS), *N,N'*-dihexyl-4,4'-bipyridinium dibromide (MPTC), methanol (Avra), chlorobenzene (Avra), pyridine (Avra), 1-hexyl bromide (Avra), *n*-hexane (CDH), diethyl ether (CDH), ethyl acetate (SD fine) and other reagents were used as received without further purification.

2.2. Ultrasonic process equipment

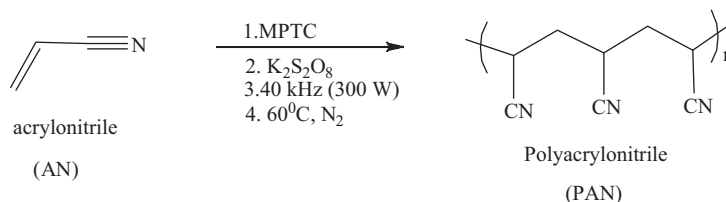
Ultrasonic energy is transmitted to the reaction vessel through the liquid medium, usually water in the tank. For safety purpose, the sonochemical reactor consisted of two layers of stainless steel sheet. The sonochemical reactor configuration used in the present work is basically an ultrasonic bath with 5 L capacity. The reactor has an operating frequency of 28 and 40 kHz both with an output of 300 W. The ultrasounds are separately produced through flat transducer mounted at the bottom of the tank. In this ultrasonic instrument there is a provision for a drain as well as an outlet at the top, which provides the facility for continuous operation of the process. The process vessel is immersed in the water present in the tank. An additional heater with a facility of temperature controller has also been provided so as to facilitate some high and low temperature conditions. From the top of the sonicator, if the water level is lower than the outlet i.e., 3 cm below the applied frequency is automatically cut off. So the water fill is important. The reactor is made of Pyrex glass polymer tube fitted with an inlet and outlet for nitrogen. An inert atmosphere is maintained inside the reaction tubes by closing the inlet and outlet with rubber gaskets. This reaction vessel is supported at the center of the ultrasonic cleaning bath 2 cm above from the position of the transducer which is fixed at the bottom of the ultrasonicator to get the maximum ultrasonic energy. All the experimental parameters were done at 40 kHz with output power of 300 W.

2.3. Synthesis of soluble multi-site phase-transfer catalyst

A mixture of 1.56 g (10 mmol) of 4,4'-bipyridine, 10 mL of *n*-hexyl bromide, and 60 mL of ethanol was placed in a 250 mL three necked round bottomed Pyrex flask. The reaction was carried out at 60 °C for 24 h and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, i.e., *N,N'*-dihexyl-4,4'-bipyridinium dibromide (MPTC) was washed with *n*-hexane (3 × 20 mL). The white solid MPTC was stored in CaCl₂ desiccators. m.pt. 198 °C; Yield: 90%;



Scheme 1. Preparation of MPTC.



Scheme 2. Polymerization of acrylonitrile.

¹H NMR (400 MHz, D₂O); δ 0.82–0.85 (t,6H–CH₂–CH₃), 1.26–1.34 (m,12H–CH₂–CH₃), 1.99–2.11 (m,4H–N⁺–CH₂–CH₂), 4.63–4.67 (t,4H–N⁺–CH₂), 8.52–8.59 (d,d 4H, pyCH), 8.95–9.15 (d,d 4H, N⁺–pyCH); ¹³C NMR (100 MHz, D₂O): δ 15.79 (CH₃), 24.28, 27.46, 32.85, 33.06 (CH₂), 64.21 (N⁺–CH₂), 124.64, 144.78, 147.28 (bipy-C). MS (EI, 70 Ev.%): m/z 486; Elemental analysis Calc.: C, 54.33%; H, 7.05%; N, 5.76%; Found, C, 54.30%; H, 7.01%; N, 5.72% (Scheme 1).

2.4. Polymerization procedure under sonocatalyzed condition

The reaction tubes for the polymerization are long Pyrex glass tubes with inlet and outlet for nitrogen gas. The polymerization reactions are carried out in an inert atmosphere at constant temperature of 60 °C with ultrasonic energy (40 kHz, 300 W). The mixture consists of aqueous and organic phases. The monomer in acrylonitrile is the organic phase and the phase-transfer catalyst, potassium peroxydisulphate, potassium sulphate (for adjusting ionic strength) and sulphuric acid (for maintaining [H⁺]) were taken in aqueous phase. The reaction tube containing the reaction mixture is suspended at the center of the ultrasonic cleaning bath for 50 min to get the maximum ultrasound energy. The reaction is arrested by pouring the reaction mixture into ice-cold methanol containing traces of hydroquinone (Scheme 2).

The polymer formed was filtered quantitatively through a sintered crucible (G-4) washed several times with distilled water and methanol, and dried at 60–70 °C in a vacuum oven to constant weight. The rate of polymerization (Rp) was determined gravimetrically. The Rp was calculated from the weight of the polymer obtained using the formula:

$$R_p = \frac{1000 m_m}{V \times t \times M_m}$$

where, m_m – weight of the polymer in gram, V – volume of the reaction mixture in mL, t – reaction time in seconds, M_m – molecular weight of the monomer (acrylonitrile (AN)).

3. Results and discussion

The polymerization of acrylonitrile (AN) initiated by PDS–MPTC in chlorobenzene/water biphasic medium with ultrasonic energy (40 kHz, 300 W) was studied under different experimental conditions to evaluate the various parameters, which influence the polymerization reaction.

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