

# Solvent and kinetic penultimate unit effects in the copolymerization of acrylonitrile with itaconic acid

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## Abstract

Copolymerization of acrylonitrile (AN) with itaconic acid (IA) in dimethylformamide (DMF) and DMF/water mixture was investigated at enhanced concentrations of the latter. Analysis of the copolymer composition revealed the existence of a marked penultimate unit effect with respect to radicals terminated in AN. The reactivity of IA was considerably less than that of AN, manifested as a negative reactivity ratio for the former. The  $r_{IA}$  values ranging from  $-0.28$  to  $-0.50$  and  $r_{AN}$  values ranging from  $0.53$  to  $0.70$ , were obtained by Kelen–Tudo's (KT) and extended KT methods. The penultimate reactivity ratios were determined by both linear and non-linear methods. The values ranged from  $r_1 = 0.009$  to  $0.01$ ,  $r'_1 = 0.0015$  to  $0.0043$ ,  $r_2 = 0.54$  to  $0.69$  and  $r'_2 = 0.9$  to  $1.03$ . The reactivity of AN radical towards IA decreased about twofold when the latter formed the penultimate group. The penultimate model explained an acceptable rational feed-copolymer composition profile for the whole composition range. Addition of water decreased the reactivity of IA slightly. IA caused a decrease in the apparent copolymerization rate in agreement with the observed trends in the reactivity ratios; presence of water caused a further decrease in the rate of polymerization. A statistical prediction of monomer sequences based on reactivity ratios implied that IA existed as a lone monomer unit between the long sequences of AN units.

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## 1. Introduction

Carbon fibers find an important place in hi-tech areas like, the aerospace industry and defence applications due to their excellent properties such as ability to withstand high temperature, resistance to chemical and environmental effects etc. [1–4]. Among the precursors available, polyacrylonitrile (PAN) based fibers remain one of the best materials for making carbon fibers [2–20]. The quality of the ultimate carbon fiber depends largely on the quality of the precursor material. PAN homopolymer as precursor results in poor quality of the carbon

fibers [2–4]. PAN precursor is modified to improve its properties by incorporation of suitable acidic comonomer during polymerization, which increases its hydrophilicity and catalyses the cyclization of nitrile groups during the heat treatment of PAN precursors, producing thermally stabilized acrylic fibers [3–16]. One of the key comonomers recommended for the copolymerization with AN for this purpose is itaconic acid (IA), which has been a subject of some previous studies [3–12]. The major reason for the superiority of IA over other acidic comonomers is the presence of two carboxylic groups, which increases the possibility of interaction of the carboxylic group and the nitrile group during cyclization reaction [3]. The copolymerization of AN with other comonomers can be done by various methods such as solution, emulsion, aqueous suspension and solvent–water suspension polymerization [3–9]. Among these,

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solution polymerization is the most advantageous since it yields a precursor with lower stabilization temperature and fewer molecular defects. In addition, the polymer solution can be converted directly to the spinning dope for fiber production [2–4].

The quality of the final carbon fiber from PAN depends upon the nature of the comonomer, its proportion and distribution in the polymer precursor chain, which in turn depends upon the copolymer composition, decided by the monomer reactivity ratios. The earlier published results on reactivity ratios of AN and IA appear to be ambiguous; different authors reporting different values [4–7]. In majority of the cases, the reported parameters explain the copolymerization behaviour at very low concentrations of IA, but fail to describe the behaviour at relatively higher concentrations of IA. This may be arising from the fact that the parameters have been determined for compositions containing very low concentrations of IA. The present work examines the copolymerization kinetics at extended concentrations of IA. DMF is the solvent usually recommended for the copolymerization of AN and IA. The effect of reaction medium on radical polymerization has been well documented in previous reported studies, suggesting factors like electrostatic interactions, hydrogen bonding, polar–polar interactions etc as responsible for monomer and radical reactivities in copolymerizations [21]. DMF is highly hygroscopic and the presence of water in it could affect the reactivity ratio, as solvents are known to affect the reactivity ratio [22]. Hence the objective of the present work includes examination of the effect of water in DMF on the reactivity ratio.

## 2. Experimental

### 2.1. Materials

AN (Ottokemi, Mumbai) was purified by alkali washing followed by distillation. IA (Spectrochem, Mumbai) was recrystallised from acetone. Dimethylformamide

(DMF) (Ranbaxy, New Delhi) was dried over phosphorous pentoxide and distilled under vacuum.  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN) (Spectrochem, Mumbai) was recrystallised from methanol. The water bath used was Julabo make digital water bath with a temperature precision of  $\pm 0.1$  °C.

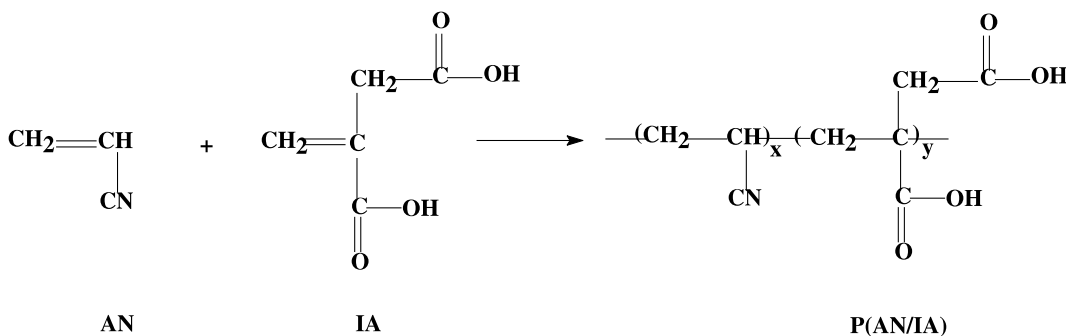
### 2.2. Polymerization

All polymerizations were performed in 100 ml round bottomed flasks under vacuum. In a typical experiment, freshly distilled AN (98 mol%, 16.12 g), IA (2 mol%, 0.81 g) together with AIBN (20 mg) were dissolved in 20 ml DMF and charged into a flask fitted with a vacuum adaptor. The contents of the flask were thoroughly de-aerated for 30 min at  $-25$  °C, vacuum-sealed and then polymerized at 60 °C. After the reaction, the polymer was isolated by precipitation into excess of methanol and was purified by reprecipitation from DMF into methanol. The polymer was further purified by soxhlet extraction using methanol for 8 h. It was dried in vacuum at 50 °C. The copolymer composition was determined from the acid value analysis of the copolymer, by dissolving it in dimethyl sulfoxide and titrating against standard alcoholic KOH ( $\approx 0.1N$ ) using thymol blue as indicator.

## 3. Results and discussion

AN and IA were copolymerized according to Scheme 1.

The solvent usually recommended for the polymerization is DMF, which is polar. Copolymerization reactivity ratios of AN/IA pair have been reported in some of the previous works and the reported values predict a moderately good reactivity for IA. Different reports give varying reactivity ratios for IA, thus Bajaj et al. [4,5] have reported the reactivity ratios of AN/IA pair as ranging from  $r_{IA} = 2$  to 6.8 and  $r_{AN} = 0.55$  to 0.88, The Polymer Handbook, by Brandrup [6] has reported the



Scheme 1. Polymerization of AN with IA.

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