

Synthesis, reactivity ratios and characterization of hydroquinone promoted CT co-polymerization of styrene and methyl methacrylate in a room temperature ionic liquid

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Abstract

For the first time, charge transfer (CT) co-polymerization of styrene and methyl methacrylate, promoted by hydroquinone (HQ) at various feed compositions, has been achieved in a hydrophobic ionic liquid. The co-polymers have been characterized for thermal and molecular weight properties. The molecular weights obtained for the co-polymers made in ionic liquid were found to be slightly lower than the corresponding polymers synthesized in conventional solvent. The reactivity ratios of the co-polymers have been computed and compared with conventional CT polymerization. The reactivity ratios of Sty-MMA indicate that the co-polymerization has a tendency to alternate and to produce a higher styrene content in the co-polymers. The numerical values of the inverse of r_1 and r_2 indicate that both monomer radicals have a distinct cross propagation tendency.

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1. Introduction

In many instances, different monomers exhibit different tendencies towards co-polymerization. Some monomers are more reactive in co-polymerization than indicated by their rate of homopolymerization [1]. Several workers [2–4] have determined co-polymer composition by assuming the chemical

reactivity of the propagating chain (which may be a free radical or ion) in a co-polymerization to be dependent only on the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit. Mayo et al. [3] proposed that the composition formed at any instant is dependent not only on the concentration of monomer species present in the system but also on the reactivity ratios. The reactivity ratios are dependent on the type of monomers, polymerization temperature, type of initiation (free radical/ionic) and also on the solvent used in the polymerization [5]. The nature of the solvent can thus affect free-radical

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co-polymerization through polarity, radical-solvent complexation and monomer-solvent complexes [6–8].

The use of ionic liquids (ILs) as solvents for clean synthesis has been studied for many chemical and biochemical reactions [9–11]. There are numerous properties of ILs which are distinctly advantageous compared to molecular solvents like DMSO and thus they have appeared in numerous applications, including polymerization reactions [12–17]. For example, ILs enhance the rate of many reactions. The polarity of these solvents also makes them a distinct class of their own in stereo-selective reactions. The main objective of the present study was to investigate the co-polymerization reactivity of styrene and methyl methacrylate (MMA) in ionic liquids by estimating their reactivity ratios, as well as characterising the co-polymers for thermal and molecular weight properties.

In earlier studies [18] we have shown that enhanced reaction rates were obtained in hydroquinone (HQ) promoted CT polymerization of homopolymers involving vinyl and acrylic monomers in a room temperature ionic liquid. The reactivity ratios for the free radical polymerization of Sty-MMA in ionic liquid has been studied recently [19]. However the CT polymerization of Sty-MMA in ionic liquid and the effect of HQ in the conventional and ionic liquid solvents have not been explored. Hence, in this study an attempt has been made to investigate the reactivities of styrene and methyl methacrylate in the HQ promoted co-polymerization of Sty-MMA in a room temperature ionic liquid as compared to a conventional molecular solvent. The co-polymers obtained were also characterized for their thermal and molecular weight properties and compared with the conventional system.

2. Experimental

2.1. Materials and methods

The analytical grades of MMA (Aldrich), Styrene (Sigma), DMSO (Aldrich), carbon tetrachloride, *n*-butyl amine (Merck) and HQ (Merck) were used. The purification of the monomers and the synthesis of the butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)amide (known as [p_{1,4}][tf₂N]) ionic liquid followed the procedures in the literature [20,21]. Typically the CT co-polymerization promoted by HQ was carried out by adding 0.013 g

of HQ (0.18 mmol) to the mixture containing 0.47 g CCl₄ (3.05 mmol) and 0.73 g of either DMSO (9.34 mmol) or IL (1.72 mmol) solvent. Then 0.05 g of styrene (0.48 mmol) and 0.95 g of MMA (9.48 mmol) was added to the contents and mixed well to obtain a homogenous solution. Finally 0.30 g of *n*-butyl amine (4.28 mmol) was added and the contents were thermostated at 60 °C. The polymerization was restricted to less than 10% conversion. The polymers, after a desired reaction time, were precipitated in excess methanol, filtered and washed several times with fresh methanol. They were then vacuum dried at 30 °C. The methanol was evaporated from the filtrate to recover the ionic liquid. In a similar manner the CT co-polymerization was also carried out for different feed compositions of styrene and MMA.

2.2. Characterization

2.2.1. ¹H NMR spectroscopy

¹H NMR spectra of co-polymer samples were recorded using a Bruker 300 MHz FT-NMR instrument with CDCl₃ as solvent and TMS as internal standard.

2.2.2. Gel permeation chromatography (GPC)

The polymer samples were characterized using a Waters gel permeation chromatograph (GPC) for molecular weights and distribution. The instrument was calibrated with different polystyrene standards using a μ ultrastayrex column and tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 ml/min.

2.2.3. Differential scanning calorimetry (DSC)

Glass transition temperatures (*T_g*) were recorded by Perkin–Elmer DSC and the instrument was calibrated using Indium as a standard. DSC used sample sizes of 5–10 mg and a heating rate of 5 °C/min in an argon atmosphere.

3. Results and discussion

3.1. Evidence of co-polymer formation

The ¹H NMR spectrum is not only used for identifying individual monomeric units in the co-polymer, but also employed for determining the co-polymer composition. Typical spectra with varying feed compositions of styrene and MMA, synthesized in presence of HQ and employing ionic liquid as solvent, are shown in Fig. 1. The backbone

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