Use of phase transfer catalysts to aid initiation in suspension vinyl polymerization

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In suspension vinyl polymerization of water immiscible monomers, the polymer yield is very low when water soluble initiator is used, because the free radicals generated in the aqueous phase do not get the opportunity to initiate polymerization. However, in conjunction with a phase transfer catalyst, the radical precursor is transferred into the organic phase, where the generated free radicals cause vinyl polymerization, just as an organic soluble initiator does.

(Keywords: phase transfer catalyst; water soluble initiator; vinyl polymerization; suspension polymerization)

Introduction

Phase transfer catalysts (PTC) have found interesting applications in polymer functionalization[1,2] and polymer functional group transformations[3,4]. There have been several reports about the use of PTC for the synthesis of step polymers involving interfacial reactions[5].

However, there is no report of PTC-aided free radical vinyl polymerization. Mohanraj and Ford[1] have reported the phase transfer of the hypochlorite anion, a free radical precursor, for the chlorination of the methyl group of poly(*p*-methylstyrene). This suggested that a PTC could be used to phase transfer an anionic free radical precursor into the organic phase, where it will generate free radicals to initiate vinyl polymerization. It has been reported that the persulphate ion is sufficiently lipophilic[6] to be phase transferred into the organic phase using a quaternary ammonium salt. Since the persulphate anion is a good source of free radicals to initiate vinyl polymerization, we have used potassium persulphate, a water soluble free radical precursor, for bringing about this type of polymerization of an organic solvent soluble vinyl monomer.

Experimental

Materials and chemicals. The monomers styrene and divinylbenzene (DVB; Thermax Corp., Pune, India), methyl methacrylate (MMA; IPCL, Baroda, India) and glycol bisacrylate (GBA; Aldrich Chemical Co., Milwaukee, WI, USA) were freed from stabilizers by the usual methods and distilled[7]. Potassium persulphate (Sigma Chemical Co., St Louis, MO, USA), poly(vinyl pyrrolidone) (PVP; MW, 25,000 SD Lab-Chem. Industry, Bombay, India) and benzyltriethylammonium chloride (BTEAC; synthesized) were used as received.

Polymerization procedure. A suspension polymerization technique was used for preparing crosslinked polystyrene beads. A four-necked reaction vessel (500 ml capacity) was fitted with a mechanical stirrer, nitrogen inlet tube, reflux condenser and a dropping funnel. The reaction vessel, containing 200 ml distilled water, 0.5 g PVP (as suspension stabilizer), 0.27 g (0.001 mol) potassium persulphate and 0.23 g (0.001 mol) BTEAC (as PTC), was kept in a thermostatically controlled water bath at 70°C (*Table 1*). The mixture was then flushed with nitrogen gas. The organic phase consisting of 10.4 g (0.1 mol) styrene monomer, 0.26 g (0.002 mol) DVB and 10 ml toluene as diluent was added dropwise to the aqueous phase using the dropping funnel. During the addition, the mixture was stirred at a rate (~ 300 rev min^{-1}) sufficient to disperse the organic phase as fine droplets in the aqueous phase. After the addition was complete, stirring was continued for 16 h. The suspension mixture was poured into 200 ml water, stirred with a glass rod for a few minutes and allowed to settle, and decanted. The polymer beads were then washed with acetone, ethyl acetate and chloroform in order to remove unreacted monomer, and other constituents. Finally, the beads were filtered through a sintered glass funnel under low pressure, and were dried.

Polymerization of MMA was also carried out using GBA as the crosslinking agent (*Table 1*).

Results and discussion

Basically, suspension polymerization is a bulk polymerization in which the organic reaction phase is dispersed into spherical droplets in the aqueous phase.

Table 1 Reaction conditions and yields in PTC vinyl polymerization

Expt no.	Quantity of monomer (g)	Initiator ($K_2S_2O_8$) (g)	PTC^a (BTEAC) (g)	Yield (%)
1^b	Styrene, DVB (10.4, 0.2)	0.27	–	8–10
2^b	Styrene, DVB (10.4, 0.2)	0.27	0.27	80–85
3^c	Styrene, DVB (10.4, 0.2)	2.70	2.27	90
4^b	MMA, GBA (10.0, 0.3)	0.27	–	5
5^b	MMA, GBA (10.0, 0.3)	0.27	0.27	70–75
6^c	MMA, GBA (10.0, 0.3)	2.70	2.27	85

In all the experiments 200 ml of water were used and the temperature was kept at ~ 70°C; 10 ml toluene (diluent) and 0.5 g PVP (stabilizer) were added in each case
[a] PTC: initiator molar ratio, 2:1
[b] Monomer: initiator molar ratio, 1:0.01
[c] Monomer: initiator molar ratio, 1:0.1

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In normal suspension polymerization, a lipophilic initiator, such as dibenzoyl peroxide (DPO), remains in a homogeneous phase, dissolved in the monomer (and diluent, if any) droplets. Hence, when the polymerization is initiated, it starts simultaneously in the whole bulk of a droplet. At a particular instant (low conversions) monomer-swollen polymer beads are produced, which are extremely tacky and therefore likely to coalesce into an aggregated product.

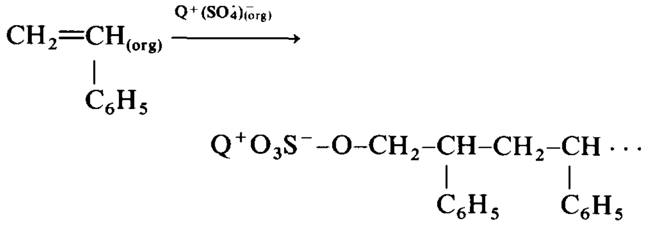
In our case, the diffusion-controlled polymerization begins at the surface of the monomer droplet producing a polymer film at the surface of the droplet, thus enclosing the still uncovered monomer. Hence, the dead surface is less tacky and prevents coalescing of beads. The polymerization of the whole monomer in a bead is diffusion controlled and is likely to yield tough and uniform beads.

Some perbisulphate ions are also likely to break into free radicals in aqueous medium, but these will not be effective in initiating polymerization.

Nature of polymer end groups. The polymer produced under the polymerization conditions employed is likely to have anionic sulphate as the end group[8,9] while DPO-polymerized polystyrene will have no charged end group. The various steps in the polymerization reaction are given below:

$$K_2S_2O_{8(aq)} + 2QCl \rightarrow (Q^+)_2S_2O^{2-}_{8(org)} + 2KCl_{(aq)}$$

$$(Q^+)_2S_2O^{2-}_{8(org)} \xrightarrow{\Delta} 2(Q)^+(SO_4^{\cdot})^-_{(org)}$$



$$\underset{\displaystyle C_6H_5}{CH_2{=}CH_{(org)}} \xrightarrow{Q^+(SO_4^{\cdot})^-_{(org)}} Q^+O_3S^- {-} O {-} CH_2 {-} \underset{\displaystyle C_6H_5}{CH} {-} CH_2 {-} \underset{\displaystyle C_6H_5}{CH} \cdots$$

where Q^+ is the quaternary ammonium cation.

To verify this, the polymer beads were suspended in a 1.0% aqueous solution of a cationic dye, i.e. methylene blue. The dye was taken up by the beads, and was not removed by several washings, thereby indicating the presence of an ionic group. In the case of DPO-polymerized polystyrene, the polymer beads absorbed very little dye which was subsequently washed out by water. Further, the polymer with the anionic end group also has a quaternary ammonium group as the counter ion. Hence, it was necessary to employ an excess of the PTC. The presence of the quaternary ammonium cation in the polymer was also demonstrated by extracting the beads with methylene chloride and aqueous potassium iodide. The lipophilic cation–anion (Q^+I^-) pair was readily extracted with methylene chloride exchanging the counter ion Q^+ in the polymer by K^+.

The polymer beads produced had diameters of 0.25 mm and their surface area was found to be comparable to those produced in conventional suspension polymerization. The lower conversions observed (*Table 1*) indicate that some initiator is lost due to the inevitable free radical formation in aqueous medium. Increase in the initiator:PTC ratio beyond 1:2 did not significantly improve the conversion yield.

Conclusions

Conventionally, some neutral and lipophilic free radical precursors, e.g. DPO and azobisisobutyronitrile, are used as initiators for vinyl polymerization of lipophilic monomers[10]. This experiment demonstrates that a water soluble free radical precursor can also be used for such polymerization, in conjunction with a PTC. Without a PTC, however, such initiators are unsuccessful.

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