ABSTRACT

Phase transfer catalysis is a broadly useful tool in all branches of chemistry especially in synthetic organic and polymer chemistry owing to its high reaction rates even at low temperatures. In this technique, two mutually insoluble reagents in organic/aqueous biphasic system react with the help of a phase transfer catalyst (PTC). The phase transfer catalyst plays the role of transporting reactive species from aqueous phase to organic phase where reactions get initiated. This technique offers a convenient synthetic route to various industrially important polymers. A large scale production of polymers by the new synthetic method needs an understanding of kinetics and mechanism of polymerization.

In the present investigation, a phase transfer catalyst (PTC) viz a quaternary ammonium salt has been synthesised, characterised and used for the study of kinetics and mechanism of free radical polymerization of six different vinyl monomers. The polymerization reactions of the six vinyl monomers viz methylmethacrylate (MMA), ethylmethacrylate (EMA) butylmethacrylate (BMA), glycidylmethacrylate (GMA), Butylacrylate (BA) and acrylonitrile (AN) were carried out under inert and unstirred conditions at 60°C in cyclohexanone/water biphasic media using K₂S₂O₈ as initiator and propiophenonebenzyldimethylammonium chloride as phase transfer catalyst.
The steady state rate of polymerization of all monomers was ascertained by carrying out the experiments at different intervals of time. Generally an increase in $R_p$ was obtained, which thereafter decreased and then attained a constant value.

The rate of polymerization of vinyl monomers was determined at different experimental conditions such as different concentrations of monomer, initiator and catalyst and different ionic strength, temperature and aqueous phase volume.

The rate of polymerization of vinyl monomers increased with increase in concentration of monomer, initiator and phase transfer catalyst. From the plot of log $R_p$ versus log concentration of variables, the reaction order with respect to monomer, initiator and phase transfer catalyst were calculated.

The order for alkylmethacrylates viz MMA, EMA, BMA and GMA was found to be 1.0 and in the case of butyl acrylate the order was 1.5 and for acrylonitrile it was found to be 2.0. The order of more than unity with respect to monomer may be attributed to the dependence of initiator rate on the monomer concentration and to the primary radical termination. The order with respect to the initiator for almost all the monomers were found to be 0.5. However, in the case of EMA it was 0.7. The order with respect to the phase transfer catalyst for all the six monomers were found to be 0.5.
The effect of variation in the volume fraction of aqueous phase on $R_p$ with a constant volume of organic phase at fixed concentrations of monomer, peroxodisulphate, phase transfer catalyst and at constant acid and ionic strength was studied for all the six systems. It has been observed that $R_p$ increased slightly with increase in $V_w/V_o$. No significant change in the rate of polymerization was observed by varying ionic strength and acid strength.

Activation energies for the polymerization of various monomers were calculated from the slope of log $R_p$ versus $1/T$ in the temperature range 50°C to 65°C. The other thermodynamic parameters were also calculated for each monomer.

Molecular weight of the polymers obtained in this work were determined by viscometry using the appropriate Mark - Houwink relationship to find the dependency of degree of polymerization on the initiator concentration. Based on the kinetic results suitable mechanism has been proposed.