

Phase-Transfer-Catalyzed Polymerization of Acrylonitrile

The use of phase transfer catalysis (PTC) for free radical polymerization is recent. The first reports on the use of PTC for free radical polymerization were due to Rasmussen and Smith,^{1,2} who demonstrated the superior efficiency of PTC for polymerization of vinyl monomers as compared to initiators such as AIBN. We recently reported on the polymerization of methyl methacrylate using ammonium peroxydisulfate and hexadecyl pyridinium chloride in ethyl acetate/water.³ The reaction was found to be not truly phase transferred in character since, in the absence of water, no polymerization took place when the quaternary persulfate which was isolated in the solid form was used as the initiator. In this study, the use of PTC has been extended to the polymerization of acrylonitrile using hexadecyl trimethyl ammonium bromide and ammonium peroxy disulfate in toluene/water two-phase systems.

EXPERIMENTAL

Kodak practical grade acrylonitrile (AN) was used without further purification. Toluene (Fisher, AnalaR), 2,2'-azobisisobutyronitrile (AIBN, Eastman Kodak), benzoyl peroxide (Bz_2O_2 , Fisher), ammonium peroxydisulfate (Fisher, AnalaR), hexadecyl pyridinium chloride (K&K Laboratories, Inc.) and hexadecyl trimethyl ammonium bromide (HTAB, K&K Laboratories, Inc.) were used as received. Water employed was laboratory distilled. Solutions of HTAB and $(NH_4)_2S_2O_8$ were prepared in water. Unless indicated, all the reaction mixtures contained 18 mL of the organic phase and 2 mL of the aqueous phase. The polymerization procedure has been reported before.³ Unlike the system methyl methacrylate (MMA)/ethyl acetate, polyacrylonitrile precipitated continuously during polymerization. The rates of polymerization reported are time average rates for 60 min reaction. Viscosity of polymer solutions were measured in an Ubbelohde viscometer at 35°C using dimethyl formamide as the solvent. The following equation was employed to calculate the average degree of polymerization from the intrinsic viscosity data⁴: $\log \bar{M} = 1.3405 \log[\eta] + 4.6902$.

RESULTS AND DISCUSSION

Figure 1 shows the percentage conversions in the polymerization of acrylonitrile using various initiator systems. Under identical conditions, the conversion attained using PTC is nearly twice that of AIBN or Bz_2O_2 . Figures 2 and 3 illustrate the variation of the rate of polymerization with changes in concentration of HTAB, $S_2O_8^{2-}$, and AN. Unlike MMA in ethyl acetate/water where a simple kinetic model could be derived based on the observed kinetic data, the kinetic data in the present investigation could not be fit into a model which would explain all the experimental observations. Whereas hexadecyl pyridinium persulfate was found to be virtually insoluble in the MMA/ethyl acetate system, hexadecyl trimethyl ammonium persulfate was found to be soluble in AN/toluene and was capable of initiating polymerization in the absence of any water present. The solid hexadecyl trimethyl ammonium persulfate was prepared by mixing an aqueous solution of HTAB with a saturated aqueous solution of $(NH_4)_2S_2O_8$. The precipitated quaternary persulfate was filtered, washed several times with water and dried. The percent conversion obtained using this quaternary persulfate as well as using hexadecyl pyridinium persulfate in the polymerization of acrylonitrile is shown in Table I. It can be seen that, unlike hexadecyl pyridinium persulfate with MMA/ethyl acetate, water has very little effect on the rate of polymerization. The hexadecyl pyridinium persulfate was not found to be phase transferred in MMA/ethyl acetate.³ But, the polarity of the medium AN/toluene appear to favor the transfer of both quaternary persulfates as demonstrated by the data in Table I. This observation is further strengthened by the fact that when hexadecyl trimethyl ammonium persulfate was used with MMA/ethyl acetate, very little polymerization took place (Table I). Thus it appears that the polarity of the medium is an important criterion

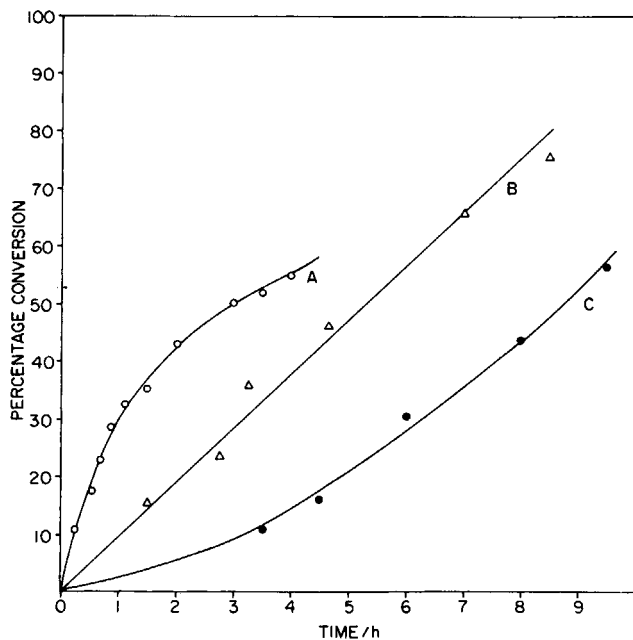


Fig. 1. Percent conversion vs. time plots for polymerization of MMA using various initiators at 55°C. (A) $[AN]=3.77$, $[(NH_4)_2S_2O_8]=0.0125$, and $[HTAB]=0.00625$ mol-dm⁻³. (B) $[AN]=3.77$ and $[AIBN]=0.0125$ mol-dm⁻³. (C) $[AN]=3.77$ and $[Bz_2O_2]=0.0125$ mol-dm⁻³.

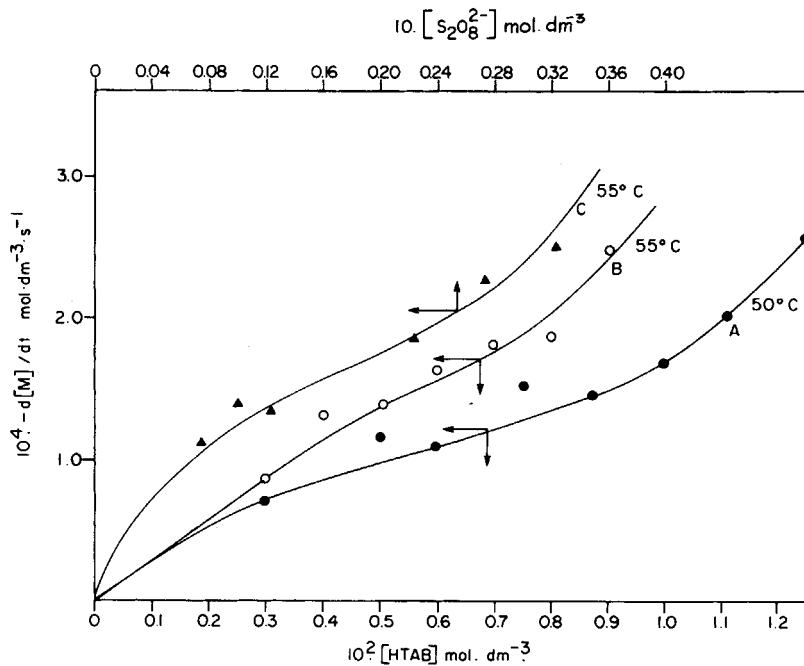


Fig. 2. Plot of polymerization rate vs. $[HTAB]$ and $[(NH_4)_2S_2O_8]$ (A) and (B) $[AN]=3.77$ and $[(NH_4)_2S_2O_8]=0.0125$ mol-dm⁻³. (C) $[AN]=3.77$ and $[HTAB]=0.005$ mol-dm⁻³.

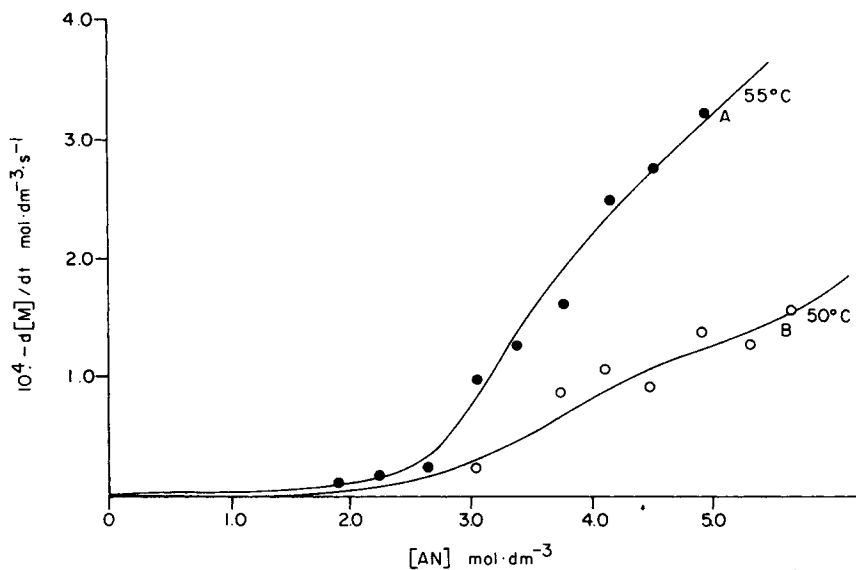


Fig. 3. Plot of polymerization rate vs. [AN]. [HTAB]=0.00625 and $[(\text{NH}_4)_2\text{S}_2\text{O}_8]=0.0125$ mol-dm⁻³.

TABLE I
Percent Conversion Attained in Polymerization of AN and MMA Using Hexadecyl Trimethyl Ammonium Persulfate (HTAP) and Hexadecyl Pyridinium Persulfate (HPP) at 50–60°C^a

System	Percentage conversion in 2 h
An=5.0 mL Toluene= 10.0 mL Water= 2.0 mL HTAP=0.25 g Temp= 50°C	69.2
An=5.0 mL Toluene=10.0 mL HTAP=0.25 g Temp=50°C	66.3
An=5.0 mL Toluene=10.0 mL HPP=0.25 g Temp=50°C	58.3
MMA=5.0 mL Ethylacetate=5.0 mL HTAP=0.1 g Temp=60°C	7.9

^a Distilled monomers free of inhibitor were employed.

for the transfer of the dianions such as $S_2O_8^{2-}$, which are normally resistant to transfer into the organic phase. The quaternary persulfate was found to yield polyacrylonitrile of very high molecular weight. The viscosity-average degree of polymerization of the polymer obtained through PTC was found to give a value of 2721 as opposed to 1504 produced by AIBN initiation under identical conditions. Thus, quaternary persulfates which can easily be prepared and stored in the solid form may find application as better initiators for vinyl polymerization to yield high molecular weight polymers as compared to commonly used initiators such as AIBN or Bz_2O_2 .

References

1. J. K. Rasmussen and H. K. Smith, II, *J. Am. Chem. Soc.*, **103**, 730 (1981).
2. J. K. Rasmussen and H. K. Smith, II, *Makromol. Chem.*, **182**, 701 (1981).
3. A. Jayakrishnan and D. O. Shah, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 3201 (1983).
4. *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1966.

A. JAYAKRISHNAN

Department of Materials Science and Engineering
University of Florida
Gainesville, Florida 32611

D. O. SHAH

Department of Chemical Engineering
University of Florida
Gainesville, Florida 32611

Received November 30, 1983

Accepted January 30, 1984