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Reactions

Rate of Radical Polymerization of N,N-Dimethylaminoethyl Methacrylate in Cyclohexane

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SUMMARY

Dilatometric measurements of the rate of polymerization of N,N-dimethylaminoethyl methacrylate(DMAEMA) gave $k_p/k_t^{1/2}=7.67\mathrm{x}10^{-2}$ (mole. sec/l)$^{1/2}$ at $[\mathrm{DMAEMA}]_0=2.000$ M in cyclohexane at 60°C. The rate was proportional to the first order and 0.5 order of DMAEME and AIBN concentrations,respectively,in cyclohexane. The initial rate of polymerization varied little in organic solvents.

INTRODUCTION

Poly(N,N-dimethylaminoethyl methacrylate)(poly(DMAEMA)) is a useful polymer with the tertiary amine substituent but only a few observations of the rate of polymerization have been reported. Egoyan and co-workers measured the rate constants of propagation,k_p,and bimolecular termination,k_t,in acetone and acetone/water mixed solvent at 40°C. The rate was proportional to 0.8 order and 0.5 order of the monomer and initiator concentrations,respectively(EGOYAN et al,1979a, 1979b). The rate was found to be proportional to 0.48 order of 2,2'-azobisisobutylonitrile(AIBN) concentration in bulk(GERDVILITE,1979) and to 1.0 order of the monomer concentration in aqueous solution (RUZIEV,1979).

A dilatometric study of the polymerization of DMAEMA is carried out in a non-polar solvent, cyclohexane, at 60°C.

EXPERIMENTAL

Reagent grade DMAEME(Fluka) was distilled and chromatographed through alumina(Woelm N,Akt.1) before use. AIBN was recrystallized from methanol and reagent grade solvents were dried and distilled or chromatographed through the alumina.

The solution of the monomer and AIBN was degassed under vacuum by the freeze-thaw method before being placed in a glass dilatometer whose capacity,v_0,was 17.1638 cm^3 at 60°C. The density of DMAEMA and poly(DMAEMA) at 60°C was measured by pycnometry to be 0.8982 $\mathrm{g/cm}^3$ in neat and 1.2471 $\mathrm{g/cm}^3$ in acetone solution,respectively. The conversion was assumed to be proportional to the relative volume decrease,$(v_0-v_t)\mathrm{x}100/(v_0-v_\infty)$ in %,where v_t and v_∞ were the volume of the system at time t and infinity,respectively. The dilatometer was placed in an oil bath of 60.0±0.1°C and the volume contraction at the capillary part was followed. The polymer was not soluble in nonpolar solvents but no fine precipitate was formed in the course of the polymerization presumably because of the strong solvation by the monomer molecules. Highly swallen, homogenously dispersed colloidal solution was formed slowly in cyclohexane and CCl_4 when the conversion was less than 20 %.

Fine powder of poly(DMAEMA) sample was obtained by freeze-drying the benzene solution; A polymerization mixture was dropped in petroleum ether. Only solvated viscous precipitate was formed, which was placed in a pouch of a semi-permeable membrane and the unreacted monomer and initiator were extracted with acetone in a Soxhlet apparatus for a few days. Then the solvent was replaced with benzene in the same apparatus by refluxing it. This benzene solution of the polymer was freeze-dried under a high vacuum.

RESULTS AND DISCUSSION

Smoothly curving time-conversion curve based on the volume contraction was observed in all runs. The initial part of the time-conversion curves was almost straight-line up to 6 % conversion. As shown in Fig.1 and Fig.2, the initial rate of polymerization was proportional to 0.5 order of AIBN concentration and the first order of the monomer concentration in cyclohexane. The rate in CCl_4 was very closely similar to that in cyclohexane indicating little difference in solvent effect between the two nonpolar solvents(Fig.2).

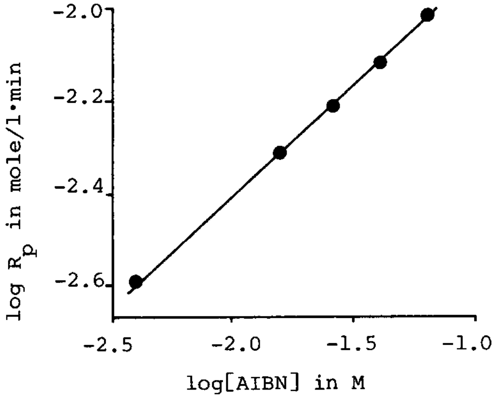

Fig.1. Dependency of the rate of polymerization of DMAEMA,R_p,on AIBN concentration. [DMAEMA]= 2.000 M,incyclohexane,at 60°C. The slope of the best-fit straight-line is 0.501.

It is regarded that the polymerization of DMAEMA follows the classical radical polymerization scheme of bimolecular propagation between a growing radical and a monomer molecule, and the bimolecular termination reactions between the radicals:

$$R_p=k_p(2f\cdot k_d[AIBN]/k_t)^{1/2}[DMAEMA] \quad (1)$$

where, R_p is the rate of polymerization, k_d is the rate constant of decomposition of the initiator and f is the efficiency of initiation. Good first-order plot with respect to the monomer concentration was obtained from every rate observation in this experiment.

The rate of initiation,R_i,in cyclohexane at 60°C at [DMAEMA]= 2.000 M was determined by the inhibitor method with p-benzoquinone (BQ) in Table 1 from R_i=2[BQ]/(induction period). The efficiency of initiation,f,was calculated by $f=R_i/(2k_d[AIBN])$. Average of two

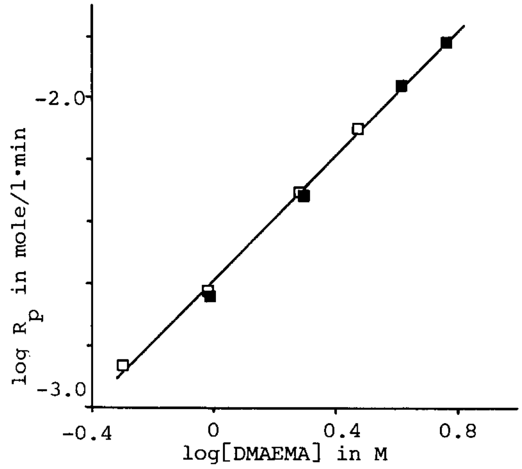

Fig.2. Dependency of the rate of polymerization of DMAEMA, R_p, on the monomer concentration. [AIBN]=1.580×10^{-2} M, at 60°C. (■) in cyclohexane; (□) in CCl_4. The slope of best-fit straight-line is 1.02.

reported values of k_d measured in benzene at 60°C was employed. These were $k_d=8.48\times10^{-6}$ sec^{-1} (BROWN and VERDIN,1960) and $k_d=9.15\times10^{-6}$ sec^{-1} (VAN HOOK and TOBOLSKY, 1958). The large value of f indicates very efficient initiation at this DMAEMA concentration by AIBN radical in cyclohexane. The ratio of $k_p/k_t^{1/2}$ was calculated from Eqn.(1). The value had been reported to be 0.162 and 0.346 in acetone and in acetone/water mixed solvent, respectively, at 40°C at [DMAEMA]=4.25 M (EGOYAN et at,1979a). Although it was suggested that the rate of termination decreased in aqueous solvents due to microheterogeneity of the growing radical(EGOYAN et al,1982), the effect of solvent polarity and solubility on the rate of polymerization of DMAEMA was only slight among organic solvents and no apparent effect of microheterogeneity was observed in cyclohexane and CCl_4 possibly due to the strong solvation by the monomer molecules(Table 2).

TABLE 1. Rate of initiation by p-benzoquinone(BQ), and $k_p/k_t^{1/2}$. [DMAEMA]=2.000 M, [AIBN]=1.580×10^{-2} M, in cyclohexane, at 60°C

$[BQ]\times10^4$ (mole/l)	Induction period (sec)
1.092	786
3.276	2360

R_i = 2.78×10^{-7} (mole/l·sec)
f = 0.996
$k_p/k_t^{1/2}$=7.76×10^{-2}(mole·sec/l)$^{1/2}$

TABLE 2. Initial rate of polymerization of DMAEMA in various solvents at 60°C. [DMAEMA]=2.000 M, [AIBN]=1.580×10^{-2} M

Solvent	Dielectric* const./Temp.	$R_p\times10^3$ (mole/l·min)
Cyclohexane	2.02/20°C	4.760
CCl_4	2.24/20°C	4.858
Butan-2-one	18.5/20°C	4.079
Propan-1-ol	20.1/25°C	5.245
Ethanol	24.3/25°C	5.277
DMF		4.662
DMSO	45	5.694

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