Polymer Bulletin 13, 459–462 (1985)

Polymer Bulletin

Rate of Copolymerization of Maleic Anhydride with Butyl Vinyl Ether in $CHCl_3$ and Relative Reactivity of Free Monomers and the Complex

Kiyohisa Fujimori

Department of Chemistry, University of New England, Armidale, N.S.W. 2351, Australia

SUMMARY

Dilatometrically measured initial rate of radical copolymerization of maleic anhydride(A) with butyl vinyl ether(D) in $CHCl_3$ at 50°C was maximum at the feed maleic anhydride mole fractions of 0.39, 0.36, and 0.32 when the total monomer concentration was 1.5 M, 1 M and 0.5 M, respectively. Both free monomers and the donor-acceptor complex appeared to be operative to give an alternating copolymer. Georgiev's method gave $\alpha=k_{AD}/k_{DA}=0.14$, $\beta_D=k_{DC}/k_{DA}=6.2$, $\beta_A=k_{AC}/k_{AD}=0.50$ and $k_{AC}/k_{DC}=0.011$.

INTRODUCTION

Copolymerization of electron donor-acceptor comonomer pairs is characterized by the strong alternating tendency. The relatively fast rate of the copolymerization is accompanied by a rate maximum. A participation of the charge-transfer complex formed between the comonomers is a strong possibility when the complex is detected by physical methods.

It may be concluded that the rate maximum always appears on one side of the equimolar feed composition depending on the stability of the radicals. Thus in the copolymerization of maleic anhydride (MA), the rate maximum appears on the MA rich compositions when the comonomer is styrene(TSUCHIDA et al,1971,1972) and on the MA poor side of feed compositions when the comonomer is an alkyl vinyl ether or a monoolefin(BALDWIN,1965;HALLENSLEBEN,1970;ZEEGERS and BUTLER, 1972). It has become apparent that the position of rate maximum approaches to the equimolar feed composition as the total monomer concentration increases(JAVNI,FLES and VUKOVIC,1982). It is generally accepted that both free monomers and the donor-acceptor complex(C) participate in the alternating copolymerization.

$$
\begin{aligned}
&\text{——A}\cdot \quad + \text{D} \xrightarrow{k_{AD}} \text{——D}\cdot \\
&\text{——D}\cdot \quad + \text{A} \xrightarrow{k_{DA}} \text{——A}\cdot \\
&\text{——A}\cdot \quad + \text{C} \xrightarrow{k_{AC}} \text{——A}\cdot \\
&\text{——D}\cdot \quad + \text{C} \xrightarrow{k_{DC}} \text{——D}\cdot
\end{aligned}
$$

where A and D are the acceptor and the donor monomers and k's are the rate constants.

The dilatometrically measured initial rate of copolymerization of MA with butyl vinyl ether(BVE) is reported here.

EXPERIMENTAL

Reagent grade BVE(Fluka) was twice distilled,reagent grade MA(Fluka) was twice recrystallized from dry benzene and 2,2'-azobisisobutyronitrile(AIBN)(Fluka) was recrystallized from methanol before use. Solvents were purified according to the usual methods(RIDDICK and TOOPS,1955).

The copolymer was prepared in sealed glass ampules under vacuum, and purified by repeatedly precipitating it from the acetone solution in dry diethyl ether. The composition of the copolymer was determined conductometrically in acetone/water mixed solvent with 0.05 M NaOH and 0.05 M HCl.

The rate of copolymerization in $CHCl_3$ was measured by using a glass dilatometer of about 17 cm^3 capacity in an oil thermostat at 50 ± 0.1°C. Required amounts of BVE,MA and AIBN were accurately weighed out and dissolved in $CHCl_3$ in a standard volumetric flask. The solution was degassed by the freeze-thaw method under vacuum before being placed in the dilatometer. The following density at 50°C in g/cm^3 was determined pycnometrically;BVE 0.7843,$CHCl_3$ 1.4123,MA 1.2816 (measured in $CHCl_3$),and 1:1 MA-BVE copolymer 1.401(measured in acetone). The initial rate was determined from the plots of the initial volume decrease,v_o-v_t,against the reaction time,which gave straight lines after a short induction period. The conversion in % was calculated by $100x(v_o-v_t)/(v_o-v_\infty)$,where v_o,v_t and v_∞ were the volume of the solution in the dilatometer at time zero,time t,and at infinite time of polymerization,respectively. The copolymer was not soluble in $CHCl_3$ but because it swelled highly in $CHCl_3$,a homogeneously dispersed colloidal solution of the well swollen,finely divided copolymer was formed when the conversion was below a few percent,which enabled the dilatometric observation.

RESULTS AND DISCUSSION

The composition of the copolymer prepared in $CHCl_3$ at 60°C was found to be 1:1 in a wide range of the feed composition as shown in TABLE 1. The conversion was less than 10 % in all cases. As both MA and BVE donot homopolymerize in ordinary conditions,it is considered that a 1:1 alternating copolymer is formed.

TABLE 1
Composition of MA-BVE copolymer prepared in $CHCl_3$ at 60°C

Mole fraction of MA	
In feed	In copolymer
0.150	0.460
0.300	0.490
0.450	0.499
0.650	0.480
0.850	0.510

MA is known to form donor-acceptor complexes with vinyl ethers. The stoichiometry of the complexation between MA and BVE was confirmed to be 1:1 spectrophotometrically;the continuous variation of the absorption by the complex at 328 nm in 1,2-dichloroethane($[MA + BVE]=6.10x10^{-2}M$) was maximum at the equimolar concentration of the electron donor(BVE) and the acceptor (MA).

The equilibrium constant of complexation in $CHCl_3$ has been reported to be 0.18 ± 0.02 M^{-1},which is measured spectrophotometrically at room temperature(SMIRNOV et al,1975).

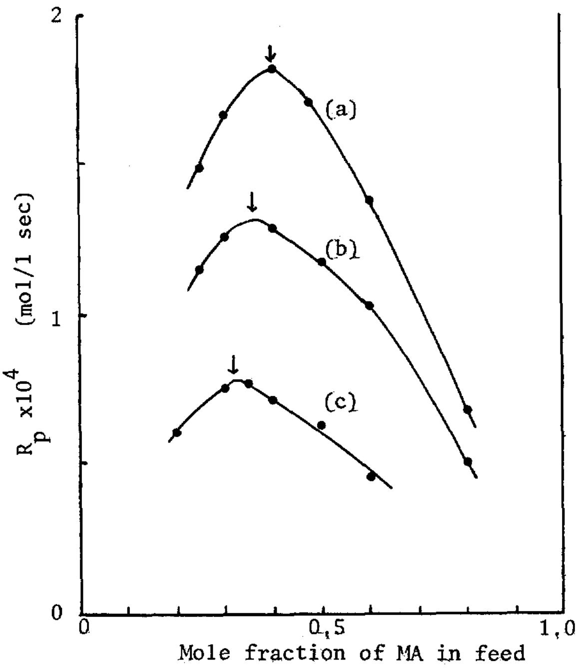

Fig.1. Initial rate (R_p) of copolymerization of MA with BVE in $CHCl_3$ at 50°C, [AIBN]=1.220×10^{-2}M.
(a) [MA+BVE]=1.5 M,
(b) [MA+BVE]=1 M,
(c) [MA+BVE]=0.5 M.

The arrows indicate the positions of rate maxima

The rate of copolymerization is shown in Fig.1. It is confirmed that the rate is maximum not at the equimolar feed composition but always in BVE rich feed, and that the position of the maximum shifts toward the equimolar feed composition as the total monomer concentration increases indicating increasing contribution of the complex.

The rate was found maximum at the MA feed mole fractions of 0.32, 0.36 and 0.39 when the total monomer concentration was 0.500 M, 1.000 M and 1.500 M, respectively.

The overall rate of copolymerization (R_p) is thought to be a sum of free monomer propagations (R_f), and polymerization of the complex (R_c), viz. $R_p = R_f + R_c$. The rate expression by Georgiev is in Eqn.(1) (GEORGIEV and ZUBOV, 1978).

$$R_p = k_{AD}(R_i/k_{to})^{\frac{1}{2}}\{[A]([D]+2\beta_D[C])+[D]([A]+2\beta_A[C])\}/\{\alpha[D]+[A]\} \qquad (1)$$

where, R_i is the rate of initiation, $\alpha = k_{AD}/k_{DA}$, $\beta_D = k_{DC}/k_{DA}$ and $\beta_A = k_{AC}/k_{AD}$. The termination is considered to be diffusion-controlled. The overall rate constant of termination (k_{to}) is defined to be $k_{to} = (k_{tAA}+k_{tAD}+k_{tDD})/4$, which is independent of feed composition, and the rate of termination is $R_t = k_{to}[m\bullet]^2$, where $[m\bullet]$ is the total radical concentration. According to Georgiev's method (see Method I in GEORGIEV and ZUBOV, 1978), α=0.14, β_D=6.2 and β_A=0.50 are obtained from the shift of the rate maximum with the total monomer concentration. The small value of α indicates much larger resonance stabilization of MA radical than BVE radical. The values of β_D and β_A indicate that the less stable BVE radical reacts with the complex overwhelmingly and that the complex has a comperable reactivity to BVE monomer in reacting with stable MA radical. As $\alpha\beta_A/\beta_D = k_{AC}/k_{DC} =$ 0.011 shows, the complex is about 100 times more reactive toward a

BVE radical than toward a MA radical.

The rate expression by Shirota is in Eqn.(2)(YOSHIMURA et al, 1976),where A(x) is a function of the mole ratio of acceptor to donor x=[A]/[D], and is a constant at a fixed x and initiator concentration.

$$R_p = A(x)[D] + A(x)K(\beta_D + \beta_A x)[D]^2 \qquad (2)$$

where,K is the equilibrium constant of the complexation. The general bimolecular termination reactions formulated by Walling in his derivation of overall rate of copolymerization(WALLING,1949) is adopted in this expression. According to Eqn.(2), a participation of the complex should result in a rate enhancement over the first-order rate with respect to the monomer concentration. However, the initial rate of MA-BVE copolymerization in $CHCl_3$ was found to be slower than the first-order dependency. It is possible that,in $CHCl_3$ where the copolymer precipitates out, the termination reaction is diffusion-controlled.

Caze and Loucheux have proposed that,in some cases, the more stable radical undergoes the termination process exclusively(CAZE and LOUCHEUX,1975). This model gives a relation between the feed mole fraction of the monomer of more stable radical at which the rate is maximum(x_{max}), and the total monomer concentration, as in Eqn.(3).

$$x_{max} = \tfrac{1}{2} - a/(2b[A+D]) \qquad (3)$$

where, a and b are constants. Caze and Loucheux applied this model successfully to the copolymerization of MA with vinyl acetate(1975). The rate maxima observed in the MA-BVE system did not conform to Eqn.(3) indicating that their model of termination reaction was an oversimplification for this system.

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Accepted May 13, 1985