Polymer Bulletin 15, 223–226 (1986)

Polymer Bulletin

Overall Rate of Alternating Copolymerization of Vinyl Acetate with Maleic Anhydride in Methyl Ethyl Ketone

Relative Reactivity of the Complex and Free Monomers

Kiyohisa Fujimori* and Anthony S. Brown

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

SUMMARY

The initial rate of radical copolymerization of vinyl acetate(D) and maleic anhydride(A) was measured dilatometrically in methyl ethyl ketone at 50°C. The rate was found to be maximum at the feed maleic anhydride mole fraction of 0.40,0.44 and 0.47 when the total monomer concentration was 0.75 M,1.50 M and 2.25 M,respectively. Participation of both free monomers and the complex was considered. Georgiev and Zubov's method gave $\alpha=k_{AD}/k_{DA}=0.24$, $\beta_A=k_{AC}/k_{AD}=35$, $\beta_D=k_{DC}/k_{DA}=2.2$ and $k_{AC}/k_{DC}=3.9$. The equilibrium constant of donor-acceptor complexation between vinyl acetate and maleic anhydride was determined to be 0.030 in acetonitrile at 27°C.

INTRODUCTION

Vinyl acetate(VA) and maleic anhydride(MA) are well known to form 1:1 alternating copolymer with radicals(DeWILDE and SMETS,1950). Caze and coworkers reported that VA and MA formed 1:1 donor(D)-acceptor(A) complex and that the maximum of the overall rate of copolymerization in benzene always appeared on VA-rich side of the feed monomer composition, with the rate maximum shifting toward the 1:1 feed composition as the total monomer concentration increased(CAZE and LOUCHEUX,1975;GHESQUIERE et al,1979; ARNAUD et al,1980). However, there appears to be no reliable data of the initial rate of the copolymerization. As gravimetric determination of rate usually involves an enormous uncertainty, a dilatometric determination of the overall rate is carried out for the copolymerization in methyl ethyl ketone(MEK).

EXPERIMENTAL

Reagent grade VA,MA and 2,2'-azobisisobutyronitrile(AIBN) (all from FLUKA) were fractionally distilled,recrystallized from dry benzene and recrystallized from methanol,respectively at least twice before use. Solvents were purified by the usual methods(RIDDICK and TOOPS,1955).

Unicam SP8-100 spectrophotometer was used for the UV determination of the equilibrium constant(K) of complexation with 1 cm path length. The absorptivity of VA was subtracted mechanically by placing the same concentration of VA in the reference cell as in the sample cell. A very small and constant concentration of MA was used.

Dilatometric measurements were carried out in dilatometers whose capacity was about 9 cm^3. It was assumed that an alternating coplymer was formed when the mole fraction of MA in feed(x_{MA}) is larger than 0.3(DeWILDE and SMETS,1950). Pycnometrically measured density at 50°C were

---

* To whom offprint requests should be sent

0.8935, 1.2816 and 1.4570 in g/cm^3 for VA, MA(measured in chloroform) and the copolymer which was prepared from x_{MA}=0.5 feed(measured in MEK),respectively. Required amounts of the components were measured out on an analytical balance and dissolved in MEK in a 10 cm^3 standard volumetric flask. The solution was degassed by the freeze-thaw method under vacuum before being placed in a dilatometer. As the copolymer dissolved in MEK, the system remained homogeneous throughout the measurement. The initial rate was determined with four significant figures from the slope of the plot of the volume decrease against the reaction time. There was a good corelation between the calculated conversion by dilatometry and the amount of the copolymer recovered from precipitating the dilatometer content in a large amount of boiling petroleum ether.

RESULTS AND DISCUSSION

The equilibrium constant of 1:1 charge-transfer complex between VA and MA in acetnitrile(dielectric constant,DC=37.5/20°C(RIDDICK and TOOPS, 1955)) was determined to be 0.030 by Ketelaar's equation(KETELAAR et al, 1952) in Fig.1, because this equation accounted for the absorptivity due to free and complexed MA separatedly.

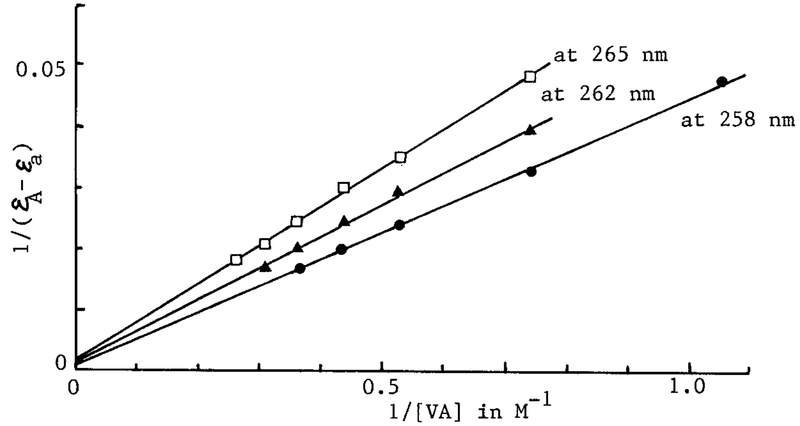

Fig.1. Ketelaar plot for the determination of the equilibrium constant of complexation in acetonitrile at 27°C. [MA]=3.437x10^{-3}M.

$$1/(\epsilon_A-\epsilon_a) = 1/\,K[D](\epsilon_c-\epsilon_a) + 1/(\epsilon_c-\epsilon_a) \qquad (1)$$

where,[D] is the concentration of the donor(VA), ϵ_A is related to the measured absorptivity,d_A, and to the total concentration of both free and complexed acceptor(MA) by the expression $d_A=\epsilon_A[A]$. ϵ_c and ϵ_a represent the extinction coefficients of the complexed and free acceptor. The results are in Table 1. The λ_{max} of the complex was not detected because VA,in the concentration used here,absorbed too much at wave lengths shorter than 258 nm. The equilibrium constant has been reported to be 0.56 M^{-1} in cyclohexane(DC=2.023/20°C)(GHESQUIERE et al, 1979) and 0.06 in chloroform(DC=4.806 /20°C)(CAZE and LOUCHEUX,1975) both at 25°C. The magnitude of K decreases

TABLE 1

K and ϵ_c values in acetonitrile at 27°C

λ(nm)	K(M^{-1})	ϵ_c
258	0.032	670
262	0.031	590
265	0.028	510

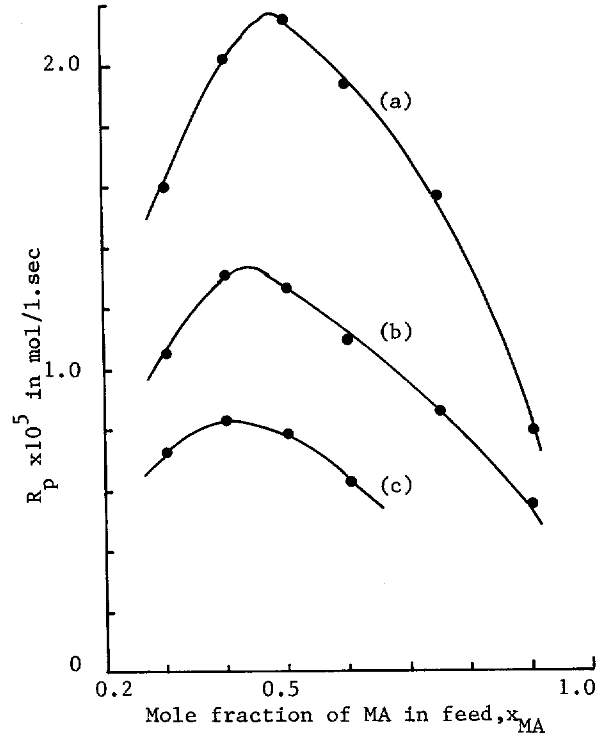

Fig.2. Initial rate(R_p) of copolymerization of VA with MA in MEK at 50° C ± 0.1°C. [AIBN]=2.439x10^{-2}M.

(a)[VA+MA]=2.250 M.
(b)[VA+MA]=1.500 M.
(c)[VA+MA]=0.750 M.

generally with increasing polarity of the solvent, suggesting polar nature of the association. Determination of the equilibrium constant in MEK was not successful because,in ^{1}H-NMR, the vinyl resonance peaks of VA overlapped with the MA peak, and because the solvent MEK absorbed overwhelmingly at wavelengths shorter than 327 nm in UV.

The overall initial rate in MEK at 50°C is shown in Fig.2. It is seen that the rate maxima appear on the VA-rich side of the feed monomer composition. This suggests that the rate depends more critically on the VA concentration. The fact that the maximum shifts toward 1:1 feed composition as the total monomer concentration increases, is consistent with a participation of the complex because the concentration of the complex, $[C]\cong K[A][D]$,increases geometrically as the total monomer concentration increases. Asymmetry of the overall rate has been recognized for many donor-acceptor comonomer pairs(for example,RATZSCH and STEINERT,1984). Since the rate maximum does not coincide with the 1:1 feed composition, the pure complex addition mechanism is not compatible. The rate is continuous over the entire range of feed composition,which is contrary to what has been reported(CAZE and LOUCHEUX,1975). The position of the rate maximum is estimated to be at x_{MA}=0.40,0.44 and 0.47, when [VA+MA]=0.75 M,1.5 M and 2.25 M,respectively.

It is generally agreed that both the complex and the free monomers participate in alternating copolymerization(TSUCHIDA et al,1972;YOSHIMURA et al,1978;GEORGIEV and ZUBOV,1978). The propagation includes cross-propagations of free monomers,(2) and (3), and the addition of the complex(C),(4) and (5). Georgiev and Zubov(1978) wrote the overall rate,R_p, as a function of α, β_A and β_D.

$$—A\cdot + D \xrightarrow{k_{AD}} —D\cdot \qquad (2)$$

$$—D\cdot + A \xrightarrow{k_{DA}} —A\cdot \qquad (3)$$

$$—A\cdot + C \xrightarrow{k_{AC}} —A\cdot \qquad (4)$$

$$—D\cdot + C \xrightarrow{k_{DC}} —D\cdot \qquad (5)$$

$$R_p=k_{AD}(R_i/k_{to})^{0.5}\{[A]([D]+2\beta_A[C])+[D]([A]+2\beta_D[C])/(\alpha[D]+[A])\} \qquad (6)$$

where,$\alpha=k_{AD}/k_{DA}$, $\beta_A=k_{AC}/k_{AD}$, $\beta_D=k_{DC}/k_{DA}$,R_i was the rate of initiation and k_{to} was the rate constant for overall termination. R_p is maximum when the concentrations of the donor and acceptor are $[\bar{D}]$ and $[\bar{A}]$. By applying the condition of a maximum to Eqn.(6), the following relation is obtained.

$$a\alpha\beta_A + b\alpha\beta_D + c\alpha + d\beta_A + e\beta_D = f \qquad (7)$$

where,$a=2K[\bar{A}][\bar{D}]$,$b=k([\bar{D}]^2-[\bar{A}][\bar{D}])$,$c=[\bar{D}]$,$d=(1/[\bar{D}])K[\bar{A}]^2([\bar{D}]-[\bar{A}])$,$e=-2K[\bar{A}]^2$ and $f=[\bar{A}]^2/[\bar{D}]$. Eqn.(7) is solved for α, β_A and β_D by knowing $[\bar{A}]$'s and $[\bar{D}]$'s at three different total monomer concentrations of 0.75 M.1.5 M and 2.25 M(Fig.2). The average value of $K=0.030\ M^{-1}$ measured in acetonitrile is used for the calculation because MEK(DC=18.51/20°C) is a polar solvent with a very good solvation capability. $\alpha=0.24$, $\beta_A=35$ and $\beta_D=2.2$ are obtained. The small α value is consistent with the fact that MA radical is much more stabilized radical through conjugation than VA radical,thus making reaction (2) slower than reaction (3) due to a large activation energy required for reaction (2)(EVANS,1948). As MA radical is more stable and longer living,more MA radical may be present in the copolymerization system. Thus,in MEK where the concentration of the complex is small,the overall rate depends more heavily on the VA concentration, making the rate maxima to appear in VA-rich side of feed composition. Both β_A and β_D are larger than 1.0 indicating that the complex is much more reactive than free monomers. β_A is far larger than β_D because VA radical,being less resonance stabilized, is already fairly reactive toward MA monomer. It is estimated from $\beta_A\alpha/\beta_D=k_{AC}/k_{DC}=3.9$ that the complex is about four times more reactive toward MA radical producing the resonance stabilized MA radical again than toward VA radical.

REFERENCES

ARNAUD,R.,CAZE,C. and FOSSEY,J.,J.Macromol.Sci.-Chem.,A14,1269(1980)
CAZE,C. and LOUCHEUX,C.,J.Macromol.Sci.-Chem.,A9,29(1975)
DeWILDE,M.C., and SMETS,G.,J.Polym.Sci.,5,253(1950)
EVANS,M.G.,J.Polym.Sci.,3,866(1948)
GEORGIEV,G.S. and ZUBOV,V.P.,Eur.Polym.J.,14,93(1978)
GHESQUIERE,D.,ARNAUD,R. and CAZE,C.,J.Phys.Chem.,83,2029(1979)
KETELAAR,J.A.A. et al,Rec.trav.chim.,71,1104(1952)
RATZSCH,M. and STEINERT,V.,Makromol.Chem.,185,2411(1984)
RIDDICK,J.A. and TOOPS,E.E.,"Organic Solvents"2nd ed.,Interscience,1955
TSUCHIDA,E.,TOMONO,T. and SANO,H.,Makromol.Chem.,151,245(1972)
YOSHIMURA,M.,MIKAWA,H. and SHIROTA,Y.,Macromolecules,11,1085(1978)

Accepted March 5, 1986

C