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The Alternating Copolymerization of n-Butyl Vinyl Ether with Maleic Anhydride

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Abstract : n-Butyl vinyl ether (BVE) and maleic anhydride (MA) copolymerized in chloroform with a radical initiator to give 1 : 1 alternating copolymer. The initial rate of copolymerization was maximum at 1 : 1 feed composition and the limiting conversion was close to the theoretical limiting conversion. The charge-transfer (CT) complex of BVE and MA showed a UV absorption maximum at 270 nm in 1, 2-dichloroethane. The stoichiometry of the complex was 1 : 1. The equilibrium constants of the complexation were found to be 0.37 dm^3/mol in carbon tetrachloride at 37°C by NMR, and 0.27 dm^3/mol in chloroform and 0.11 dm^3/mol in 1, 2-dichloroethane both by UV at 23°C. The participation of the CT complex of BVE and MA into their alternating copolymerization was discussed.

1. Introduction

It has been known that polar monomers which do not homopolymerize individually, could be copolymerized with radical initiators to give alternating copolymers when the polarities of the comonomers are opposite and large.[11,14,18] Participation of the charge-transfer (CT) complex formed between the comonomers, has been proposed for the alternating copolymerizations of some vinyl ethers such as 2-chloroethyl vinyl ether,[9] p-dioxene,[6] 1, 2-dimethoxyethylene,[10] ethyl vinyl ether[3] and dihydropryran[3] with maleic anhydride (MA), which has a strongly positively polarized C=C double bond (Alfrey-Price $e = 2.25$ and $Q = 0.23$).[4] The mechanism suggested is that the CT complex formed between the comonomers is the species that polymerizes to give an alternating copolymer.[9]

In this paper, the CT complexation of n-butyl vinyl ether (BVE) (Alfrey-Price $e = -1.20$ and $Q = 0.087$)[4] and MA is studied in chloroalkanes to explain the radical copolymerization of BVE with MA.

2. Experimental

2.1. Materials

Reagent grade MA (British Drug House) was recrystallized from benzene, reagent grade BVE (B.D.H.) was fractionally distilled and reagent grade 2, 2'-azobisisobutylonitrile (AIBN) (Tokyo Kasei) was recrystallized from methanol before use. All solvents were purified by the usual methods.[17]

2.2. Spectroscopy

The ultraviolet (UV) spectra of the CT complex were taken by using a UNICAM SP8—100 spectrophotometer with quartz cells of 1 cm path length. The nuclear magnetic resonance (NMR) spectra were taken by a Varian EM-360 60 MNz NMR spectrophotometer at 37°C. JASCO J-0001 infra-red (IR) spectrophotometer was used to take the IR spectra of the copolymer from KBr pellets.

2.3. Polymerization

The copolymerizations were carried out in chloroform solutions with AIBN as the radical initiator in glass ampules of approximately 15 cm^3 capacity, which were sealed after degassing by the freeze-thaw method on a vacuum line. The sealed ampules were then immersed in an oil bath at 60° ± 0.1°C. The polymerizations were stopped at the end of the reaction periods by immediately pouring the reaction mixtures in large amounts of diethyl ether, in which the polymers were precipitated out. The polymers were purified by reprecipitation from the acetone solutions in diethyl ether. The rate of the polymerization was measured gravimetrically.

The compositions of the copolymers were determined by conductometrically titrating the MA units with Philips PR9500 conductivity bridge. The copolymers were dissolved in water with 0.1 M NaOH and back-titrated with 0.1 M HCl.

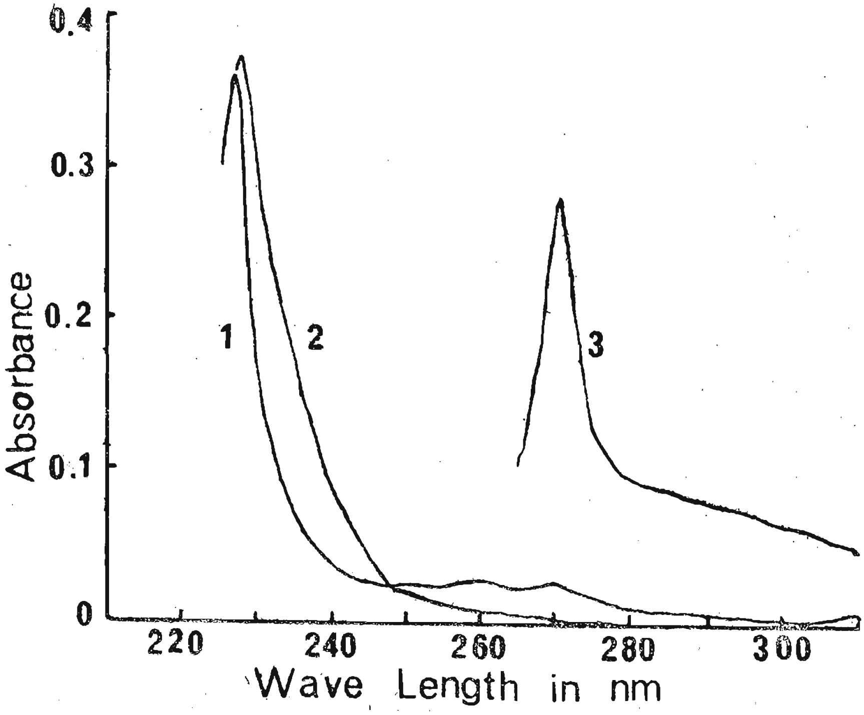

Figure 1. The UV absorption of BVE-MA charge-transfer complex in CH_2ClCH_2Cl at 23°C.
(1) [BVE] = 6.25 × 10^{-3} mole/dm^3 v.s. solvent
(2) [MA] = 1.01 × 10^{-4} mole/dm^3 v.s. solvent.
(3) Charge-transfer complex only, [BVE] = 1.20 M and [MA] = 1.02 × 10^{-4} mole/dm^3.

3. Results and Discussion

3.1. The charge-transfer complexation between n-butyl vinyl ether and maleic anhydride

An enhancement of absorption is observed in the UV region when BVE and MA are mixed in 1, 2-dichloroethane. When the absorptions of BVE and MA are subtracted from the overall absorption, the enhancement becomes an absorption maximum at 270 nm as shown in Figure 1. This new absorption maximum is attributed to a weak CT complexation between BVE and MA, BVE acting as the electron donor and MA as the acceptor, considering the polarities of the compounds.

The stoichiometry of the complexation was determined in 1, 2-dichloroethane by the Job's continuous variation method.[7] As shown in Figure 2, the maximum of the absorbance-composition plot indicates that BVE and MA form a 1 : 1 CT complex.

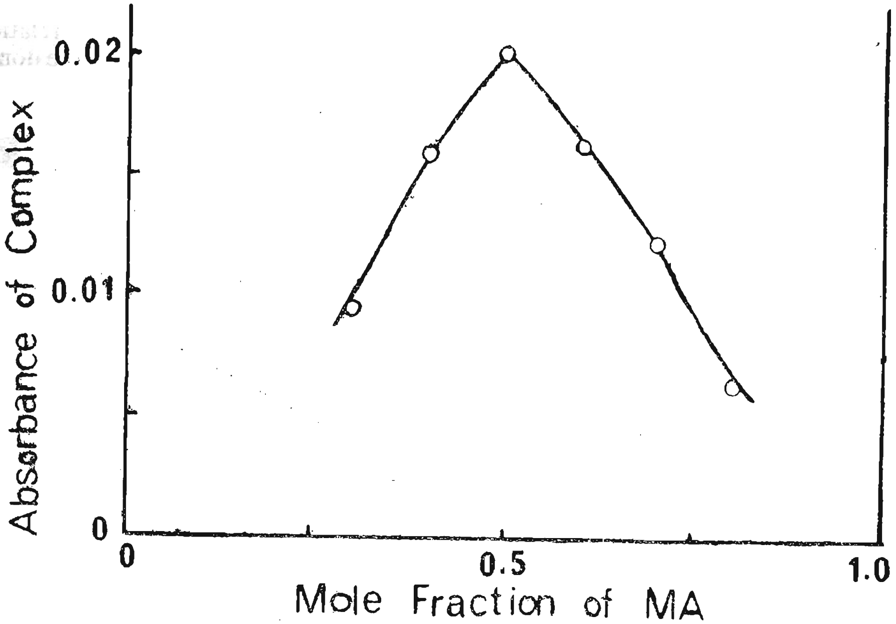

Figure 2. UV determination of the stoichiometry of the charge-transfer complex of BVE and MA by Job's continuous variation method in CH_2ClCH_2Cl at 328 nm. [BVE] + [MA] = 0.0610 mole/dm.3

The equilibrium constant (K) of the CT complexation can be determined by UV and NMR spectroscopy. In the case of a 1 : 1 complexation, the relation between the absorptivity of the complex and the concentrations of the components has been derived by Ketelaar *et al.*[8]

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

where [D] is the concentration of the donor and EA is related to the measured optical density, dA, and to the total molar concentration of both free and complexed acceptor [A] by the expression $d_A = \log_{10} I_0/I = E_A[A]l$. Ec and Ea represent, respectively, the extinction coefficients of the complexed and uncomplexed acceptor.

When a very small concentration of an acceptor and a large excess concentration of a donor are used, it can be assumed that all the acceptor is complexed. Under this condition, K can be determined through either the equation by Bensi and Hildebrand[1] (Equation (2)), or the equation by Scott[16] (Equation (3)).

$$[A]l/d_c = 1/\epsilon_c K[D] + 1/\epsilon_c \qquad (2)$$

$$[A][D]l/d_c = [D]/\epsilon_c + 1/\epsilon_c K \qquad (3)$$

where, $[A] << [D]$, d_c is the absorbance due to the complex only, i.e., $d_c = d(\text{overall}) - d(\text{donor})$ and l is the pathlength in cm.

When the donor is always in large excess compared to the acceptor, the relation between the chemical shift of the acceptor in NMR and the concentration of the donor is Equation (4) by Hanna and Ashbough.[5]

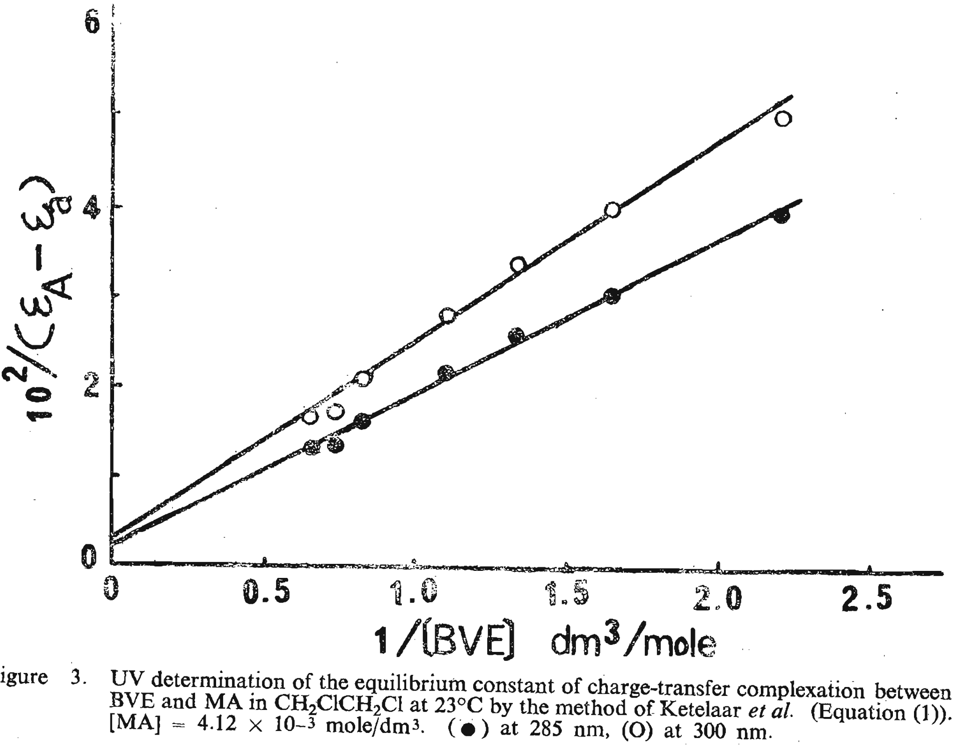

Figure 3. UV determination of the equilibrium constant of charge-transfer complexation between BVE and MA in CH_2ClCH_2Cl at 23°C by the method of Ketelaar *et al.* (Equation (1)). [MA] = 4.12 × 10^{-3} mole/dm³. (●) at 285 nm, (O) at 300 nm.

$$1/\Delta^{A}{}_{obs} = 1/K\Delta^{A}{}_{c}[D] + 1/\Delta^{A}{}_{c} \qquad (4)$$

where, $\Delta^{A}{}_{obs} = \delta^{A}{}_{obs} - \delta^{A}{}_{o}$ is the difference between the chemical shifts of the acceptor proton in complexing media (δ_{Aobs}) and that of the acceptor in uncomplexed form ($\delta^{A}{}_{o}$), and $\Delta^{A}{}_{c} = \delta^{A}{}_{c} - \delta^{A}{}_{o}$ is the difference in the acceptor proton chemical shifts in pure complex ($\delta^{A}{}_{c}$) and free acceptor.

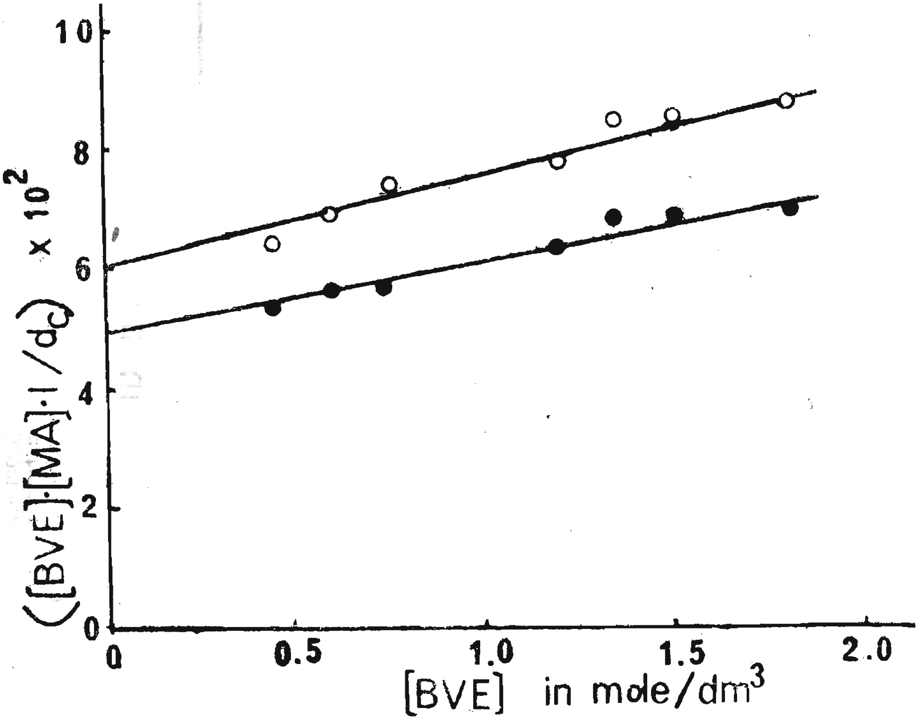

Figure 4. UV determination of the equilibrium constant of charge-transfer complexation between BVE and MA in $CHCl_4$ at 23°C by the method of Scott (Equation (3)). [MA] = 4.12×10^{-3} mole/dm^3. (●) at 285 nm, (○) at 300 nm.

The equilibrium constants of the CT complexation between BVE and MA were determined in 1, 2-dichloroethane by equation (1), in chloroform by Equation (3), and in carbon tetrachloride by Equation (4). The results are shown in Figs. 3, 4 and 5, respectively. In all cases, the concentration of MA was kept small and constant, while the concentration of BVE was increased. The chemical shift of chloroform was used as the inner standard in measuring the chemical shift of MA.

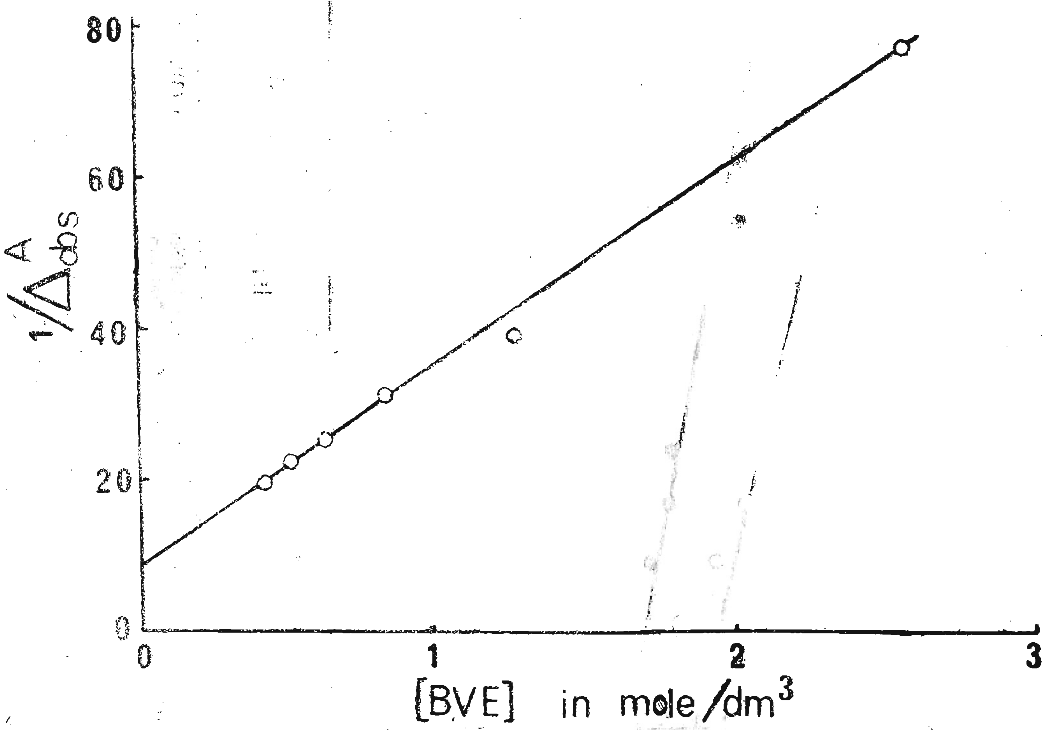

Figure 5. NMR determination of the equilibrium constant of charge-transfer complexation between BVE and MA in CCl_4 at 37°C by the method of Hanna and Ashbough (4)). [MA] = 1.00×10^{-2} mole/dm^3

TABLE 1. Relation between the polarity of the solvents and the equilibrium constants (K) of — charge-transfer complexation between BVE and MA in chloroalkanes.

Solvent	Dielectric constant[15]	Method	K (dm³/mole)	εc or δAc
CCl_4	2.238 (20°C)	NMR at 37°C	0.37	6.988 ppm
$CHCl_3$	4.806 (20°C)	UV at 23°C	0.27 (at 285 nm) 0.26 (at 300 nm)	75 67
CH_2ClCH_2Cl	10.36 (25°C)	UV at 23°C	0.11 at (285 nm) 0.11 (at 300 nm)	560 450

As seen in Table 1, the magnitude of the K values found in various chloroalkanes indicate that the CT complex between BVE and MA is a weak one. The decrease of K values with increasing solvent polarity suggests that the CT complexation follows a polar association of the components, and that the complex is predominantly at its no-bond state.[12,13] The more polar solvent reduces the magnitude of K, because in more polar solvents, the free components are better stabilized than the complex of the components. It is considered that the planar vinyl ether part of BVE molecule complexes with the planar MA molecule parallel each other achieving the maximum overlapping of the orbitals.[12,13]

Radical copolymerization of n-butyl vinyl ether with maleic anhydride BVE and MA readily underwent copolymerization at 60°C with AIBN in chloroform solution, although both BVE and MA were incapable of homopolymerization individually under the same conditions. The copolymer precipitated out in chloroform as the polymerization proceeded. The copolymer was soluble in polar solvents such as acetone, N, N-dimethyl formamide and dimethylsulphoxide, but was insoluble in non-polar solvents.

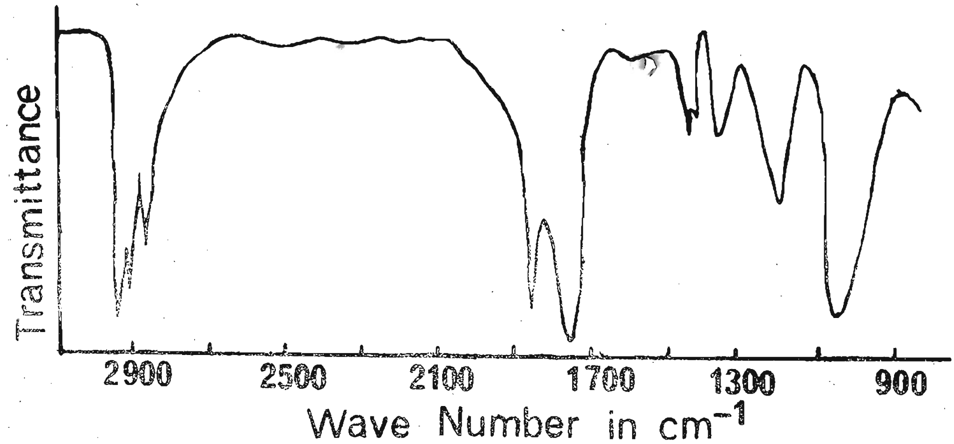

Figure 6. The IR absorption spectrum of the copolymer of BVE and MA. The mole fraction of the MA units in this copolymer is 0.49.

The IR spectrum of the copolymer in Fig. 6 shows large absorptions of five-membered anhydride group at 1770 and 1860 cm^{-1}. The absorption due to the unsaturated ether linkage $CH_2{=}CH{-}O{-}C$ of BVE monomer which appears at 1220 cm^{-1} is shifted to 1080 cm^{-1} in the copolymer, showing that the ether linkage in the copolymer is saturated, $-CH_2{-}CH{-}O{-}C$. The sp^3 C—H stretching of BVE appears at 2860 and 2940 cm^{-1} both in the monomer and the copolymer. The sp^2 C—H stretching of BVE monomer at 3100 and 3040 cm^{-1} and that of MA at 3160 cm^{-1} are completely absent in the copolymer, indicating the consumption of C=C double bonds in the copolymerization.

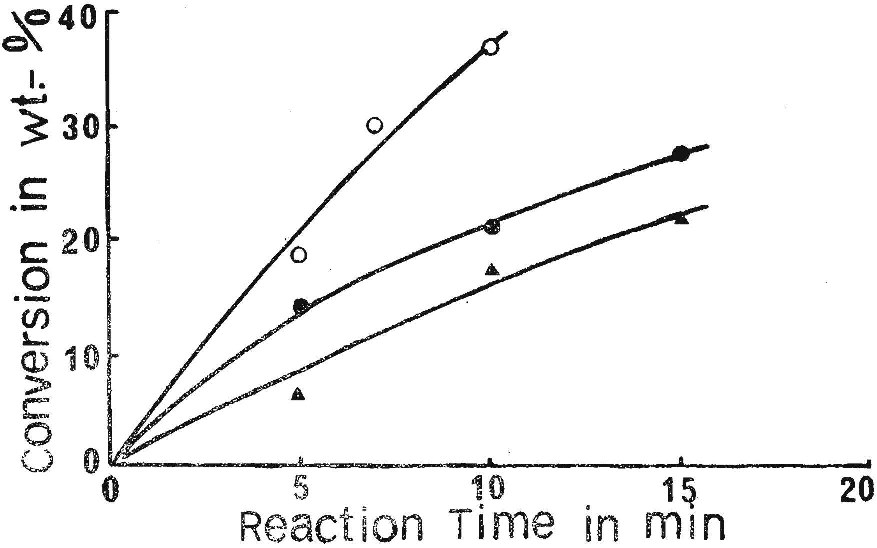

Figure 7. The conversion in the copolymerization of BVE with MA with respect to the polymerization time in $CHCL_3$ at 60°C. [BVE] + [MA] = 1.50 mole/dm^3, [AIBN] = 3.00×10^{-2} mole/dm^3. The mole fraction of MA in the monomer mixture was 0.50 (O), 0.65 (●) and 0.80 (▲).

The time-conversion curves of the copolymerization are shown in Figure 7. It is seen that the polymerization is rapid and that the rate is fairly constant up to a high conversion under the conditions used.

The copolymer composition based on the titration of the MA units of the copolymer is shown in Figure 8. The composition of the copolymer is found to be 1 : 1 over a wide range of the monomer composition. Since neither BVE or MA homopolymerizes individually under the present conditions, the copolymer of BVE and MA is considered to be a 1 : 1 alternating copolymer.

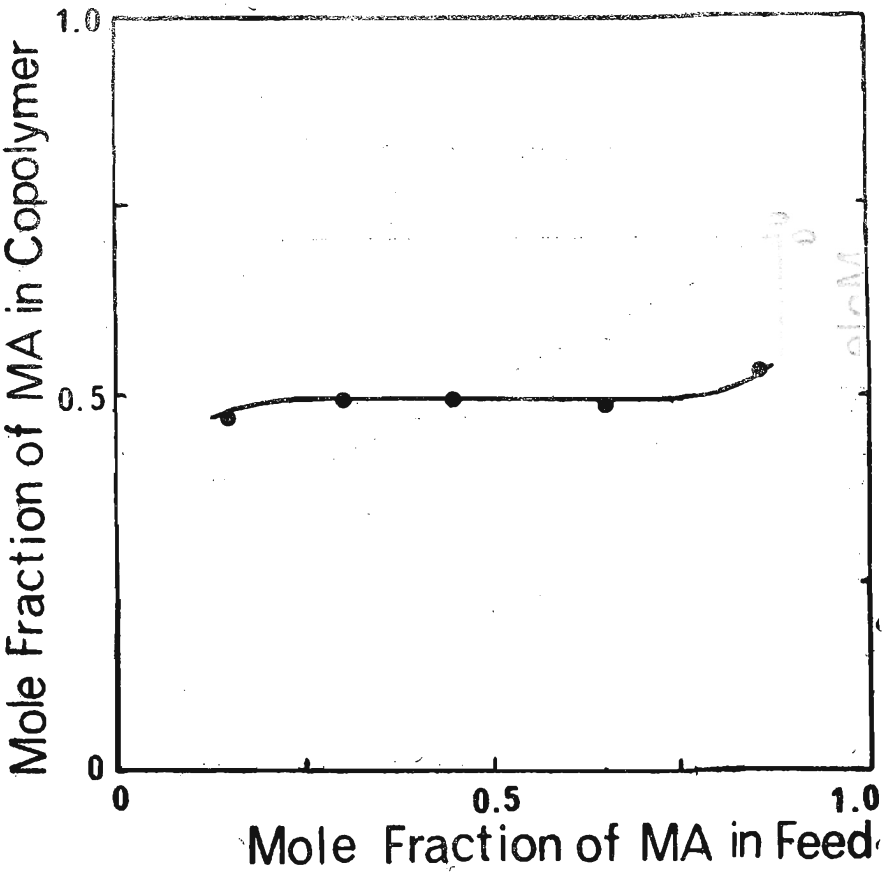

Figure 8. The copolymer composition curve for the copolymerization of BVE with MA in $CHCl_3$ at 60°C. [BVE] + [MA] = 3.00 mole/dm^3, [AIBN] = $6.00 \times 10^{-}$ mole/dm^3.

The initial rate of the copolymerization and the conversion of the polymerization after a prolonged reaction period (24 hours), are shown in Figure 9, with respect to the feed monomer composition. Both the initial rate of the copolymerization and the limiting conversion are maximum at 1 : 1 monomer composition of the feed. If the 1 : 1 CT complex of BVE and MA is the species that polymerizes to give the 1 : 1 alternating copolymer, the rate of the copolymerization should be proportional to the concentration of the complex.[2] Since the concentration of a 1 : 1 complex becomes maximum at 1 : 1 feed monomer composition, the rate should be maximum at 1 : 1 feed monomer composition, which is consistent with the experimental observation. The theoretical limiting conversion is calculated assuming the polymerization is an alternating copolymerization. The observed limiting conversion is within the theoretical limiting conversion and is closely parallel to it.

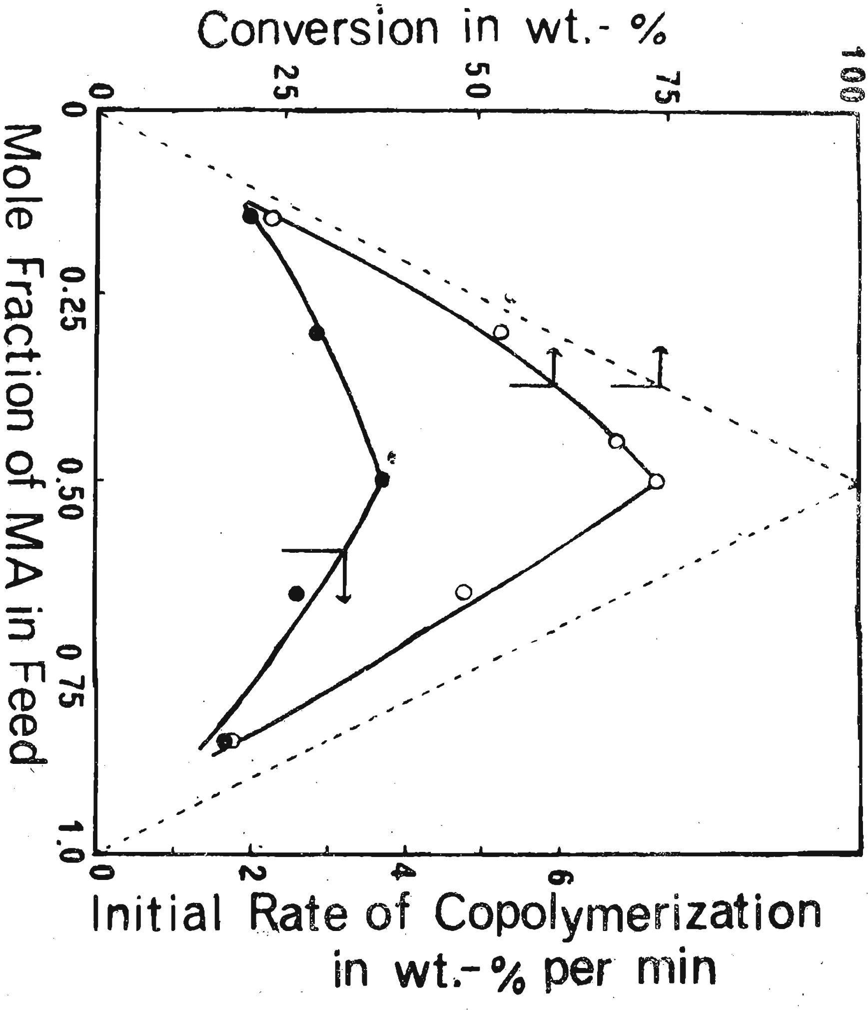

Figure 9. The initial rate of copolymerization of BVE with MA (●), and the limiting conversion after 24 hours of polymerization (O). The dotted lines are calculated for the maximum possible conversion for a pure alternating copolymerization. (BVE) + (MA) = 1.50 mole/dm^3, (AIBN) = 3.00 × 10^{-2} mole/dm^3 in $CHCl_3$ at 60°C.

Thus the copolymerization of BVE with MA can be explained when the 1 : 1 alternating copolymer is thought to be formed through the polymerization of the 1 : 1 CT complex of BVE and MA, the complex being considered to be much more reactive than the free monomers.

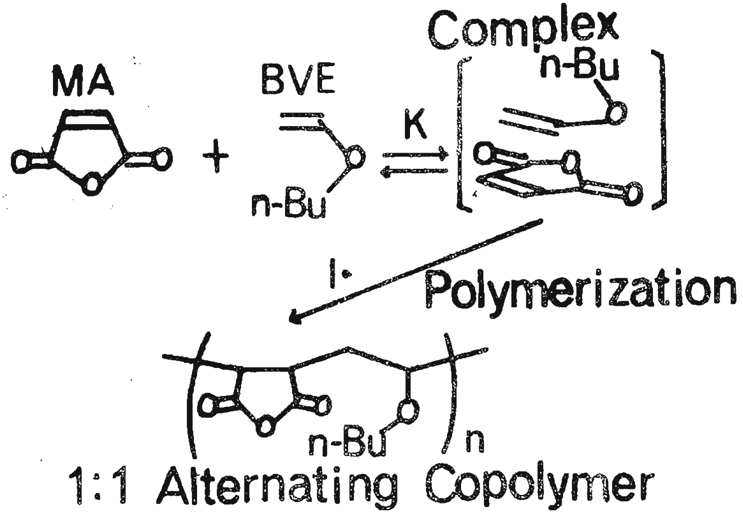

Fig. 10.

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