## Studies on the Charge-Transfer Complex and Polymerization. XVII. The Reactivity of the Charge-Transfer Complex in Alternating Radical Copolymerization of Vinyl Ethers and Maleic Anhydride

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ABSTRACT: After mixing a donor and an acceptor monomer, a development of color and the formation of an alternating copolymer are often observed. An example is the copolymerization of 1,2-dimethoxyethylene, pdioxene or 2-chloroethyl vinyl ether with maleic anhydride. Such systems can be described in terms of a mechanism which involves a charge-transfer complex formation equilibrium. It is found that the reactivity of the complex increases with the equilibrium constant for the complex formation.

To date two mechanisms have been proposed for alternating radical copolymerizations: (1) the transition state of the cross-propagating step is stabilized either by electron transfer<sup>1</sup> or electrostatic interaction,<sup>2</sup> and (2) the charge-transfer complex between a donor and an acceptor monomer is more reactive than a free monomer and can polymerize preferentially (i.e., the complex mechanism theory).8 We favor the latter mechanism because of the evidence of physical association (the formation of the charge-transfer complex) in the alternating radical copolymerization systems of p-dioxene (PD),<sup>4</sup> vinyl ethers,<sup>5</sup> and 1,2-dimethoxyethylene (DME)6 with maleic anhydride (MAnh), and in terpolymerizations such as PD-MAnh-acrylonitrile (AN),7 PD-MAnh-2-chloroethyl acrylate (2-CEA).8 2-chloroethyl vinyl ether (CEVE)-MAnh-An,9 and dodecyl vinyl ether-fumaronitrile (FN)-2-CEA,10 in which the third monomer has little or no interaction with the other monomers. In these cases the resulting terpolymers always had an equimolar composition of the donor and the acceptor monomers, and the DEVE-MAnh-FN, CEVE-PD-MAnh systems could be treated as binary copolymerizations of only two different complexes.<sup>11</sup> Dilution effects upon the terpolymer composition, which would be expected in the copoly-

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merization of a complex and an indifferent monomer, were observed in the terpolymerization<sup>12</sup> and kinetic evidence for the participation of the complex in initiation and propagation was established in the spontaneous copolymerization of 1-methylcyclopropene-SO $_{2}^{13}$  and cyclopentene-SO<sub>2</sub><sup>14</sup> systems. Also, the microstructure observed in butadiene copolymers supported the complex mechanism.15

Although in such alternating copolymerizations between donor and acceptor monomers the development of color is observed in many cases, indicating the formation of the charge-transfer complexes (and Walling, et al., observed a relationship between apparent color and copolymerization reactivities in the case of ringsubstituted styrenes<sup>1</sup>), no quantitative studies have been made to correlate complex formation equilibria with copolymerization reactivities.

We have already reported two systems, CEVE-PD-MAnh and CEVE-MAnh-FN,11 in which the modified monomer reactivity ratios,  $r_{\rm I}(K_1/K_2)$  and  $r_{\rm II}(K_2/K_1)$ , of the complexes could be calculated by regarding them as the copolymerization of two complexes. If the equilibrium constants for complex formation,  $K_1$ and  $K_2$ , could be measured by a proper method, the reactivities of the complexes could then be evaluated. This terpolymerization technique should thus be useful in relating K values and reactivities of the complexes considered as the activated monomers.

In these studies, solvent effects in complex formation equilibria were examined spectrophotometrically. Values of K were measured in benzene, toluene, mxylene, chlorobenzene, chloroform, and acetone. The relative reactivities of the complexes were then estimated and discussed for the systems DME-MAnh, PD-MAnh, and CEVE-MAnh.

## **Experimental Section**

Materials. DME was prepared by modification of the

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<sup>(6)</sup> S. Iwatsuki, S. Iguchi, and Y. Yamashita, ibid., 69, 145 (1966). (7) S. Iwatsuki and Y. Yamashita, *ibid.*, **68**, 1138 (1965).

<sup>(12)</sup> S. Iwatsuki and Y. Yamashita, J. Polym. Sci., Part A-1, 5, 1753 (1967).

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<sup>(14)</sup> S. Iwatsuki, T. Okada, and Y. Yamashita, ibid., in press. (15) Y. Yamashita, S. Iwatsuki, and T. Kokubo, J. Polym. Sci., Part C, in press.

preparative method of 1,2-diethoxyethylene by McElvain, et al.,<sup>16</sup> as follows.

A. Preparation of Bromoacetaldehyde Dimethyl Acetal (I). A 3-1. three-necked round-bottomed flask A was equipped with a mechanical stirrer and a thermometer and an exit glass tube leading through a safety trap to a water pump. In the other neck was fitted a 7-mm glass tube, extending to the bottom of the flask, and attached to a 500ml bottle containing 900 g of bromine. This bottle was connected to a 500-ml wash bottle containing 250 ml of sulfuric acid. The inlet tube was connected to a calcium chloride tube. A solution of 500 g of vinyl acetate in 1.5 l. of absolute methanol was placed in A. The solution was cooled to about  $-10^{\circ}$  by an ice-salt mixture, and stirring was started. Bromine vapor was introduced into A by suction of a water pump. The rate of introduction was regulated so that 10-20 hr were required to volatilize all the bromine. Stirring was stopped, and the reaction mixture was allowed to stand overnight at room temperature. The mixture was poured into 2.0 l. of ice water and the lower layer of I and methyl acetate was separated, washed twice with 300-ml portions of cold water and once with 300 ml of cold 10% sodium carbonate solution, and dried over calcium chloride. The crude product was purified by distillation under reduced pressure (55° (26 mm) to  $62^{\circ}$  (32 mm), 550 g, 57.5%).

B. Preparation of Methoxyacetaldehyde Dimethyl Acetal (II). A cooled solution of sodium methoxide, prepared by the reaction of 106 g of sodium with 2.5 l. of absolute methanol, was placed under nitrogen in a three-necked 5-l. round-bottomed flask fitted with condenser and stirrer, and 550 g of I was added over a period of 1 hr. A slow stream of nitrogen was passed over the mixture for 24 hr while it was refluxing. The precipitated sodium bromide was filtered off and approximately 1.5 l. of methanol was removed from the filtrate by careful distillation. The remaining solution was refluxed overnight and the precipitated sodium bromide filtered off. After removal of the methanol from this filtrate, fractionation of the residue yielded ca. 170 g of II (bp 120–124.5°). From an ether extract of the solid residue from the above distillation an additional 60 g of II was obtained, bringing the total yield of 230 g (58.5%).

C. Preparation of DME. In a vertical glass column,  $44 \times 2.5$  cm, were placed 25 g of alumina pellets prepared from alumina obtained by the hydrolysis of aluminium isopropoxide and heated at 600° for several hours. II (120 g) was then dropped at a rate of 25 ml/hr from a dropping funnel into the alumina column at 190°. The products were collected in a flask immersed in an ice bath. After all the acetal was added, nitrogen was passed through the tube for about 10 min. Fractionation of the reaction products yielded 24 g of DME, bp 95–108°, and 63 g of unchanged acetal. The crude yield of DME based on unrecovered II was 60%. The crude product was fractionally distilled by 95–105° through a Widmer column. Analysis by gas chromatography (PEG, 80°) gave a composition of 90% *cis* and 10% *trans* isomer.

CEVE, which was prepared by the Japan Oil Seal Co., was distilled carefully from calcium hydride (bp  $108^{\circ}$  <sup>17</sup>) before use.

PD was prepared from *p*-dioxane according to the method of Summerbell, *et al.*,<sup>18</sup> which involves conversion of *p*-dioxane to 2,3-dichloro-*p*-dioxane (mp  $28 \sim 30^{\circ}$ ) by chlori-

nation and then reaction with magnesium iodide in ethyl ether to yield PD (bp  $94 \sim 94.7^{\circ}$ , 74% yield). MAnh was purified by distillation under reduced pressure and stored in a desiccator over calcium chloride.

**Spectrophotometric Measurements.** For the determination of the equilibrium constants of the complex formation, transmittances were measured at 350 and 340 m $\mu$  with a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer using 0.5-cm Pyrex cells and a thermostated cell holder. The temperature of the cell was kept constant to  $\pm 1.0^{\circ}$ .

Two solutions, prepared by dissolving in appropriate solvents a certain amount of a donor or an acceptor monomer, respectively, were mixed just before the spectrophotometric measurement at a ratio chosen to give the desired concentration. Changes of the absorbance by polymerization during the times required for measurement were negligible, even in the case of the most reactive system (DME-MAnh) because of the low monomer concentration.

**Polymerization Procedure.** A 30-ml glass ampoule was charged with a measured amount of monomer and diluted with benzene to the desired concentration. No initiator was added. The ampoule was cooled to  $0^{\circ}$ , flushed with nitrogen and sealed. It was then maintained without stirring at  $30^{\circ}$  (DME-MAnh) or  $60^{\circ}$  (PD-, CEVE-MAnh). The polymer was precipitated by adding excess ethyl ether, washed with ethyl ether, and dried under vacuum to constant weight.

#### Results

By using the continuous variation method<sup>19</sup> we have previously established that DME, PD, and other vinyl ethers form 1:1 complexes with MAnh.<sup>4-6</sup> As only the 1:1 complex should be considered, the equilibrium constant for association is determined by using the Benesi-Hildebrand equation,<sup>20</sup> eq 1, and/or Scott's equation,<sup>21</sup> eq 2. When  $[A] \ll [D]$ 

$$[\mathbf{A}]l/d = (1/K\epsilon[\mathbf{D}]) + (1/\epsilon) \tag{1}$$

$$[A][D]l/d = (1/K\epsilon) + ([D]/\epsilon)$$
(2)

where [D] and [A] are the concentrations of donor and acceptor, respectively, d is the absorbance due to complex and l is the path length. According to eq 1, a plot of [A]l/d vs. 1/[D] should be linear with slope and intercept equal to  $1/K\epsilon$  and  $1/\epsilon$ , respectively. On the other hand, according to eq 2, if a plot of [A][D]l/d vs. [D] is made,  $1/K\epsilon$  and  $1/\epsilon$  are obtained from the intercept and slope, respectively. By using both equations simultaneously, errors in  $1/\epsilon$  from eq 1 and of  $1/K\epsilon$  in eq 2 can be minimized.

Since the charge-transfer band of a complex between MAnh and a donor monomer (*i.e.*, DME, PD, or CEVE) appears in the same region of the near-uv region where MAnh itself absorbs, it is difficult to determine  $\lambda_{max}$  and  $\epsilon_{max}$  of the charge-transfer band precisely. Therefore, measurements were carried out at 350 m $\mu$  for the DME-, PD-MAnh systems and at 340 m $\mu$  for the CEVE-MAnh system. At these wavelengths the overlapping of both bands is comparatively small (the DME and PD-MAnh systems have charge-transfer band maxima at about 350 m $\mu$ ). Absorbances due to

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			-DME	MAnh <sup>n</sup> -		~	-CEVE-	MAnh <sup>h</sup> -			-PD-	MAnh <sup>a</sup> —	
Solvent	Dielectric constant, $D_{25}^{\circ}$	€350, <sup>c</sup> l. mol <sup>-1</sup> cm <sup>-1</sup>	12.5°	- <i>K</i> , l./mc 25°	ol <u></u>	$\epsilon_{340},^{c}$ l. mol <sup>-1</sup> cm <sup>-1</sup>	<u> </u>	K, l./mo 30°	l 51 °	ε <sub>350</sub> , <sup>c</sup> l. mol <sup></sup> cm <sup>-1</sup>	<sup>1</sup> 10°	- <i>K</i> , l./mo 25°	<u>51.5°</u>
Benzene	2.27	250	0.33	0.294	0.22	25	0.114	0.10 <sup>d</sup>	0.076	500	0.074	0.069	0.058
Toluene	2.38	410	0.20	0.164	0.14					820	0.042	0.040	0.035
<i>m</i> -Xylene Chlorobenzene	2.37 5.62	100 420	0.21	0.73 0.175	0.136					830		0.051	
Chloroform	4.70	345	0.164	0.15	0.13	33	0.13	0.105	0.096	690	0.055	0.0545	0.040
Acetone	20.7	330	0.098	0.09	0.082					670		0.047	

Table I Equilibrium Constants of Complex Formation in Various Solvents at Various Temperatures

<sup>*a*</sup> [MAnh] = 0.025 mol/l., [DME] or [PD] = 0.25  $\sim$  0.8 mol/l. <sup>*b*</sup> [MAnh] = 0.025 mol/l., [CEVE] = 0.5  $\sim$  1.90 mol/l. <sup>*c*</sup> Independent of temperature. <sup>*d*</sup> At 21.5<sup>*c*</sup>.

TABLE II

	IHERMO	DDYNAMIC C	ONSTANTS <sup>4</sup> O	OF COMPLEX F	ORMATION I	N VARIOUS S	OLVENTS		
	]	DME-MAn	h——-	~C	EVE-MAn	h—		-PD-MAnh	
	$\Delta F$ ,	$-\Delta H$ ,		$\Delta F$ ,	$-\Delta H$ ,		$\Delta F$ ,	$-\Delta H$ ,	
	kcal/	kcal/	$-\Delta S$ ,	kcal/	kcal/	$-\Delta S$ ,	kcal/	kcal/	$-\Delta S$ ,
Solvent	mol	mol	eu	mol	mol	eu	mol	mol	eu
Benzene	0.72	1.91	8.9	1.37	1.55	9.8	1.58	1.11	9.0
Toluene	1.07	1.74	9.4				1.91	0.92	9.5
Chlorobenzene	1.03	2.04	10.3				1.77		
Chloroform	1.13	0.99	7.1	1.32	0.86	7.3	1.73	0.65	8.0
Acetone	1.42	0.90	7.8				1.81		

<sup>a</sup> At 25°, calculated from  $\Delta F = -RT \ln K$  and  $\Delta F = \Delta H - T\Delta S$  using K and  $\ln K vs. 1/T$ .



Figure 1. Determination of equilibrium constants K using the Benesi-Hildebrand equation (A) and the Scott equation (B) for the system DME-MAnh, measured at 350 m $\mu$ :  $\bigcirc$ , 25°;  $\bullet$ , 50°, in toluene.

the complex, d, were calculated from eq 3, where d'

$$d = d' - d'' \tag{3}$$

and d'' are the apparent absorbance observed and that of MAnh, respectively. An example of the use of eq 1, 2, and 3 is shown in Figure 1 for the case of the system DME-MAnh in toluene. Good linear relationships are found.

In Table I, the equilibrium constants for complex formation, K, are given for various solvents and at

various temperatures. Since solvents such as *m*-xylene show comparatively strong donor character and interact with MAnh to give charge-transfer bands in the same uv region as the CEVE-MAnh system, measurements of *K* values were difficult for such cases. Hence we did not measure *K* values in *m*-xylene and toluene. Assuming that the molar extinction coefficient,  $\epsilon$ , is independent of temperature, the bonding energy between a donor and an acceptor can be calculated from the slope of a curve of log *K* vs. 1/T (Figures 2 and 3). Values of  $\Delta F$  and  $\Delta S$ , calculated from the equations  $\Delta F = -RT \ln K$  and  $\Delta F = \Delta H - T\Delta S$ , are summarized in Table II.

The comparison of spontaneous copolymerization rates in the DME, CEVE, and PD systems is shown in Table III. Here in runs 1, 2, and 3 the monomer feeds were the same but, of course, the complex concentrations are different. In runs 2 and 4 the complex concentrations were the same, being calculated from the K values at 60° (the polymerization temperature). The order of the apparent polymerization rates is DME > CEVE > PD according to the data of Table III. Table IV shows the relation between K values and the polymerization rates for the same system, DME-MAnh, in different solvents. These data indicate that the larger the K values, the more rapid the rates.

In terpolymerizations generally, there are three possible methods of monomer combination, *i.e.*, donor-donor-acceptor, donor-acceptor-acceptor, and donor-acceptor- $M_3$  (in which  $M_3$  has little interaction with the other two monomers). Table V shows examples of the first and third types. In these three systems, the calculations of the modified monomer reactivity ratios considered as two component systems were performed





1.6

Figure 2. Relation between equilibrium constant and temperature in various solvents for the system DME-MAnh: ●, benzene; ①, toluene; ⊇, chloroform; O, chlorobenzene; ⊙, acetone.

Figure 3. Relation between equilibrium constant and temperature in various solvents: PD-MAnh-O, benzene; zene

TABLE III RATES OF SPONTANEOUS COPOLYMERIZATION

Run	System	Total feed, <sup>a</sup> mmol	Solvent, benzene, ml	Polymerizn temp, °C	Mean polymerizn rate, %/min
1	DME-MAnh	9.0	2.5	30	0.0925
2	CEVE-MAnh	9.0	2.5	60	$0.089_{4}$
3	PD-MAnh	9.0	2.5	60	0.0027
4	PD-MAnh	$10.4^{b}$	2.5	60	0.0060

<sup>a</sup> Equimolar with respect to donor and acceptor monomers. <sup>b</sup> Complex concentration equal to that of run 2.

TABLE IV COMPARISON OF COPOLYMERIZATION RATE AND KFOR THE SYSTEM DME-MAnh<sup>a</sup>

		Conversion, 2	7
Time, min	Benzene	Toluene	<i>m</i> -Xylene
22	2.41	2.03	2.32
75	6.98	6.55	8.19
120	10.3	11.2	19.4
180	18.0	11.7	15.2
Mean <sup>b</sup> rate	0.093	0.080	0.110
$K^c$	0.29	0.16	0.73

"  $30^{\circ}$ ; feeds, [DME] = 0.397 g, [MAnh] = 0.441 g; solvent, 2.5 ml. <sup>b</sup> Per cent per minute. <sup>c</sup> Values at 25°.

by the application of the modified Mayo-Lewis equation (the intersection method) and the true monomer (complex) reactivity ratios are calculated using the K values determined from spectrophotometry. Table VI indicates the relative reactivities of two complexes toward AN radical calculated from the monomer reactivity ratios of Table V and of binary copolymerization systems.<sup>9, 22, 23</sup> The Alfrey-Price Q and e values calcu-

lated from the monomer reactivity ratios for the complexes obtained from the terpolymerizations containing AN are summarized in Table VII.

#### Discussion

Solvent Effects on Equilibrium Constant. It is clear from Table I that the values of K decrease with increasing polarity of the solvent, indicating that the complexes are not sufficiently polar to initiate ionic polymerizations, and also that the contribution of dative structures may not be very significant. In the case of the complex of N-vinylcarbazole with p-chloranil, the K value is very large (3 - 6) in toluene acetonitrile), it increases with the solvent polarity, and initiates cationic polymerization, indicating that the contribution of a dative structure may be significant.<sup>24</sup> All this is the opposite of the situation in our present work.

The data in Table II show at once the different influence of the aromatic and the nonaromatic solvents. The aromatic solvents are known generally to act as  $\pi$ donors; on the other hand nonaromatic solvents, e.g., acetone, act as an n donor, due to the lone pair electrons of oxygen, and chloroform as a  $\sigma$  acceptor, due to the  $\sigma$  bonds between carbon atom and chlorine

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Chem. Soc., 70, 1529 (1948).

TABLE V TERPOLYMERIZATIONS OF CEVE-PD-MANH, CEVE-MANH-AN, PD-MANH-AN SYSTEMS IN BENZENE AT 60°

System	First component	Second component	Modifie	d mrrª	$r_1$	$r_2$	Ref
CEVE-PD-MAnh	C <sub>1</sub> (CEVE-MAnh)	C <sub>2</sub> (PD-MAnh)	$r_1K_1/K_2$	2.05	1.52	0.46	11
CEVE-MAnh-AN	C (CEVE-MAnh)	AN	$r_2 K_2 / K_1$	0.34	4.8	0.093	9
PD-MAnh-AN	C (PD-MAnh)	AN	$r_1K$	0.36	5.0	0.189	7
			$r_2/K$	1.25			
			$r_1K$	0.28			
			$r_2/K$	3.4			

<sup>a</sup> Monomer reactivity ratio recalculated from the data of reference cited by the intersection method using the equations

$$-\frac{\mathrm{d}[\mathbf{C}]}{\mathrm{d}[\mathbf{AN}]} = \frac{[\mathrm{donor}][\mathrm{MAnh}]}{[\mathrm{AN}]} \left(\frac{r_1 K[\mathrm{donor}][\mathrm{MAnh}] + [\mathrm{AN}]}{[\mathrm{donor}][\mathrm{MAnh}] + (r_2/K)[\mathrm{AN}]}\right)$$

for the systems containing AN and

$$-\frac{\mathrm{d}[\mathrm{C}_{1}]}{\mathrm{d}(\mathrm{C}_{2})} = \frac{[\mathrm{CEVE}]}{[\mathrm{PD}]} \left\{ \frac{r_{1}(K_{1}/K_{2})[\mathrm{CEVE}] + [\mathrm{PD}]}{[\mathrm{CEVE}] + r_{2}(K_{2}/K_{1})[\mathrm{PD}]} \right\}$$

for the CEVE–PD–MAnh system. <sup>b</sup> Equilibrium constants used for the calculation of  $r_1$ ,  $r_2$ , are 0.0747 for CEVE–MAnh and 0.0556 for PD-MAnh.

TABLE VI REACTIVITIES OF THE COMPLEXES TOWARD AN RADICAL<sup>a</sup>

	$k_{\rm AN} \cdot c_{\rm i}/k_{\rm AN} \cdot c_{\rm EVE}$	kan·c <sub>1</sub> /kan·manh	$k_{\rm AN} \cdot c_2 / k_{\rm AN} \cdot p_D$	$k_{\mathrm{AN}} \cdot {}_{\mathrm{C}_2}/k_{\mathrm{AN}} \cdot {}_{\mathrm{MAnl}}$	$k_{\rm AN} \cdot {\rm ceve}/k_{\rm AN} \cdot$	PD $k_{AN} \cdot c_1 / k_{AN} \cdot c_2$
	10.8	64.5	31.2	31.7	5.9	2.03
<sup>a</sup> Ca	lculated from PD(M	$(r_1 = 0.000)$	$3, r_2 = 5.9$ ), CEV	$E(M_1)-AN(r_1 = \cdot$	$-0.07 \pm 0.1, r_2$	= 1.0), $MAnh(M_1)-AN$ , ( <i>r</i> )

= 0,  $r_2$  = 6.0), and the terpolymerizations containing AN in Table V;  $C_1$ , CEVE-MAnh complex;  $C_2$ , PD-MAnh complex.

	TABLE V $Q$ and $e$ Values of 1	'II the Complexe	s
	PD-MAnh complex	CEVE– MAnh complex	AN
Q e	$2.4 \\ 0.98 (\sim 0.5^{a})$	2.2 0.31	0.60 1.20

<sup>a</sup> From the chain transfer to solvents or/and the PD-MAnh-2-CEA system.

atoms, or as an acceptor, which donates a proton. Therefore, the remarkable difference in  $\Delta H$  and  $\Delta S$ may depend upon whether they are  $\pi$  donors or not. The small differences in bonding energies  $(-\Delta H)$ of the complexes in  $\pi$  donor solvents such as toluene, benzene and chlorobenzene are due to the chargetransfer interactions of such solvents with the MAnh monomer, *i.e.*, the bonding energies decrease with the increase of their donor characters of solvents. The order observed in the values of  $-\Delta H$ , *i.e.*, chlorobenzene > benzene > toluene, is the expected trend.

Good correlations are observed between  $-\Delta F$  and  $-\Delta H$  in the three systems. For both quantities the order observed is DME > CEVE > PD. This relation between  $\Delta F$  and  $\Delta H$  is generally observed in complex formation.<sup>25</sup> On the other hand,  $-\Delta S$  must either vary linearly with  $-\Delta F$  and  $-\Delta H$  or be invariant. In Table II, a linear relation of  $-\Delta S$  with  $-\Delta F$  or  $-\Delta H$  is not observed. Because of large errors accumulated from  $-\Delta F$  and  $-\Delta H$  in calculation it is difficult to say whether  $-\Delta S$  is invariant. Since the change of  $\Delta F$  and  $\Delta H$  with solvent medium is not

(25) R. M. Keefer and L. J. Andrews, J. Amer. Chem. Soc., 77, 2164 (1955).

negligible, the comparisons should be made in the same solvent.

In general, a K value is composed of a sum of  $K_i$ values, where  $K_i$  denotes the equilibrium constant of the *i*th complex, because there will be all sorts of complexes of different bonding states. If large percentages of two or more complexes of very different bonding states exist then  $\ln K vs. 1/T$  would not be linear and the molar extinction coefficient  $\epsilon$  would depend on temperature.<sup>26</sup> But the systems used here showed an almost linear relationship between  $\ln K$  and 1/T and  $\epsilon$  was independent of temperature to within the limit of experimental error, as shown in Figure 1. Moreover the magnitude of the decrease in entropy,  $-\Delta S$ , upon complex formation corresponds to that of a complex in which the components are tightly bound to each other. Hence complexes which have fixed orientations of components predominate in the systems used here, and such complexes are not simple transitory contact charge-transfer complexes.<sup>27</sup> But if such complexes exist, they may affect the molar extinction coefficients but not the K values as determined by eq 1 and 2. Therefore the K values obtained are correct to within experimental error. The existence of complexes having fixed orientations of components is supported by the fact that the K values are so large as to enable them to be measured.

Solvent effects in terpolymerizations such as in the systems PD-MAnh-AN and CEVE-MAnh-AN, where the reactivities of complexes were largest in chloroform, have been reported12 already. These may be due to the positive *e* values of the complexes (Table VII)

(26) D. Booth, *Sci. Progr.* (London), 48, 435 (1960).
(27) C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworth and Co., Ltd., London, 1961, p 111.

and to the acceptor property of chloroform, *i.e.*, solvation to the reaction sites of the complex may be less in acceptor solvents than in donor solvents such as aromatics and acetone.

Relative Reactivities of Charge-Transfer Complexes. The order observed in Table III, DME > CEVE > PD, and the order of solvents found from the polymerization rates, *m*-xylene > benzene > toluene in Table IV, agrees with the order of K values in different systems and solvents, respectively (Table I). One might ask whether the differences in spontaneous copolymerization rates depend upon the differences in the concentrations of the complexes or in the reactivities of the complexes or both, and moreover upon the difference in initiation rates or in propagation rates, etc. To give a partial answer to these questions, the difference in propagation rates was evaluated by using the terpolymerization technique (Table V).

The relative monomer reactivity ratios of two complexes in the DME-PD-MAnh system indicate that the CEVE complex is about three times as reactive toward radicals as the PD complex (compare  $r_1$  and  $r_2$ ). This is consistent with the reactivities obtained from analysis of the CEVE-MAnh-AN and PD-MAnh-AN systems (Table V). That is, in the CEVE-PD-MAnh system the values of  $r_1$  (1.52) and  $1/r_2$  (2.17) may be equal to the reactivities of both complexes  $C_1$  and  $C_2$  for the radical produced from the  $C_1$  and  $C_2$  complex. These values are consistent with that for AN radical (2.03) as seen in the last column of Table VI, indicating that the  $C_1$ complex will be two times as reactive as a  $C_2$  complex for the propagating radicals. Hence, this indicates also that the reactivities of the complex increase with the K values and the order observed in the apparent copolymerization rates (Table III), i.e., CEVE > PD, is the same in the propagation step, *i.e.*, the order of the reactivities of the complexes toward radicals.

As is clear from Table I, the values of K are controlled by the solvent polarity. Therefore, it might be expected that AN, which has a large value for its dielectric constant, 38, might affect the K values when used as a solvent. Although the copolymerization reactivity ratios indicate that AN had small interactions with MAnh, PD or CEVE, respectively,<sup>9,22,23</sup> there remains the possibility of interactions with donor monomers, with accompanying effects on the terpolymerizations.

Values of e of complexes were evaluated using terpolymerization involving AN as the third component, and resulted in values 0.98 and 0.31 for the PD and CEVE complex, respectively, as seen in Table VII. Both complexes have positive e values. In the PD complex this is consistent with values found from the PD-MAnh-2-CEA system<sup>8</sup> and from chain transfer to solvents<sup>28</sup> by the method of Fuhrman,  $et al.^{29}$  The last method gives e values which correlate much more with the propagating radicals than those given by terpolymerizations. Although it is reasonable to deduce from such positive e values that in these polymerizations the MAnh radical plays an important role, the question whether or not the e values in a radical state and in a monomer state of the complex are the same remains unsolved. At the present time such values of e for the two states cannot be evaluated by a proper method.

Anyhow, in these terpolymerizations involving complexes the complex has such a very large reactivity that its low concentration can be compensated. For example, the free PD and CEVE monomers become 31 times and 11 times more reactive, respectively, by becoming the components of complexes (Table VI).

Equilibrium Constant and Charge-Transfer Complex. Generally, the strength of the charge-transfer force depends upon the ionization potential of a donor  $(I_d)$ and the electron affinity of an acceptor  $(E_a)$ , *i.e.*, the smaller the ionization potential and the larger the electron affinity are, the larger the charge-transfer force should be. On the other hand, the following relation exists between the charge-transfer band energy and  $I_d$ or  $E_a$ 

$$h\nu_{CT} = I_{\rm d} - E_{\rm a} + G + X$$

where G and X are coulomb and the resonance energies, respectively, and are considered to be constant for a given donor or an acceptor. It can thus be concluded that the donor-acceptor pairs which have charge-transfer bands at the longest wavelengths have the strongest charge-transfer interactions.

Donor-acceptor systems generally develop color because of charge-transfer interactions between them. In the DME-, PD- and CEVE-MAnh systems, the first two systems developed yellow colors, which was more intense for the former, while the third gave no visible color. If these colors are used to classify the stabilities of the complexes, the order of DME > PD >CEVE would be proposed. Such differences in color intensities could be due to either the difference in wavelengths or to differences in absorbances. The CEVE system has its charge-transfer band at a shorter wavelength than the DME and PD systems, and the DME system has a more intense absorbance than the PD system because both systems have their absorptions at the same wavelength, ca. 350 m $\mu$ . In any case, the proposed order of reactivities, DME > PD >CEVE, is inconsistent with the order deduced from the K values in Table I and the apparent polymerization rates in Table III and the relative reactivity in terpolymerization in Table V.

The fact that the monoethers, e.g., CEVE, have charge-transfer bands at shorter wavelengths than the diethers can be understood by considering the higher ionization potential of the former. In the series of vinyl ethers (monoethers), the K values at 350 m $\mu$  increase with an increase in carbon number of the alkyl groups and, therefore, with a decrease in e values.<sup>5</sup> This can be explained by the red shift of the chargetransfer band with the decrease of e values, which should be proportional to the ionization potentials. However, the inconsistency between the reactivities and the absorption maxima ( $\lambda_{max}$ ) cannot be accounted for and it might be due to the structural differences of the donor monomers, which could affect the reactivity considerably. Recently the inconsistency between the values of K and the wavelengths of the charge-transfer band has been explained in terms of the relative strengths

<sup>(28)</sup> S. Iwatsuki, K. Nishio, and Y. Yamashita, Kogyo Kagaku Zasshi, 70, 384 (1967).
(29) N. Fuhrman and R. B. Mesrobian, J. Amer. Chem. Soc.,

<sup>(29)</sup> N. Fuhrman and R. B. Mesrobian, J. Amer. Chem. Soc., 76, 3281 (1954).

K	Class	Examples'	Behavior
$\downarrow$	А		No alternating copolymerization.
0.01	В	Cyclohexene–SO₂ (0.053, <i>n</i> -heptane, 25°) <sup>a</sup> PD–MAnh (0.055, CCl₄, 25°)	Alternating copolymerization in the pres- ence of initiator.
	С	<i>cis</i> -2-Butene–SO <sub>2</sub> (0.076, <i>n</i> -heptane, $25^{\circ}$ ) <sup><i>a</i></sup> <i>trans</i> -2-Butene–SO <sub>2</sub> (0.082, <i>n</i> -heptane, $25^{\circ}$ ) <sup><i>a</i></sup> CEVE–MAnh (0.10, CCl <sub>4</sub> , $30^{\circ}$ ) DME–MAnh (0.15, CCl <sub>4</sub> , $25^{\circ}$ ) 1-Methylcyclopropene–SO <sub>2</sub> <sup><i>b</i></sup>	Spontaneous alternating copolymerization near at room temperature. (The K value decreases with increasing solvent polarity.)
1.0 ↓ 5.0	D	N-Vinylcarbazole- <i>p</i> -chloranil $(3.2 \sim 6.6, \text{ toluene } \sim \text{ acetonitrile})^{\circ}$	(Spontaneous) ionic polymerization. (The K value increases with increasing
₩	Е	N-Vinylcarbazole–SO <sub>2</sub> , $X_2^d$ 4-Vinylpyridine- <i>p</i> -chloranil (3:1 adduct) <sup><i>e</i></sup>	solvent polarity.) Formation of separable, stable complexes

TABLE VIII Classification of Charge-Transfer Polymerizations

<sup>a</sup> D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.*, **55**, 1293 (1959). <sup>b</sup> S. Iwatsuki, *et al.*, *J. Polym. Sci.*, in press. <sup>e</sup> H. Nomori, M. Hatano, and S. Kambara, *ibid.*, *Part B*, **4**, 261 (1966). <sup>d</sup> K. Tsuji, K. Takakura, M. Nishii, K. Hayashi, and S. Okamura, *ibid.*, *Part A-1*, **4**, 2028 (1966). <sup>e</sup> H. Nomori, S. Ikeda, S. Kambara, and M. Hatano, 16th Symposium of the Polymer Society of Japan, Fukuoka, IB 05, 1967. <sup>f</sup> Inside the parentheses, equilibrium constant, solvent, and temperature are shown in that order.

of the van der Waals and the charge-transfer forces.<sup>30</sup> In cases of such systems having very small values of K, many problems remain to be solved.

Finally, according to our present knowledge it is possible to make a tentative classification of charge-transfer polymerizations as shown in Table VIII. By measuring the value of K, the mode of polymerization of the system can be predicted from such a classification, and *vice versa*.

As mentioned above, the complex mechanism theory

(30) T. Matsuo and O. Higuchi, Bull. Chem. Soc. Jap., 41, 518 (1968).

can be explained without any apparent remarkable inconsistencies. Furthermore, products of the monomer (complex) reactivity ratios,  $r_1r_2$ , do not exceed unity as shown in Table V, and thus may suggest the usual free-radical copolymerization. But as to the mode of rearrangement of the complex to radicals, the question whether it is biradicals or monoradicals, and other many problems remain to be solved. These questions will be clarified eventually by investigations of the complex itself and of the polymerizations. We have obtained some kinetic data to obtain additional support for the complex mechanism theory and will report these results in another publication.

# The Efficiency of Phloroglucinol as a Trifunctional Branching Agent in Carbonate Copolymers

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ABSTRACT: Phloroglucinol is found to yield slightly less than three-fourths the maximum possible number of trifunctional branch points during the preparation of copolymers by solution condensations of bisphenol-A and phloroglucinol with phosgene in a methylene chloride-pyridine medium. This branching efficiency was determined by applying a recently developed correlation between the solution viscosities and weight-average molecular weights of randomly branched, polydisperse polymers to  $[\eta]$  and  $\overline{M}_w$  (by light scattering) data on six carbonate copolymers of phloroglucinol and bisphenol-A.

A method of evaluating the extent of branching in a polydisperse copolymer containing randomly distributed trifunctional branch points has been published recently.<sup>1</sup> The method was developed particu-(1) A. R. Shultz, J. Polym. Sci., Part A, 3, 4211 (1965).

larly for a copolymer formed by the random condensation of bifunctional and trifunctional reactants bearing functional group A with a bifunctional reactant bearing functional group B. This evaluation procedure is here applied to determine trifunctional branching