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# Copolymerization of 2-Phenyl-4-methylene-1,3-dioxolane with Methyl Methacrylate and Acrylonitrile

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# COPOLYMERIZATION OF 2-PHENYL-4-METHYLENE-1,3-DIOXOLANE WITH METHYL METHACRYLATE AND ACRYLONITRILE

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## ABSTRACT

The copolymerization of 2-phenyl-4-methylene-1,3-dioxolane (PMDO) with acrylonitrile (AN) or with methyl methacrylate (MMA) gives rise to a copolymer spontaneously or in the presence of radical initiator. Higher yield of copolymers can be got in the presence of radical initiator. The structures of the obtained copolymers, confirmed by IR, $^1$H-, and $^{13}$C-NMR spectra, indicate that no ring-opening polymerization of PMDO takes place during copolymerization with AN or MMA. PMDO would not copolymerize with styrene (ST). During copolymerization, the formation of weak charge-transfer (CT) complexes with a mole ratio of unity for PMDO-AN and with more than unity for PMDO-MMA was demonstrated by NMR. The determination of their equilibrium constants ($K$) and $\Delta^A_{comp}$ was attempted by using the Hanna-Ashbough equation with NMR spectroscopy. Based on the different $\Delta^A_{comp}$ values and chemical shifts of the accepter protons in the complex, the structural peculiarities of complexes are discussed. The contribution of the dative structure

to the CT complex was assumed to affect the reactivity of CT complex monomer.

## INTRODUCTION

It has been demonstrated that 2-phenyl-4-methylene-1,3-dioxolane (PMDO) can undergo free-radical ring-opening polymerization in the presence of radical initiators [1]. In contrast, 4-methylene-1,3-dioxolane and its aliphatic substituted derivatives are essentially inert to radical initiators [2-4], for only cationic polymerization had been reported in the literature [2-5] which describes several homo- and copolymerization systems and practical applications of the copolymers obtained. It has been shown that 4-methylene-1,3-dioxolane and 2,2-dimethyl-4-methylene-1,3-dioxolane copolymerize spontaneously with maleic anhydride on the participation of charge transfer (CT) complexes to give alternating copolymers by vinyl-type polymerization [6]. Thus, it is expected that PMDO should behave as an electron-donor monomer when it is copolymerized with MMA or AN, which are known as electron-acceptor monomers, although the *e* values of the two monomers are less than that of maleic anhydride. It would be interesting to study the chemical shifts of different protons in the same acceptor since these protons have different electron environments in the complex, and to determine the effect of the strength of the CT complex on the reactivity in copolymerization. This article deals with CT interaction and the copolymerization of PMDO with MMA and AN with or without free-radical initiators.

## EXPERIMENTAL

### Materials

Vinyl monomers and radical initiators were purified in the usual manner. 2-Phenyl-4-methylene-1,3-dioxolane (PMDO) was prepared according to our previous work [1]. THF was distilled over $CaH_2$, then over metallic sodium and benzophenone. The other reagents and solvents were reagent grade.

### Copolymerization Procedure

In the spontaneous copolymerizations, two monomers (each 0.01 mol) and 4 mL THF were placed in a test tube with a stopper, then kept in an air atmosphere at room temperature (15°C) for 72 h. In the copolymerization initiated by AIBN or DTBP, two monomers (each 0.01 mol) and 2 mol% of free-radical initiators were put in a sealed tube. After copolymerization, the copolymers were purified by pouring the reaction mixture in chloroform into *n*-hexane while stirring to precipitate white powdery copolymers. The copolymers obtained were dried *in vacuo* at 40°C for 24 h, and then identified by IR as well as $^1$H-, and $^{13}$C-NMR spectra.

### Studies of CT Complexes

Proton nuclear magnetic resonance studies of the CT complexes between PMDO and MMA or AN were done on a Varian EM-360 spectrometer with $CCl_4$ as solvent. The chemical shifts of MMA and AN in the complexing media were measured under the following conditions: the total concentration of the acceptor (MMA or AN) and donor (PMDO) was 0.25 mol/L; the mole ratio was 1:1; TMS was used as the internal standard. For the investigation of CT complexes by the Hanna-Ashbough method, the concentrations of MMA and AN were kept constant at 0.0375 and 0.064 mol/L, respectively, whereas that of PMDO varied from 1.2 to 5.2 mol/L. Ethylene dichloride was used as the internal standard.

## RESULTS AND DISCUSSION

### Structures of Copolymers

Three commercial monomers–styrene, MMA, and AN–were chosen as comonomers for the investigation of copolymerization with PMDO. The results are listed in Table 1.

In the copolymerization of PMDO with styrene, only homopolymerization of styrene took place, as ascertained by analyzing the IR, $^1$H-, and $^{13}$C-NMR spectra of the polymer. This can be explained by noting that the benzyl radical of styrene is too unreactive to add to the unreactive PMDO monomer.

The copolymers PMDO-MMA and PMDO-AN were obtained by either spontaneous or radical-initiated copolymerization. This can be verified by their IR spectra. The IR spectrum of the copolymer PMDO-MMA shows an absorption band at 1715 cm$^{-1}$, corresponding to the ester group; and bands at 700 and 750 cm$^{-1}$, corresponding to the monosubstituted phenyl group. In the IR spectrum of the copolymer PMDO-AN, the absorption bands at 2400 cm$^{-1}$ (–CN), at 1060 and 1080 cm$^{-1}$ (–C–O–), and at 700 and 750 cm$^{-1}$ (–$\phi$) indicate the existence of both monomer units in the copolymer. The $^{13}$C-NMR spectra of these copolymers indicate that PMDO really copolymerizes

TABLE 1. Copolymerization of PMDO with Various Comonomers

| Comonomer | Initiator (mol%) | Solvent (mL) | $T$, °C | $t$, h | Yield, % | PMDO/comonomer in feed, mole ratio | PMDO in copolymer,[c] mol% | $\bar{M}_n$[d] |
|---|---|---|---|---|---|---|---|---|
| ST[a] | AIBN (2) | Bulk | 55 | 30 | 37 | 1:1 | – | – |
| ST[a] | DTBP (2) | Bulk | 115 | 30 | 35 | 1:1 | – | – |
| MMA | AIBN (2) | Bulk | 55 | 8 | 36 | 1:1 | 20 | 8049 |
| MMA[b] | – | THF (4) | 15 | 84 | 4 | 1:1 | 12 | 2962 |
| AN | AIBN (2) | Bulk | 55 | 8 | 83 | 1:1 | 35 | 5729 |
| AN[b] | – | THF (4) | 50 | 7 | 2 | 1:1 | – | 1777 |
| AN[b] | – | THF (4) | 15 | 84 | 5 | 1:1 | 37 | 1731 |

[a] No copolymer was formed.

[b] Spontaneous copolymerization in the absence of initiator.

[c] Obtained from the $^1$H-NMR spectra.

[d] Measured with a Corona 117 VPO Molecular Weight Apparatus, acetone as solvent.

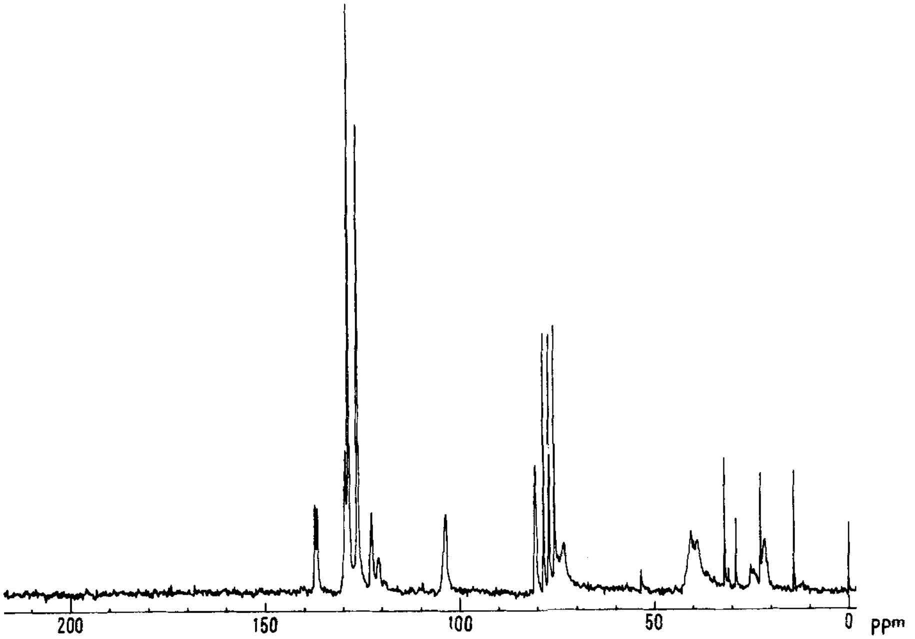
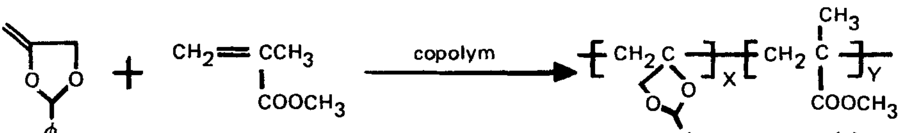


FIG. 1. $^{13}$C-NMR spectrum of PMDO-AN copolymer initiated by AIBN at 55°C in bulk.

with AN and MMA. In the $^{13}$C-NMR spectrum of PMDO homopolymer, the chemical shift of vinylidene carbon attached to the oxygen is 77.94 ppm, whereas the corresponding carbons of PMDO-AN (Fig. 1) and PMDO-MMA (Fig. 2) shift to 80.68 and 82.83 ppm, respectively. The absence of a peak at 207 ppm in the spectra of these two copolymers (Figs. 1 and 2) indicates that PMDO does not undergo ring-opening polymerization; only the addition of units of PMDO occurs in copolymers.

From above discussion, the copolymers apparently have the following structures:



$$\text{PMDO} + CH_2{=}\underset{COOCH_3}{CCH_3} \xrightarrow{\text{copolym}} \left[CH_2C\right]_x\left[CH_2\underset{COOCH_3}{\overset{CH_3}{C}}\right]_Y$$

(1)

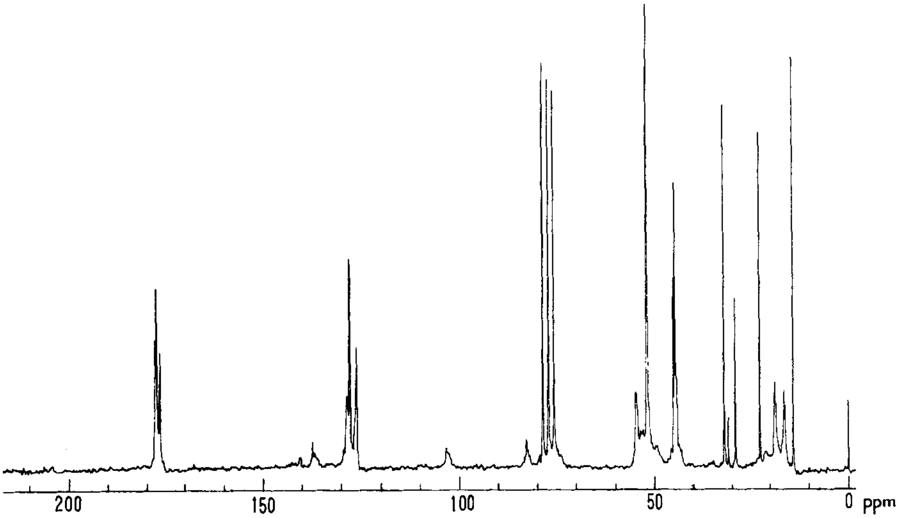
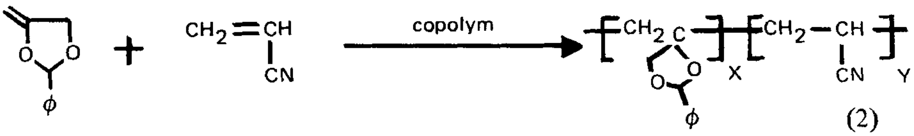


FIG. 2. $^{13}$C-NMR spectrum of PMDO-MMA copolymer initiated by AIBN at 55°C in bulk.



(2)

It is of interest to calculate the relative amount of PMDO units in the copolymers. The $^{1}$H-NMR spectrum of copolymer PMDO-MMA (Fig. 3) shows an absorption peak at 7.0-7.6 ppm, corresponding to phenyl protons of PMDO, and another peak at 4.0-3.0 ppm, corresponding to two kinds of protons: methyl protons attached to the oxygen of MMA and methylene protons next to the oxygen of PMDO. Similarly, in the $^{1}$H-NMR spectrum of copolymer PMDO-AN (Fig. 4) there is an absorption peak at 7.0-7.7 ppm, belonging to the phenyl protons of PMDO, and a peak at 2.6-3.3 ppm, corresponding to the methine proton of AN. The composition values $x$ and $y$ can therefore be calculated from the $^{1}$H-NMR integrations (Table 1). These results indicate that AN has a stronger tendency to alternating copolymerization with PMDO than has MMA.

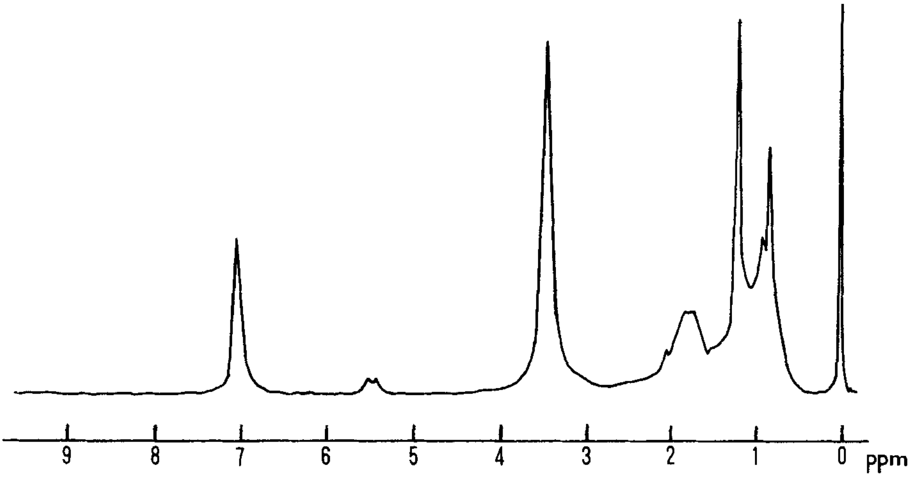


FIG. 3. ${}^1$H-NMR spectrum of PMDO-MMA copolymer obtained by spontaneous copolymerization.

### Studies of CT Complexes

It was suggested that copolymerization of unsaturated spiro-*o*-esters [7, 8] or unsaturated 1,3-dioxolanes [6] as electron donor with MA as acceptor can be attributed to the formation of charge-transfer (CT) complexes and that the radicals created initiate copolymerization [7]. The CT complexes can be detected by UV and NMR spectroscopies.

The fact that no obvious absorption band of CT complexes was found during the UV measurements of PMDO-MMA and PMDO-AN indicates there is very weak interaction between PMDO and MMA or AN. Thus the ${}^1$H-NMR method was used to obtain evidence for the formation of CT complexes. The total concentration of PMDO-AN or PMDO-MMA (mole ratio 1:1) systems is 0.25 mol/L. TMS and $CCl_4$ were used as the internal standard and the solvent, respectively. The results are listed in Table 2.

The fact that the protons of the three monomers had different chemical shifts in the complexing medium and in pure solution indicates that there are interactions between PMDO and AN or MMA [9]. According to the general assumption of CT complexing, acceptor protons should shift upfield and donor protons downfield [10]. This phenomenon happened in the PMDO-AN system,

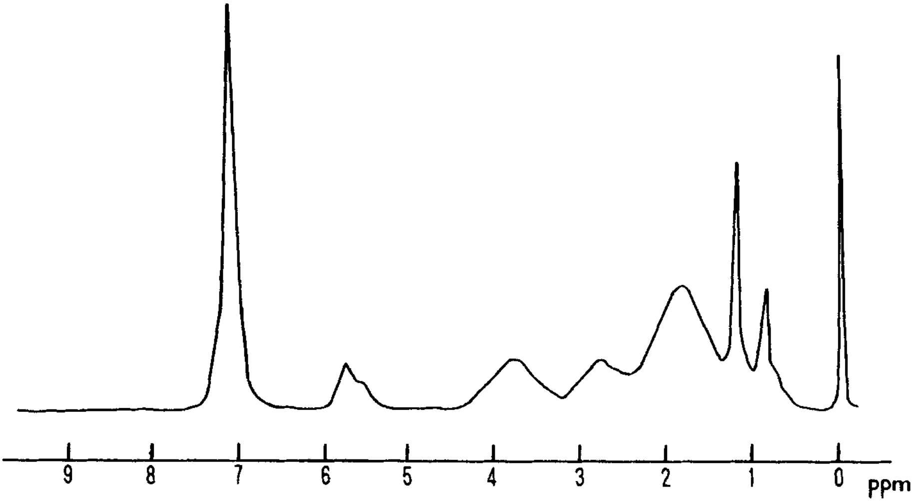


FIG. 4. $^1$H-NMR spectrum of PMDO-AN copolymer obtained by spontaneous copolymerization.

but in the PMDO-MMA system the protons in both PMDO and MMA shifted downfield, which indicates that the complex between PMDO and MMA is not the normal CT complex.

In order to determine the composition of the complex and the equilibrium constant, the Hanna-Ashbough method was used. When the ratio of donor to acceptor in the complex is 1:1, the following equation is valid [11]:

$$\frac{1}{\Delta_{\text{obs}}^{\text{A}}} = \frac{1}{K\Delta_{\text{comp}}^{\text{A}}[D]} + \frac{1}{\Delta_{\text{comp}}^{\text{A}}}, \tag{3}$$

where $\Delta_{\text{obs}}^{\text{A}}$ $(\delta_{\text{obs}}^{\text{A}} - \delta_0^{\text{A}})$ is the difference between the chemical shifts of the acceptor protons in a complexing medium $(\delta_{\text{obs}}^{\text{A}})$ and a noncomplexing medium $(\delta_0^{\text{A}})$, $\Delta_{\text{comp}}^{\text{A}}(\delta_{\text{comp}}^{\text{A}} - \delta_0^{\text{A}})$ is the difference between the chemical shifts of the pure complex $(\delta_{\text{comp}}^{\text{A}})$ and $\delta_0^{\text{A}}$, $D$ is the concentration of donor, and $K$ is the equilibrium constant. Obviously, plot of $1/\Delta_{\text{obs}}^{\text{A}}$ against $1/D$ should be linear, and $K$ may be calculated from the slope by using $\Delta_{\text{comp}}^{\text{A}}$ obtained from the intercept of the line.

In our experiments the concentrations of MMA and AN were kept constant at 0.0375 and 0.0643 mol/L, respectively, while that of PMDO was varied from 1.2 to 5.2 mol/L using $CCl_4$ as the solvent and $CH_2Cl_2$ as the internal reference. By plotting the $1/\Delta_{\text{obs}}^{\text{A}}$ of different protons of the same acceptor against $1/[D]$, straight lines (except $H_a$ of MMA) were obtained, as shown in Figs. 5 and 6. The values of $\Delta_{\text{comp}}^{\text{A}}$ and $K$ so obtained are listed in Table 3.

For PMDO-AN, the chemical shifts of all protons in AN shift upfield as the concentration of PMDO increases. The linearity of the plots (see Fig. 6) indicates that the stoichiometry of the CT complex is 1:1. Because of the different electron environment of each proton of AN in its complex, $\Delta_{\text{comp}}^{\text{A}}$ is quite different for each one. However, the equilibrium constant obtained by plotting different protons is quite similar (Table 3). For PMDO-MMA, the absence of linearity of the plots (Fig. 5) indicates that the stoichiometry of the PMDO-MMA complex is not 1:1. Since the linearity for $H_b$ and $H_c$ is also not very satisfactory (Fig. 5), their $K$ values are not consistent with each other (Table 3). When the concentration of PMDO was much greater than that of MMA at the start, $H_a$ shifted upfield, then downfield with increasing PMDO concentration. This phenomenon can be explained by the anisotropy effect of the benzene ring. At low concentrations of MMA in PMDO, $H_a$ is just at the top of benzene ring; thus, it is shifted upfield because of diamagnetic shielding. At high PMDO concentration, many benzene rings in other PMDO molecules surround $H_a$, and the paramagnetic shielding of benzene rings makes the chemical shift of $H_a$ increase. In the PMDO-MMA complex, the charge transfer is much weaker than that in PMDO-AN. So in the $^1$H-NMR measurement, the long-range shielding effect of electrons on both monomers is very important, which makes all protons of PMDO and MMA shift downfield.

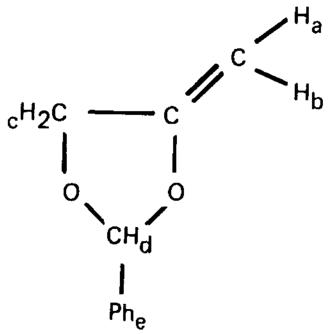
The fact that spontaneous copolymerization takes place indicates the formation of "dative" structure, which further generates radicals by a proton transfer of the dative structure [12]:

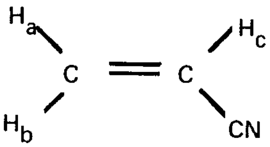
$$\text{A} + \text{D} \rightleftharpoons (\text{D}\cdot\text{A}) \longleftrightarrow (\text{D}^{+}\cdot\text{A}^{-}\cdot). \tag{4}$$

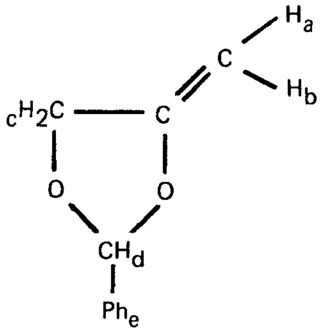
If we take into account the electron-accepting character, AN ($e = 1.20$) > MMA ($e = 0.40$), the larger $e$ value of the acceptor may cause the larger contribution of the dative structure.

Thus the greater reactivity of AN compared to MMA would be expected, and the amount of acceptor in the copolymer increases in the following order: AN (35-37%) > MMA (20-10%). Therefore, the CT complex of PMDO-AN has a stronger tendency toward alternating copolymerization than does that of PMDO-MMA.

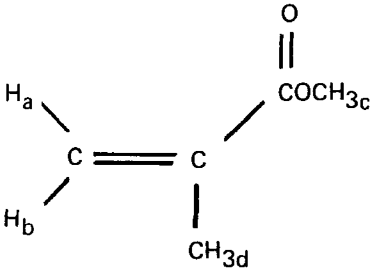
TABLE 2. Chemical Shifts of PMDO, MMA, and AN in Pure Solution and in the Complexing Medium

| Compound | | Chemical shift, Hz | | | | |
|---|---|---|---|---|---|---|
| | | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ |
|  | In pure solution | 229.4 | 257.4 | 264.0 | 357.0 | 435.2 |
| | In complexing medium | 232.0 | 258.0 | 269.0 | 359.6 | 438.0 |
| | Δ | 2.6 | 0.6 | 4.0 | 2.6 | 2.8 |

| | | $H_a$ | | | $H_b$ | | $H_c$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
|  | In pure solution | 380.2 | 378.2 | 361.4 | 365.2 | 358.2 | 348.2 | 337.2 | 331.8 | 320.8 |
| | In complexing medium | 378.6 | 376.0 | 360.0 | 361.2 | 353.0 | 344.4 | 334.0 | 328.2 | 317.6 |
| | Δ | -1.6 | -2.2 | -1.4 | -4.0 | -5.2 | -3.8 | -3.2 | -3.6 | -3.2 |



| | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ |
|---|---|---|---|---|---|
| In pure solution | 229.4 | 257.4 | 264.0 | 357.0 | 435.2 |
| In complexing medium | 233.4 | 260.2 | 269.6 | 362.8 | 422 |
| Δ | 4.0 | 2.8 | 5.6 | 5.8 | 6.8 |



| | $H_a$ | $H_b$ | $H_c$ | $H_d$ |
|---|---|---|---|---|
| In pure solution | 358.0 | 326.6 | 220.6 | 113.6 |
| In complexing medium | 362.0 | 329.4 | 223.0 | 113.4 |
| Δ | 4.0 | 2.8 | 2.4 | -0.2 |

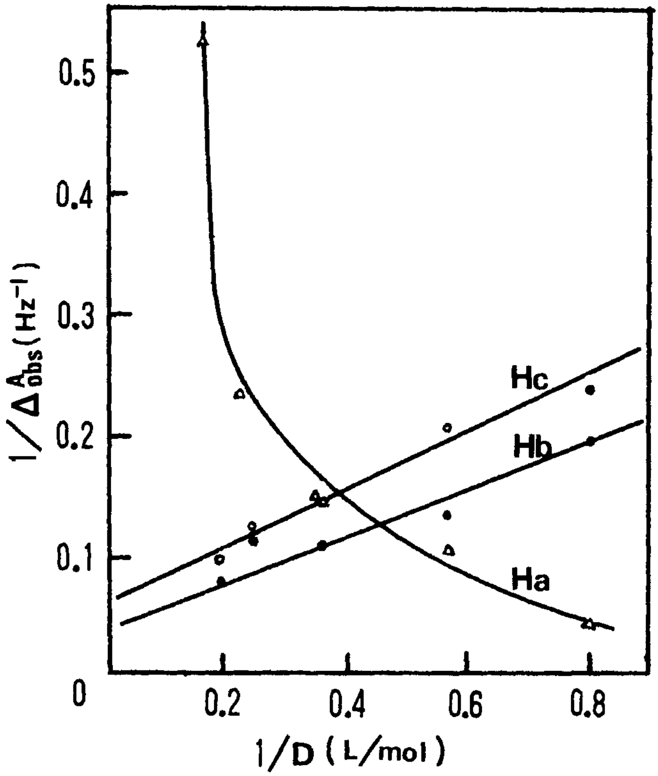


FIG. 5. Hanna-Ashbough plots: PMDO-MMA system. $1/\Delta^{A}_{obs}$ values for $H_a$ are negative.

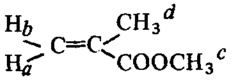

$$\underset{H_a}{\overset{H_b}{>}}C{=}C\underset{COOCH_3{}^{c}}{\overset{CH_3{}^{d}}{<}}$$

TABLE 3. Physicochemical Properties of the Complexes

| Complex | Proton traced | $\Delta^{A}_{comp}$, Hz | $K$, L/mol |
|---|---|---|---|
| PMDO-AN | $H_a$ | -27 | 0.016 |
| | $H_b$ | -16 | 0.014 |
| | $H_c$ | -18 | 0.019 |
| PMDO-MMA | $H_b$ | 31 | 0.041 |
| | $H_c$ | 18 | 0.062 |

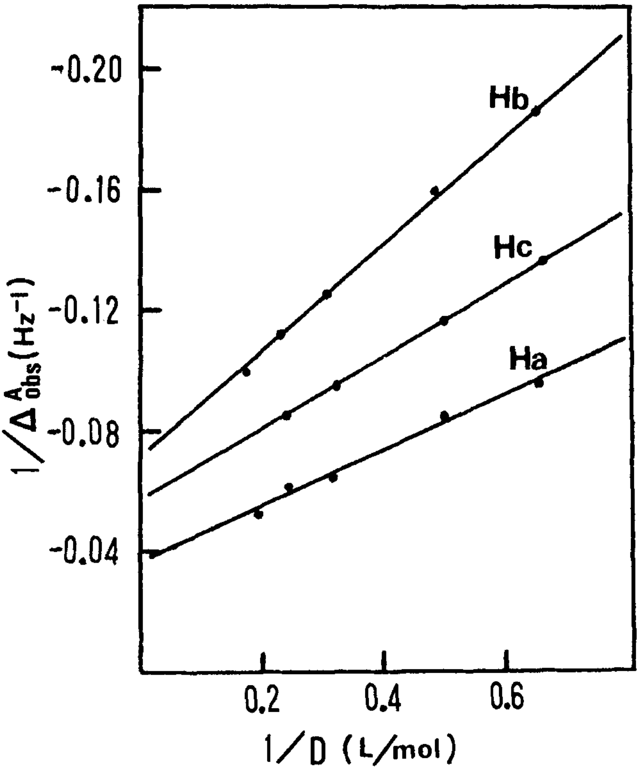
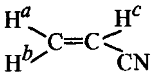


FIG. 6. Hanna-Ashbough plots: PMDO-AN system.



## REFERENCES

[1] C. Y. Pan, Z. Wu, and W. J. Bailey, *J. Polym. Sci., Polym. Lett. Ed.*, *25*, 243 (1987).

[2] W. O. Kenyon and T. F. Murray Jr., U.S. Patent 2,415,638 (1937).

[3] M. Goodman and A. Abe, *J. Polym. Sci., Part A*, *2*, 3471 (1964).

[4] H. J. Dietrich, *J. Polym. Sci., Part A-1*, *6*, 2255 (1968).

[5] M. K. Akkapeddi and H. K. Reimschuessel, *Macromolecules*, *12*, 827 (1978).

[6] H. Fukuda, M. Hirota, and Y. Nakashima, *J. Polym. Sci., Polym. Chem. Ed., 20,* 1401 (1982).
[7] H. Fukuda, M. Hirota, T. Endo, M. Okawara, and W. J. Bailey, *Ibid., 20,* 2935 (1982).
[8] Y. K. Han and S. K. Choi, *Ibid., 21,* 353 (1983).
[9] N. G. Gaylord, *J. Macromol. Sci.-Chem., A6*(2), 259 (1972).
[10] H. Hirai, *J. Polym. Sci., Macromol. Rev., 11,* 47 (1976).
[11] M. W. Hanna and A. I. Ashbough, *J. Phys. Chem., 68,* 811 (1964).
[12] N. Nagai and S. Machida, *J. Polym. Sci., Polym. Chem. Ed., 19,* 571 (1981).

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