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COPOLYMERIZATION OF METHYL METHACRYLATE WITH *N*-PHENYLMALEIMIDE IN DIFFERENT SOLVENTS*

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ABSTRACT

The copolymerization of methyl methacrylate (MMA) and *N*-phenylmaleimide (NPMI) in various solvents has been studied. It has been shown that monomer-monomer interaction exists and leads to the formation of a weak charge-transfer complex (CTC). The CTC concentration is found to depend on the type of solvent, and its equilibrium constant depends on the dielectric constant of the solvent and increases in the order DMSO < chloroform < benzene < CCl₄. NMR and dipole moment measurements have been used to investigate interaction between the monomers. The monomer reactivity ratios are found to vary appreciably with the type of solvent. The data obtained indicate that changes in the reactivity ratios are due to monomer solvation or to the solvent effect on the propagating radical, rather than to the participation of the CTC in the propagation step.

*Dedicated to Professor R. W. Lenz on his 60th birthday.

INTRODUCTION

The copolymerization of MMA with NPMI was investigated by several authors [1-3] and different reactivity ratios were reported. In these investigations, monomer-monomer interaction and solvent effects have been neglected, which could be the reason for the differences in the reported reactivity ratios.

In some cases, monomer interaction leads to the formation of a charge-transfer complex (CTC), which participates together with the free monomers in the propagation step of the copolymerization process. Solvents usually compete with the monomers in the formation of such CTC and, consequently, will affect the copolymer composition and its rate of formation.

It is the aim of this work to investigate the aforementioned types of interactions, especially when one of the monomers acts as a donor (MMA) and the other as an acceptor (NPMI) [4-6]. Their interaction in different solvents should have a strong effect on the copolymerization behavior.

EXPERIMENTAL

Materials

Methyl methacrylate was obtained from Merck and was distilled just before use. The synthesis of *N*-arylmaleimides was carried out according to the original method developed by Searle [7] (mp: *N*-phenylmaleimide (NPMI) 89°C, *N*-*p*-chlorophenylmaleimide (4CMI) 110°C).

Azobisisobutyronitrile (AIBN) was obtained from TCI, Tokyo Kasei, Japan, and it was recrystallized several times from ethanol before use.

The solvents dioxane, chloroform, and benzene (Prolabo) were purified according to standard methods. Carbon tetrachloride (Merck) and dimethylsulfoxide (BDH) were used as received. The purity was checked by refractive index measurements.

Copolymerization Procedure

Ampules of Pyrex glass were charged with the monomer mixtures, the solvent, and the initiator (AIBN). The ampules were then cooled and closed with a rubber stopper through which passed a needle for purified nitrogen bubbling. The copolymerization was carried out in a water Ultrathermostat adjusted to 60°C with periodical stirring for periods of time chosen to keep

the conversion below 10%. It was then brought to a stop by opening the glass ampules and pouring the contents into a large excess of cold ethanol. The copolymers obtained were washed repeatedly with ethanol and dried at 60°C in an air oven to constant weight. The copolymerization was homogeneous except that for CCl₄, where the copolymers precipitated during the course of reaction.

Copolymer Analysis

The copolymer compositions were calculated on the basis of nitrogen content. The analyses were performed at the Central Microanalytical Unit, Cairo University.

Spectral Measurements

The UV spectra were measured with a Perkin-Elmer, Lambda 3 spectrophotometer. ¹H-NMR spectra were recorded on a PMX-60 spectrometer (Japan Electron Optics Laboratory). The NMR tube was connected to a vacuum line after being filled with the proper amounts of the monomers, solvent, and TMS (as internal standard). The tube was then frozen with liquid nitrogen, evacuated, and sealed before the measurement. Stock solution of 4CMI in the proper solvent together with TMS was used to prepare different solutions with increasing amounts of MMA.

Dipole Moment Measurements

The static dielectric constant ϵ_0 was measured at 2 MHz with a dipolemeter DMO1 (from WTW) to an accuracy better than $\pm 0.5\%$. The refractive index n_D was measured with an Abbé refractometer (from Carl Zeiss, Jena, Model G) to an accuracy of $\pm 10^{-4}$. The measurements were carried out for dilute solutions of MMA and NPMI in benzene and CCl₄. Three concentrations between 0.005 and 0.01 mole fraction were used. All these measurements were taken at different temperatures ranging from 20 to 40°C with the aid of an Ultrathermostat.

RESULTS AND DISCUSSION

In order to study the copolymerization behavior of the system MMA and *N*-arylmaleimides, it was necessary to investigate the extent of their interaction in solution. UV and NMR spectroscopy together with dipole moment measure-

ments were used for this purpose. No coloration was observed on mixing MMA with NPMI or 4CMI. The UV spectra of different molar ratios of these two monomers in CCl_4 , chloroform, or dioxane revealed no new independent bands and no increase in the optical density. The Benesi-Hildebrand [8] method for the determination of the equilibrium constant of the expected CTC by UV was thus inapplicable. It has been shown [9, 10] that *N*-substituted maleimides experience a large upfield chemical shift in benzene solvent, and this was attributed to the association of solute and solvent molecules. In the present study the chemical shifts of the olefinic proton of 4CMI or NPMI appeared at δ (CDCl_3) 6.84, δ (benzene) 5.7, and δ (DMF) 7.14. These data indicate a strong effect of the solvents on the protons of the double bond and, consequently, on the reactivity of the monomer.

To determine the equilibrium constant of the CTC between MMA and 4CMI in 4 different solvents, the chemical shift of the olefinic protons was monitored as a function of the MMA concentration.

The lines of Fig. 1 were plotted according to the equation [11]:

$$1/C_D = (1/\Delta_o) K \Delta_c - K, \quad (1)$$

where C_D represents the molar concentration of the donor (here the MMA), and K is the equilibrium constant, $\Delta_o = \delta_{fr}^A - \delta_o^A$, $\Delta_c = \delta_{fr}^A - \delta_c^A$, where δ_{fr}^A is the chemical shift of the free 4CMI or NPMI, δ_o^A is the observed chemical shift based on the 4CMI, and δ_c^A is the chemical shift of the complexed 4CMI. The obtained values of K are summarized in Table 1. Since the use of the phenyl protons led to negative values of K , the calculations were carried out only for the olefinic protons.

The interaction between MMA and 4CMI may be through the oxygen atom of the carbonyl group of MMA to the imide ring with the CO bond normal to the ring plane, which could explain the low field shift in terms of bond anisotropy theory.

From Table 1 it can be noticed that there is a correlation between K and the dielectric constant of the solvents, as has been reported by many investigators [12-14]. High values of K mean higher concentration of the CTC in the given solvent and, consequently, higher contribution in the copolymerization process. The concentration of the CTC can be readily obtained by using the equation derived by Braun et al. [15].

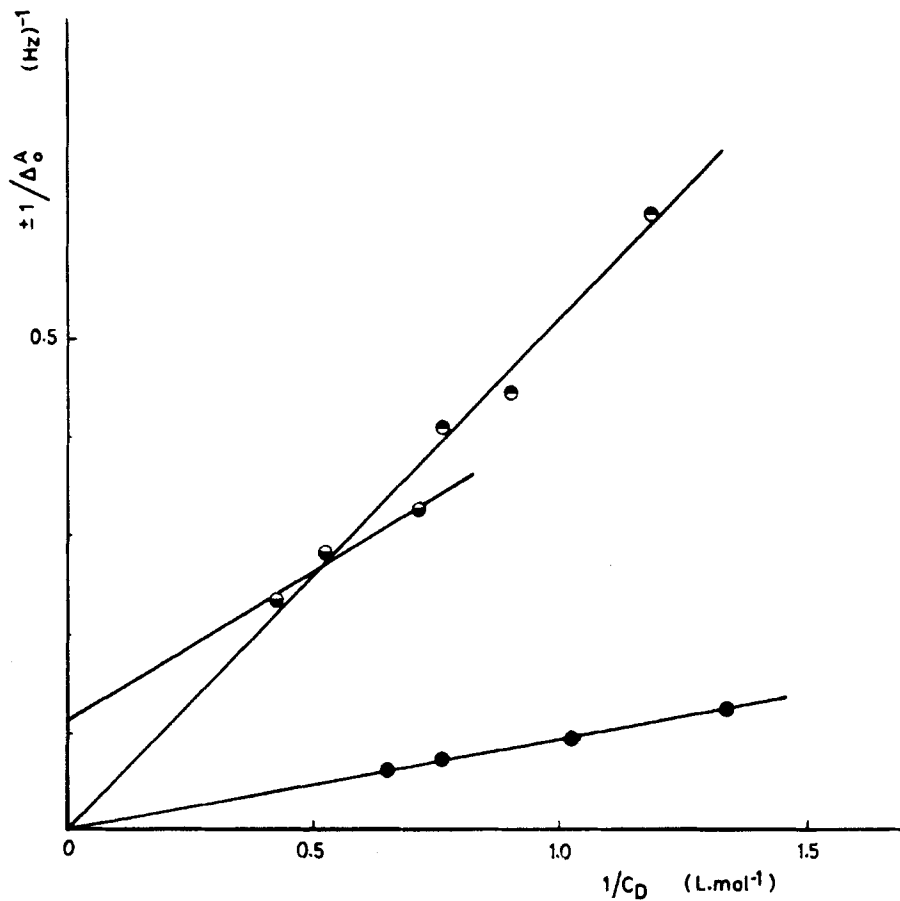


FIG. 1. Plot of $1/\Delta_0^A$ versus $1/C_D$: (○) CCl_4 , (◐) chloroform, (●) benzene.

Dipole Moment Measurements

The dipole moments μ of MMA and NPMI in different nonpolar solvents and at different temperatures are calculated by the following equation [16] and are given in Table 2,

TABLE 1. Equilibrium Constants of the MMA-NPMI Charge-Transfer Complex in Different Solvents

Solvent	K , L/mol	Dielectric constant, ^a ϵ
CCl_4	0.3730	2.238
C_6D_6	0.0394	2.284
CDCl_3	0.0050	4.806
$\text{DMSO-}d_6$	0.0	46.68

^aAt 20°C.

$$\mu^2 = \frac{27kTM}{4\pi Nd} \frac{(\Delta\epsilon_0 - \Delta n^2)x}{(\epsilon_s + 2)^2}, \quad (2)$$

where M , d , n and ϵ_0 are the molecular weight, density, refractive index, and dielectric constant of the solvent, respectively. N is Avogadro's number, k is the Boltzmann constant, and T is the absolute temperature.

The dipole moments of NPMI and MMA are in good agreement with the values given in the literature [17, 18]. From Table 2 it can be seen that the dipole moment is slightly solvent dependent. The measurements also revealed that the temperature has no effect within the range investigated. The solvent dependence reflects some sort of solute-solvent interaction.

In order to study the association between MMA and NPMI, three compositions (3:1, 1:1, and 1:3) of the two components in benzene and CCl_4 were

TABLE 2. Dipole Moments of MMA and NPMI

Compound	Solvent	μ , ^a Debye
MMA	Benzene	1.75
	CCl_4	1.78
NPMI	Benzene	1.39
	CCl_4	1.26

^aAveraged over three temperatures: 20, 30, and 40°C.

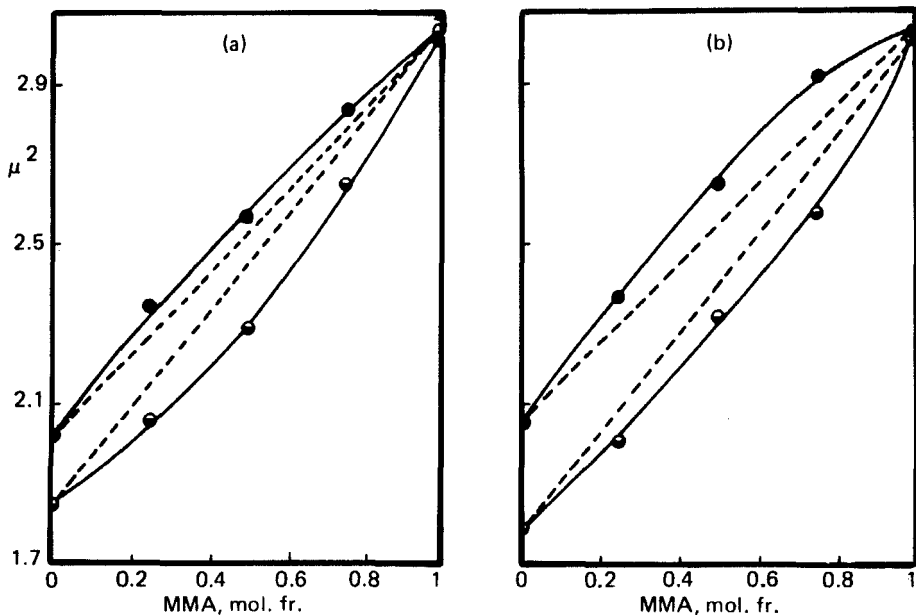


FIG. 2. Dipole moment versus composition for MMA-NPMI mixtures in (●) benzene and in (○) CCl_4 ; (a) 20°C , (b) 40°C , total monomer concentration 0.01 mole fraction.

prepared. The dipole moments are plotted versus the composition in Fig. 2. It can be noticed that the points do not lie on a straight line within the permissible error (0.5%). In other words, the measured values do not fit those calculated from the sum of the two components of $x_1\mu_1^2$ and $x_2\mu_2^2$, where x is the mole fraction and μ is its measured dipole moment. This deviation is attributed to the association of MMA with NPMI in both solvents. The dipole moments of the monomer mixture in CCl_4 are lower than the calculated values while, in benzene, they are higher. This means that the stronger association between those two components in CCl_4 leads to a decrease of the dipole moment of their mixture, probably due to an antiparallel dipole-dipole orientation. In benzene, however, the competition between the solvent and MMA to associate with the NPMI alters the orientation and leads to values slightly higher than the calculated ones.

TABLE 3. Copolymerization Data for the NPMI (M_1)-MMA (M_2) System in Different Solvents at 60°C^a

No.	Monomer composition, M_1 , mol%	Copolymer composition, m_1 , mol%				
		Dioxane	CCl ₄	Benzene	Chloroform	DMSO
1	5	7.9	10.5	3.8	13.2	3.8
2	10	13.6	19.3	7.1	23.8	8.8
3	20	23.9	31.3	15.9	34.8	16.8
4	30	31.3	38.4	21.7	40.9	23.3
5	40	38.4	48.9	28.0	44.8	29.1
6	50	41.6	54.6	36.0	50.3	36.0
7	60	46.1	62.2	42.2	56.1	42.2
8	70	51.0	68.8	50.3	59.8	48.9
9	80	55.3	78.5	60.6	66.2	57.6
10	90	69.6	87.2	75.8	77.6	70.5

^aTotal monomer concentration [M], 2 mol/L; [AIBN], 10 mol/L; except 20 mmol/L for CCl₄.

TABLE 4. Apparent Reactivity Ratios and Q - e Values for NPMI (M_1) and MMA (M_2)^a in Different Solvents (average values from the F-R and K-T methods)

Solvent	r_1	r_2	e_1	Q_1	ϵ
Dioxane	0.1446	0.6110	1.9577	2.3804	2.209
CCl ₄	0.6967	0.3866	1.5453	3.1900	2.238
Benzene	0.2750	1.3205	1.4065	0.8835	2.284
Chloroform	0.2862	0.2705	1.9995	5.4676	4.806
DMSO	0.1924	1.1367	1.6329	1.1236	46.680

^a $e_{\text{MMA}} = e_2 = 0.4 \pm 0.08$; $Q_{\text{MMA}} = Q_2 = 0.78 \pm 0.06$ [21].

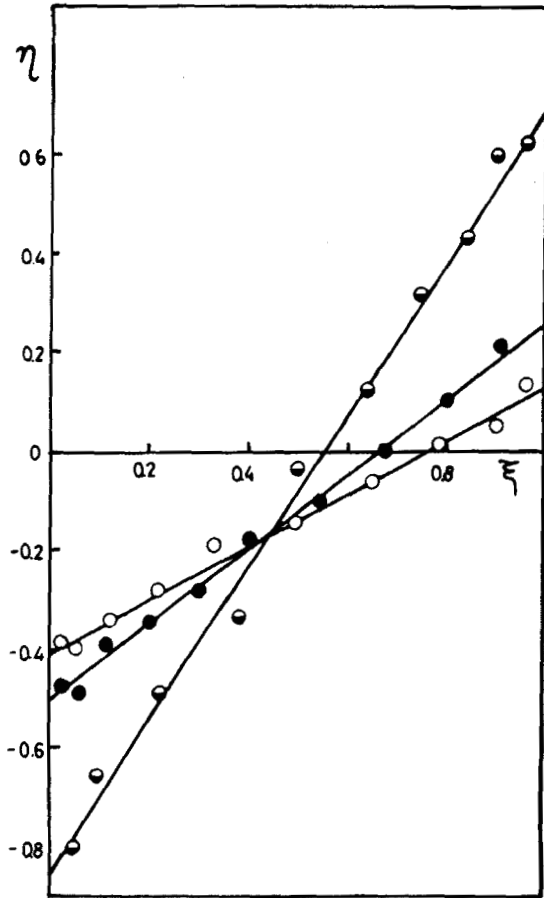


FIG. 4. Kelen-Tüdös plots for NPMI (M_1)-MMA (M_2) in (○) dioxane, (◐) CCl_4 , and (●) benzene.

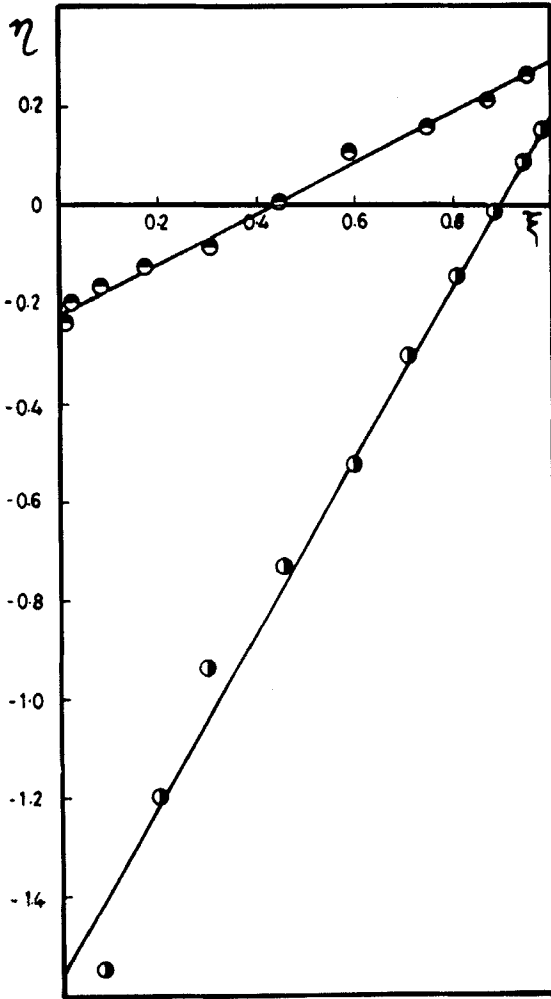


FIG. 5. Kelen-Tüdös plots for NPMI-MMA in (●) chloroform and (○) DMSO.

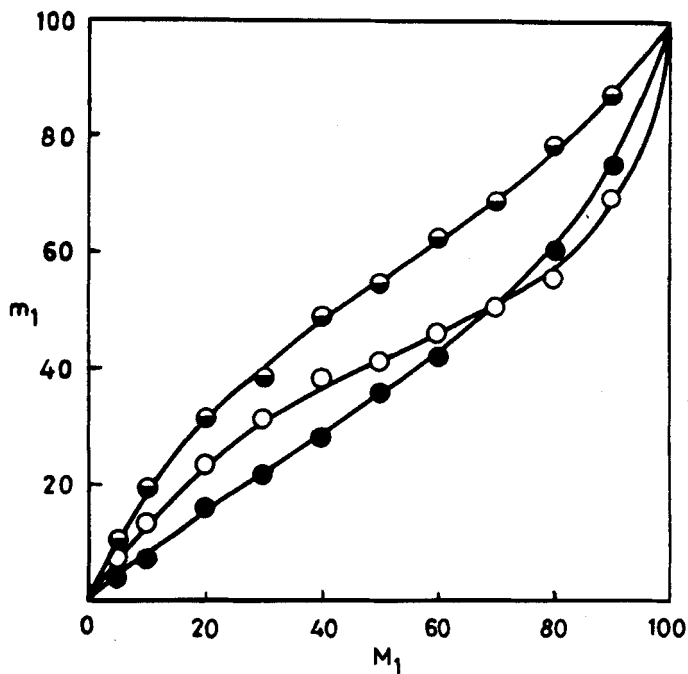


FIG. 6. Copolymer composition diagrams for NPMI-MMA in different solvents at 60°C with AIBN as initiator. Curves calculated from the reactivity ratios from Table 4. Points are experimental: (○) dioxane, (⊙) CCl₄, and (●) benzene.

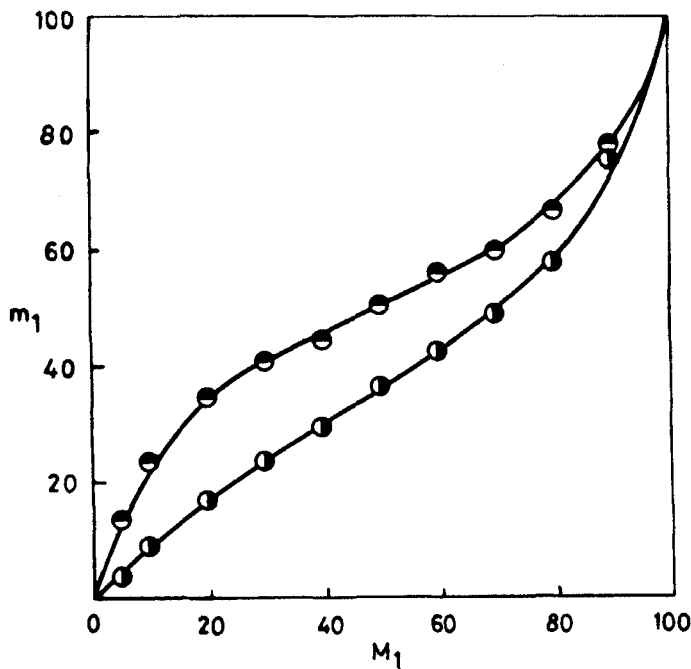


FIG. 7. The same as in Fig. 6: (●) chloroform and (○) DMSO.

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