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Electron Donor Acceptor Complexes and Copolymerization Behavior of Oxazole and Thiazole with Maleic Anhydride. A Comparison with Other Five-Membered Heterocyclic Donors

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ABSTRACT

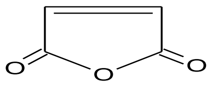
The electron donor-acceptor (EDA) complexes of oxazole (OX) and thiazole (THZ) with maleic anhydride (MAH) were detected and characterized. Radical copolymerization of OX-MAH gave nearly an alternating copolymer, while THZ-MAH gave mainly poly (MAH). EDA complexation parameters and copolymerization reactivities of MAH with various one and two heteroatom five-membered heterocycles were compared and correlated with the physicochemical properties of the heterocycles. Polymerization behavior seemed to be determined by EDA complexation, aromaticity, activity, and basicity of the heterocycle.

INTRODUCTION

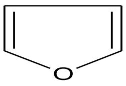
Electron donor-acceptor (EDA) complexes (sometimes called charge-transfer complexes) are formed by the weak interaction of electron donor and electron acceptor molecules(Foster,1969). These complexes show spectroscopic, and physicochemical properties (Mulliken, 1969). Donor-acceptor copolymers are being recently investigated for their optical, electrochemical, and photovoltaic properties. For example, porphyrin- furan and porphyrin-thiophene alternating copolymers were synthesized and investigated for their photophysical and photovoltaic properties (Umeyama et al.,2009). Polythiophene and polypyrrole- based copolymers were studied as conducting polymers (Berlin et al.,2008). Pyridopyrazine-based copolymers were synthesized and their photophysical and electrochemical properties were characterized (Wu et al., 2008).

Alternating copolymers were extensively studied with respect to the role of their donor and acceptor monomers in copolymer formation (Rzaev, 2000). Many of these alternating copolymers involved heterocyclic donor monomers such as furan (Ragab and Butler, 1981), and thiophene (Elmahi,1997) with the acceptor monomer maleic anhydride; or vinyl donor monomers with N-substitutedmaleimides acceptors (Zhang et al., 2006) .

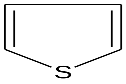
Maleic anhydride (MAH) was shown to form electron donor-acceptor (EDA) complexes with the five-membered heterocyclic donors containing one heteroatom: furan (F) (Butler et al., 1970 and Yoshida and Kobayashi, 1970), thiophene (TH) (Yoshida and Kobayashi, 1970), and pyrrole (PR) (Ragab, 1991).



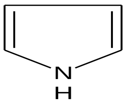
MAH



F



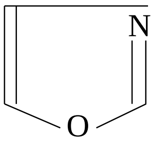
TH



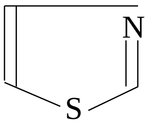
PR

MAH also forms alternating copolymers with the above donors (Gaylord et al., 1972; Ragab and Butler, 1981; and Cardon and Geothals, 1971) and their benzoderivatives (Geothals et al. 1973) by radical initiation. However, PR does not copolymerize with MAH (Ragab,1991).

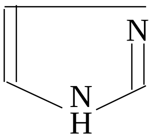
In the present work heterocyclic donors with two heteroatoms will be studied with respect to their EDA complexation and copolymerization behavior with MAH. These include oxazole (OX), thiazole (THZ), and imidazole (IMD).



OX



THZ



IMD

A comparative study will be presented involving one and two heteroatom heterocycles with respect to various parameters related to EDA complexation and copolymerization behavior with MAH.

EXPERIMENTAL

Materials

MAH was recrystallized twice from benzene or sublimed before use. OX and THZ were obtained from Aldrich and were usually distilled before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Benzene was dried by shaking three times with conc. sulfuric acid followed by distillation. Dichloromethane was dried over calcium hydride, distilled, then stored over calcium hydride.

Copolymerization

Copolymerizations were run under a nitrogen atmosphere in tightly sealed bottles; or in glass ampoules degassed three times via the freeze-thaw cycles. Copolymerizations were performed in benzene or dichloromethane as solvents; using AIBN initiator; at 60^{o}C.The polymeric products precipitated in the reaction mixture; they were collected, washed thoroughly with hot benzene or toluene, followed by diethyl ether .They were dried under reduced pressure at about 50^{o}C.

Instrumentation

IR spectra were recorded on a Shimadzu IR 435 instrument using KBr discs. UV spectra were recorded on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer using 1 cm quartz cells and spectrograde chloroform as a solvent. Reduced viscosity was determined at 30^{o}C in dimethyl sulfoxide using a Cannon – Fenske viscometer. Elemental analysis was performed by

Atlantic Microlab, Inc. or by the Analytical Services, Department of Chemistry, University of Florida.

NMR spectra were run either on a Varian XL-200 or VXR-300 spectrometers using tetramethylsilane (TMS) as an internal reference. Association constant values determined by the NMR method (K_{nmr}) were performed using the Varian VXR-300 spectrometer in chloroform-d. Temperature was controlled to within ±0.01°C of the desired degree. Samples were contained in 5 mm OD tubes and were allowed to equilibrate before acquisition was started. Freshly prepared solutions were used.

RESULTS

Detection and Characterization of EDA Complexes:

An enhanced absorption in the UV was observed on mixing OX and MAH which cannot be ascribed to either of the two compounds (Fig.1). Addition of OX caused a downfield shift in the NMR resonance of MAH protons.

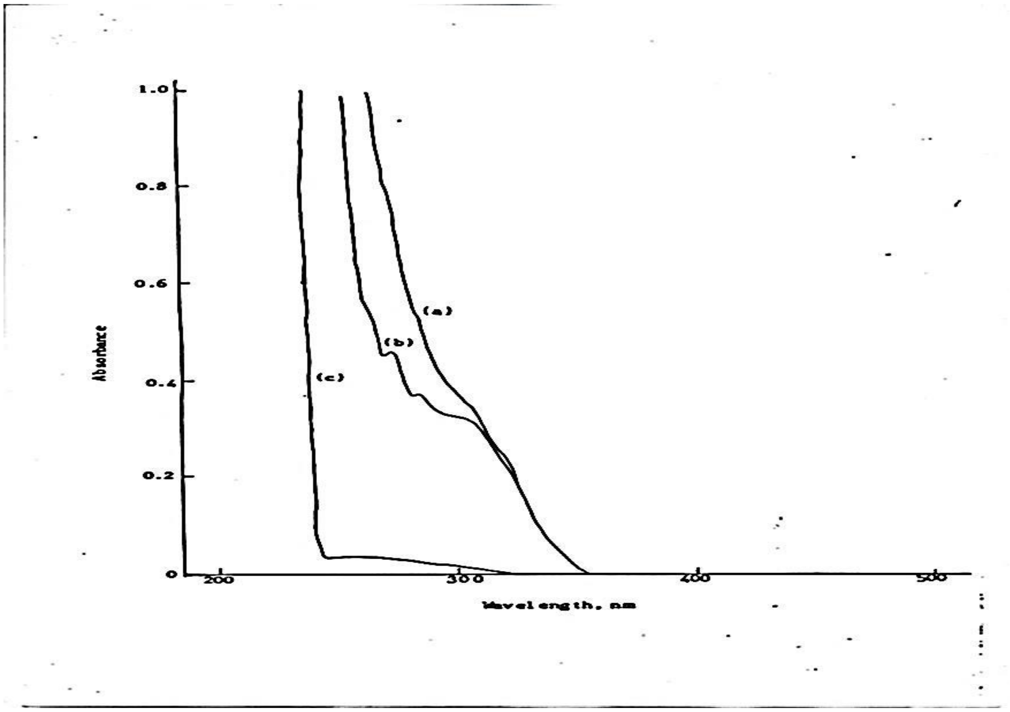


Figure 1. absorption of OX-MAH EDA complex: (a) mixture of 0.5M OX and 0.02M MAH; (b) 0.2M MAH; (c) 0.5M OX.

A yellow color was observed on mixing THZ and MAH as well as on enhanced absorption in the UV (Fig. 2). An upfield shift in the NMR resonance of MAH protons was caused by the addition of THZ.

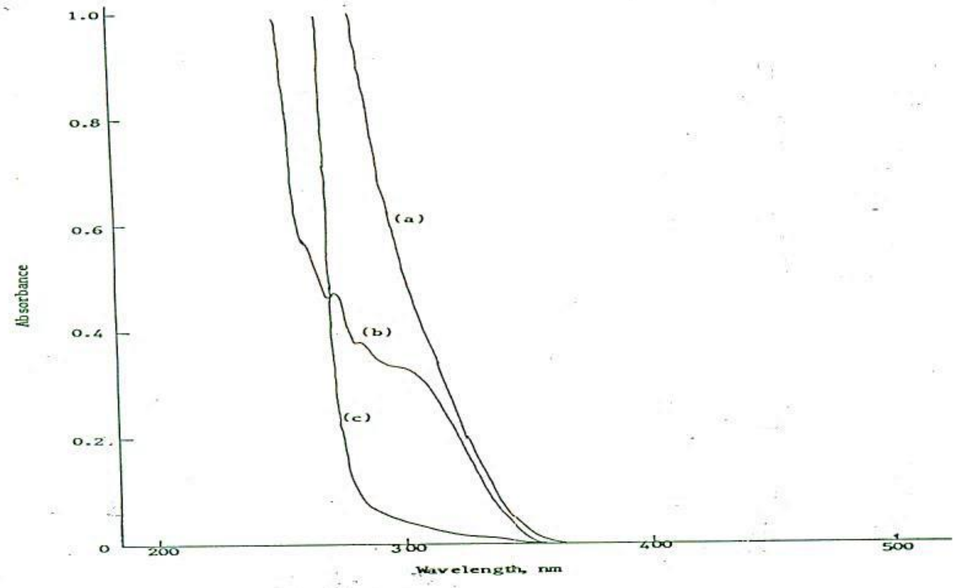


Figure 2. Absorption of THZ-MAH EDA complex: (a) mixture of 0.7M THZ and 0.02M MAH; (b) 0.02M MAH; (c) 0.7M THZ.

The association constant (K_{nmr}) values for the formation of the EDA complexes of MAH with OX and THZ were determined by the NMR method using the equation of Hanna and Ashbaugh (Hanna and Ashbaugh, 1964):

$$\frac{1}{\Delta^A_{obsd}} = \frac{1}{K\Delta^A_{AD}} \times \frac{1}{C_D} + \frac{1}{\Delta^A_{AD}}$$

Where: $\Delta^A_{obsd} = \delta^A_{obsd} - \delta^A_O$ the difference between the chemical shift of the acceptor protons in complexing media and the shift of acceptor protons in uncomplexed form; and $\Delta^A_{AD} = \delta^A_{AD} - \delta^A_O$, the difference in the chemical shift of the acceptor protons in pure complex and in uncomplexed form; C_D is the concentration of the donor; and K is the association constant.

Plots of $1/\Delta A_{obsd}$ versus $1/C_D$ for the OX-MAH and THZ-MAH systems are shown in Fig. 3. Applying linear regression the K_{nmr} values were 0.024 and 0.371 for the OX-MAH and THZ-MAH systems, respectively. Correlation coefficients were 0.998 or better.

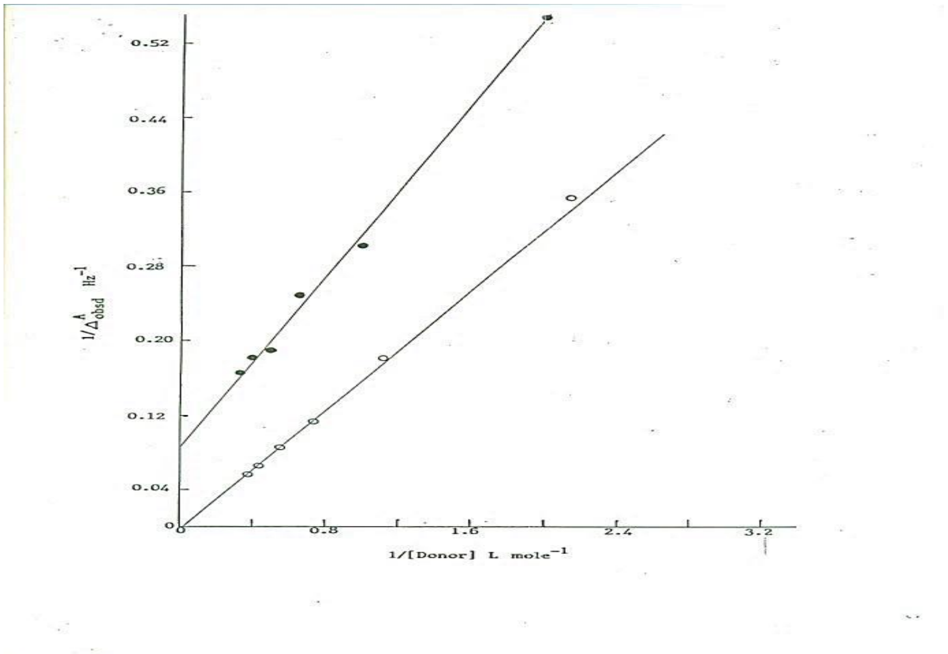


Figure 3. Plots for the determination of the association constant values of EDA complexes by NMR (K_{nmr}) at 20°C: (o) OX-MAH system; (●) THZ-MAH system.

Polymeric Products and Structure:

Table 1 summarizes the conditions for the copolymerization of OX and MAH by radical initiation. It is noticeable that reaction times are long, yields low, and reduced viscosities low. Fig. 4 shows the yield versus the fraction of OX in the feed. Maximum yield is observed at about 60% OX feed. This is usually taken as an evidence for the participation of EDA complexes in propagation. The polymer is nearly alternating since nitrogen analysis shows 35-43% OX content in the copolymer (Table 1).

Table I

Copolymerization of Oxazole and Thiazole with Maleic Anhydride

Run No.	Donor (D) (mmole)	Acceptor (A) (mmole)	Molar Ratio (D:A)	Solvent (mL)	Temp (^{0}C)	Time (hr)	Yield (%)	Elemental Analysis[a] (%)				Red (dL/g)
								C	H	N	S	
OX-MAH System[b]												
1	29.39	29.39	5:5	Bz (125)	80	9.5	2.04	-	-	-	-	-
2	5.87	22.71	2:8	Bz(50)	60	22.5	9.24	48.85	4.56	6.02	-	0.058
3	8.80	19.77	~3:7	Bz(50)	60	22.5	10.12	48.63	4.50	6.64	-	-
4	8.58	20.02	~3:7	Bz(50)	60	22.5	10.66	46.58	4.41	5.87	-	0.061
5	11.74	16.84	4:6	Bz(50)	60	22.5	10.59	48.95	4.65	6.96	-	-
6	14.29	14.29	5:5	Bz(50)	60	22.5	11.31	47.34	4.35	6.01	-	0.060
7	17.14	11.43	6:4	Bz(50)	60	22.5	12.43	47.62	4.53	6.30	-	0.065
8	22.86	5.71	8:2	Bz(50)	60	22.5	9.22	47.33	4.46	6.72	-	0.058
9[c]	14.29	14.29	5:5	CH_2Cl_2(25)	60	65	16.02	49.40	3.39	7.20	-	-

THZ-MAH System^d												
10	5.71	22.86	2:8	CH_2Cl_2(25)	60	132	12.21	48.36	3.33	2.98	5.66	0.051
11	8.57	20.00	3:7	CH_2Cl_2(25)	60	132	8.30	43.76	3.10	2.97	5.56	0.063
12	14.29	14.29	5:5	CH_2Cl_2(25)	60	132	12.75	47.57	3.79	5.23	8.82	0.049
13	17.14	11.43	6:4	CH_2Cl_2(25)	60	132	1.37	44.04	3.50	4.19	6.92	-
14	22.86	5.72	8:2	CH_2Cl_2(25)	60	132	0.78	46.32	4.17	6.69	9.49	-
15^e	23.45	23.45	5:5	CH_2Cl_2(25)	60	111	8.40	-	-	-	-	-

a Calculated elemental analysis for a perfectly alternating copolymer structure for OX-MAH: C, 50.30%; H, 2.99%; N, 8.38%; and for THZ-MAH: C, 45.90%; H, 2.73%; N, 7.65%, S, 17.49%.

b Using 5 mole% of AIBN initiator under a nitrogen atmosphere,.

c Under vacuum.

d using 4 mole% of AIBN initiator under vaccum.

e using 5 mole% of AIBN initiator.

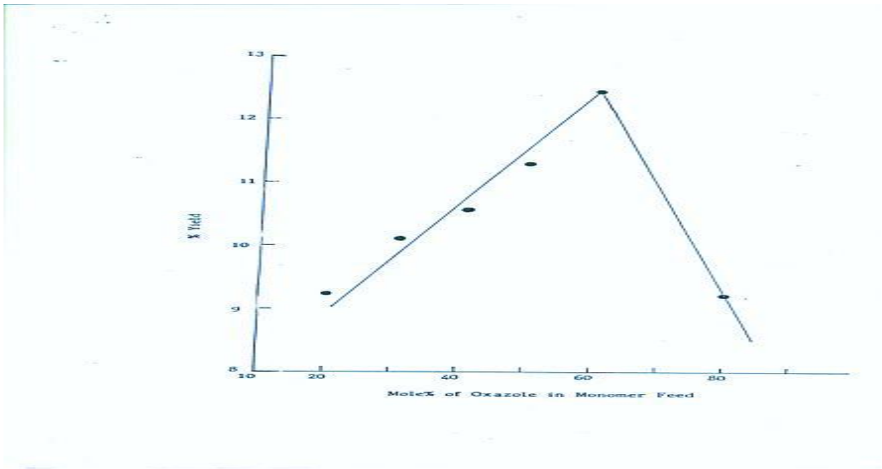


Figure 4.Plot of monomer feed versus yield for the OX-MAH system.

The OX-MAH copolymer is yellow to light brown in color; soluble in dimethlysulfoxide and dimethylformamide; but insoluble in benzene, acetone, chloroform, dichloromethane, and acetonitrile. A typical IR spectrum is shown in Fig. 5(a) where the broad peak centered at about 3200 cm^{-1} can be assigned to O-H stretches of carboxylic acid groups resulting from partial hydrolysis; the two bands at 1770 and 1720 cm^{-1} to are due to anhydride carbonyl stretches; and that at 1200 $cm^{-1}$to C-O stretches.

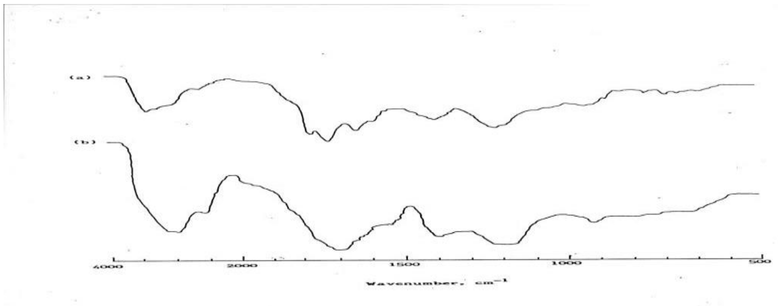


Figure 5. IR spectra of polymeric products: (a) OX-MAH; (b) THZ-MAH.

The ^1H NMR spectrum is shown in Fig. 6. The spectrum is rather broad (which is typical of polymer ^{1}H NMR spectra) and complex; and can be tentatively assigned as follows: the peak at 1-2 ppm is due to initiator fragments (the copolymer being of low molecular weight); the broad peak around 3.3 ppm is due to the methane protons of MAH units (I); the somewhat sharp peaks at 3.6-4.3 ppm are due to the methane protons of 2-oxazoline (II).The peaks at 7.6 ppm are due to olefinic protons of 2-oxazoline (II) and 3-oxazoline (III) units. These assignments are based, in part, on the ^1H NMR spectra reported for 2-oxazoline (Saegusa et al., 1972) and a derivative (Kobayashi, et al., 1981).

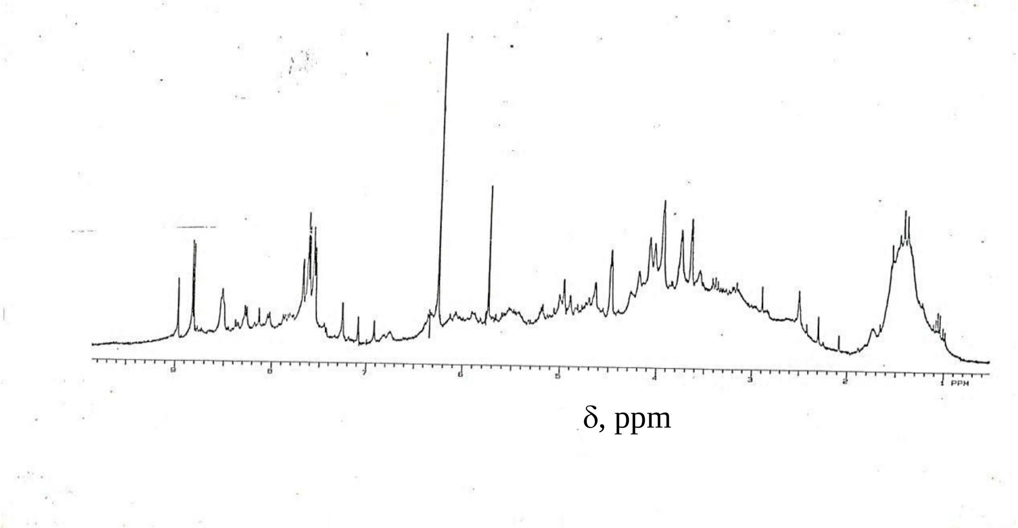
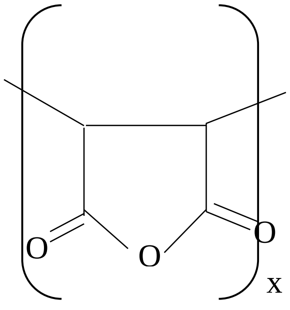
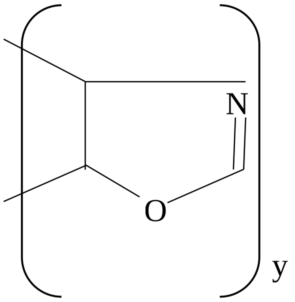


Figure 6.300 MHz 1_H NMR spectrum of OX-MAH copolymer.

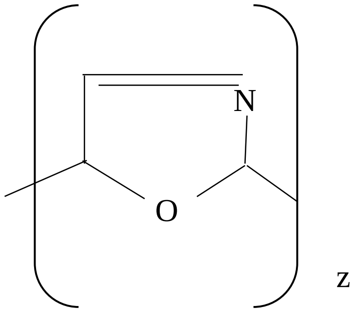
The ^{13}C spectrum of the copolymer shows carbonyl peaks at 164-174 ppm, unsaturated carbons at around 142 and 122 ppm, carbons next to oxygen at 80-90 ppm, and saturated carbons at 40-50 and 20-35 ppm. Based on the above spectral evidence, and on the fact that position 5 in OX is the most susceptible to attack by free radicals (Katritzky and Rees, 1984) it can be concluded that OX-MAH copolymer likely consists of the following units:



I



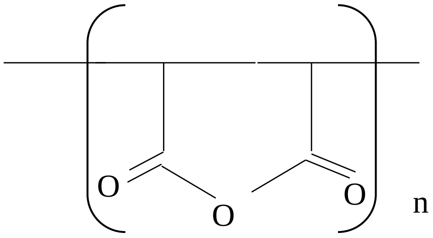
II



II

Table I shows the conditions for the reaction of the THZ-MAH system. Reaction times are very long, yields low and reduced viscosities low. The yields are higher at MAH-rich feeds, and elemental analysis shows that incorporation of THZ is only 16-27%. This suggests that the product is mainly poly (MAH) (see below). It must be noted that, under the reaction conditions, MAH cannot be homopolymerized with AIBN; nor can THZ by itself initiate the homopolymerization of MAH. May be the relatively strong THZ-MAH EDA complex is involved in the homopolymerization of MAH. A similar suggestion was presented for the homopolymerizaiton of MAH by IMD (Arakl et al., 1977).

The product of the THZ-MAH reaction is light brown; it is soluble in acetone, dimethylsulfoxide, and dimethylformamide; but insoluble in chloroform and benzene. A typical IR spectrum is shown in Fig. 5(b) where the broad band at 3500-2500 cm^{-1}can be assigned to O-H stretches of carboxylic acid groups resulting from partial hydrolysis of anhydride units. The broad band at 1830-1600 $cm^{-1}$is due to acid and anhydride carbonyl stretches; and that at 1200 $cm^{-1}$is due to C-O stretches. The ^{1}H NMR spectrum consists of a broad peak around 3 ppm due to the protons of MAH units and an acid peak around 12.6 ppm. This spectrum is similar to that obtained by pyridine-initiated poly(MAH) previously reported (Bacskai, 1976). The ^{13}C NMR spectrum consists mainly of carbonyl peaks at 168-174 ppm. Thus it can be concluded that the structure of the product of THZ-MAH reaction in the presence of AIBN is mainly poly (MAH)



Poly (MAH)

DISCUSSION

Table II attempts to the correlate EDA complexation behavior of MAH with various one and two heteroatom heterocyclic donors with relevant parameters such as the ionization potential of the donor (I.P.), wavelength of maximum UV/VIS absorption of the complex(λ_{max}),the association constant determined spectrophotometrically (K_{sp}), and the association constant determined by NMR (K_{nmr}) at different temperatures.

Table II

Parameters Related to EDA Complexation of MAH with Different Heterocyclic Donors

Donor	I.P.^{a} (eV)	λ_{max} (nm)	K_{sp}^b (L/mol)	K_{nmr} (L/mol)^c		
				-10°C	0°C	20°C

Furan	8.89	292^d	0.03^d	0.061	0.055	0.057
Thiophene	9.1	270^d	0.02^d	0.225	0.220	0.218
Pyrrole	8.2	320^e	0.63^e	0.194	0.179	0.162
N-Methylpyrrole	--	345^d	0.15^d	--	--	--
Oxazole	9.83	broad abs.	--	0.418	0.146	0.024
Thiazole	9.50	broad abs.	--	0.565	0.381	0.371
Imidazole	8.78^f	~460	$>1.5^g$	--	--	--

a Ref. (Katritzky and Rees, 1984).
b At ca. 20°C.
c Using the equation of Hanna and Ashbaugh (ref. 8) and applying linear regression. Correlation coefficients were 0.94 or better.
d Ref. (Yoshida and Kobayashi, 1970).
e Ref. (Ragab, 1991).
f Ref. (Cradock et al., 1973).
g Based on value in ref. (Arakl et al., 1977).

Generally there is a good correlation between λ_{max}, I.P., and K_{sp}. Thus I.P. increases in the order PR<IMD<F<TH<THZ<OX; while λ_{max} decreases in the order IMD>PR>F>TH; and similarly K_{sp} decreases in the order IMD>PR>F>TH. Thus λ_{max} and K_{sp} decrease with the increase of the I.P. of the donor. A similar correlation involving one heteroatom donors was reported earlier (Yoshida and Kobayashi, 1970).By far the strongest interaction is that of IMD-MAH. We observed that a yellow to red-purple color is observed on mixing solutions of IMD followed by precipitation of a polymeric product. IMD has the second lowest I.P. In contrast OX and THZ have the highest I.P. showing no distinct λ_{max}, and making it difficult to measure K_{sp}.

K_{nmr} values decrease with temperature increase as expected. The more aromatic donors (TH, PR, THZ) have the highest K_{nmr} values because of having a more effective ring current and cause MAH protons resonance to be shifted upfield. According to Hanna and Ashbaugh (Hanna and Ashbaugh, 1964) the effect of the ring current is certainly of importance and may be the principal cause of upfield shift of complexes. Most of the presently available criteria point to an order of decreasing aromaticity of: benzene>TH>PR>F (Katritzky,1985). Ring currents of TH and THZ are estimated to be very similar, and many physicochemical properties of THZ are consistent with the aromatic character of the heterocyclic ring (Katritzky and Rees,1984). The relatively more dienic donors (F and OX) have the lowest K_{nmr} values (at 20°C) because of being least aromatic and consequently having a relatively weak ring current. Delocalization of the six π electrons in OX is quite incomplete; hence it has little aromatic character, and has considerable bond fixation (Katritzky and Rees, 1984) . OX bond fixation, as in F, is indicated by its ability to undergo Diels-Alder reactions with dienophiles (Katritzky and Rees, 1984).

Table III compares the copolymerization rates of MAH with each of F, TH, OX and THZ. The reactivity decreases in the order $F >> TH \approx OX > THZ$. The oxygen-containing heterocycles F and OX react faster than their sulfur-containing counterparts TH and THZ, respectively. This is because F and OX are more dienic. On the other hand F and TH are more reactive than OX and THZ, respectively. This is because the presence of a nitrogen atom deactivates the heterocyclic ring in the same way that pyridine is deactivated relative to benzene (Katritzky, 1985).

Table III
Relative Copolymerization Rates of Heterocyclic Donors with MAH[a]

Heterocycle	Donor (g)	MAH (g)	Time (hr)	Yield (g)	Yield (%)	Relative Rate[b]	Polymn. Behavior
Furan	0.97	1.40	0.75	0.19	8.2	114	alt. copol.
Thiophene	1.20	1.40	65	0.42	16	2.6	alt. copol.
Oxazole	0.99	1.40	65	0.38	16	2.6	nearly alt. copol.
Thiazole	1.22	1.40	132	0.33	12.6	1	Mainly poly (MAH)

a Conditions: equimolar monomers (total0.0286 moles); 5 mole% AIBN; 25 mL CH_2Cl_2; 60°C; degassed.
b Calculated by dividing % yield overtime, and taking THZ-MAH as unit value.

The behavior of IMD and PR is anomalous. Some IMD derivatives were found to react with MAH to produce poly (MAH) via an ionic mechanism; and in concentrated solutions the reaction was vigorous and accompanied with the evolution of carbon dioxide (Arakl et al., 1977). We also found that IMD reacted similarly. These reactions were similar to the reaction of pyridine with MAH where pyridine acts as a basic initiator (Bacskai, 1976). It seems that the basicity of the heterocyclic donor is the crucial factor in affecting MAH homopolymerization. IMD and pyridine are the most basic among nitrogen-containing heterocyclic donors as shown in Table IV.

Table IV

Heterocycle	pk_a
Oxazole	0.8
Thiazole	2.53
Imidazole	6.95
Pyrrole	~3.8
Pyridine	5.2

Ref. (Katritzky,1985).

On the other hand, although PR forms a relatively strong EDA complex with MAH (both K_{sp} and K_{nmr}) it is weakly basic to homopolymerize MAH (see Table IV); nor can it form an alternating copolymer possibly because the PR-MAH EDA complex is too stable and/or its geometry is inappropriate (Ragab, 1991).

In conclusion it can be stated that the mode of polymerization behavior of MAH with heterocyclic donors is determined by various factors which include EDA complexation, aromaticity, activity, and basicity of the heterocycle.

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معقدات مانحات وجاذبات الإلكترون والبلمرة التشاركية بين كل من الأكسازول والثيازول مع لاماءالماليك. مقارنة مع مانحات الإلكترون الخماسية الحلقية غير المتجانسة

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الملخص

تم الكشف وتحديد خصائص معقدات مانحات وجاذبات الإلكترون بين كل من الأكسازول والثيازول مع لاماء الماليك. البلمرة التشاركية بواسطة الجذور الحرة للأوكسازول مع لاماء الماليك أنتجت بوليمر تبادلي تقريباً، أما فى حالة الثيازول فقد كان الناتج بوليمر لاماء الماليك. تم كذلك تحديد خواص المعقدات وتفاعلية البلمرة التشاركية للاماءالماليك مع مختلف المانحات الحلقية الخماسية غير المتجانسة ذوات الذرة أو الذرتين، ومقارنتها ومضاهاتها مع الخواص الفيزوكيميائية للمركبات غير المتجانسة. يبدو أن سلوك البلمرة يتحدد بواسطة عوامل مختلفة تشمل تكوين المعقد، وعطرية وتفاعلية وقاعدية المركب الحلقى غير المتجانس.