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Copolymerization of Maleic Anhydride with Benzofuran, Indole, and Benzothiophene

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ABSTRACT

Maleic anhydride (MAN) forms alternating copolymers with benzofuran (BF), indole, and benzothiophene (BT) under the influence of azobisisobutyronitrile. In all three cases the yield and molecular weight were highest when equimolar amounts of both monomers were used. The association constants of charge-transfer complex formation of MAN with the three comonomers have been measured at various temperatures by NMR. The following values were obtained (at 20°C):

MAN-BF	ca. 0.01 liter/mole (in cyclohexanone)
MAN-indole	0.28 liter/mole (in chloroform)
MAN-BT	0.30 liter/mole (in chloroform)

The results indicate that the reactivity of the comonomers to form copolymers with MAN is governed by the resonance stabilization of the monomer and to a lesser extent by complex formation. The rate of copolymerization is much higher for the MAN-BF system than for the two other systems. In the former case it is not necessary to invoke charge-complex formation to explain the copolymerization.

INTRODUCTION

It is well known that copolymerization of maleic anhydride (MAN) with a variety of electron-rich vinyl monomers leads to alternating copolymers regardless of the monomer feed ratio. This behavior has been explained by several authors [1-5] on the assumption that the two monomers form a charge-transfer complex. This complex would be more reactive than the free monomers and would therefore polymerize preferentially. The higher reactivity of the charge-transfer complex is attributed to a reduction of the activation energy as a consequence of the larger π -electron system making the whole highly polarizable [6].

Recently it was also found that some resonance-stabilized monomers which do not form polymers or copolymers with other vinyl monomers, such as furan [7] and thiophene [5], are capable of forming alternating copolymers with MAN.

In this paper another series of aromatic compounds [benzofuran (BF), benzothiophene (BT), and indole] has been studied as monomers for copolymerization with MAN. The tendency of charge-transfer complex formation of these monomers with MAN has also been investigated by measuring the values of the equilibrium constants at different temperatures.

RESULTS

Characterization of the Charge-Transfer Complexes

It is possible to determine the equilibrium constant of charge-transfer complexes either by UV spectroscopy by using the Benesi-Hildebrand equation [8] or by NMR [9, 10]. The NMR method, where it is applicable, is more accurate and easier, since in the case of weak complexes the UV absorption maximum is often near that of one of the components.

In all cases the NMR shift of the MAN protons (singlet) was followed. The concentration of MAN (the acceptor) was kept constant while the concentration of the donor was increased. The donor is always in large excess compared to the acceptor. The equation given by Foster and Fyfe [11] was used:

$$\Delta/[D]_0 = -\Delta K_c^{AD} + \Delta_0^{AD} K_c^{AD} \quad (1)$$

where $\Delta = \delta_{\text{obsd}}^A - \delta_0^A$ is the difference between the shift of the acceptor protons in complexing media (δ_{obsd}^A) and the shift of the acceptor in uncomplexed form (δ_0^A). $\Delta_0^{AD} = \delta_{AD}^A - \delta_0^A$ is the

shift for the pure complex relative to the shift for the pure acceptor in solution. $[D]_0$ is the concentration of the donor. The acceptor concentration was kept constant at 0.055 mole/liter while the donor concentration was increased from 0.46 to 3.7 mole/liter. By plotting $\Delta/[D]_0$ as a function of Δ , straight lines were obtained. The slopes of the lines give the values of K_c^{AD} . Figure 1 shows some curves obtained at different temperatures for the MAN-BT system.

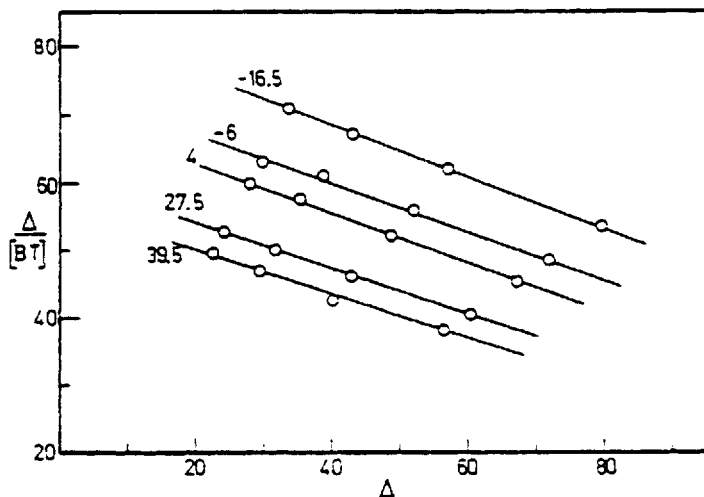


FIG. 1. Determination of K_c^{AD} for the system MAN-BT in deuterated chloroform at different temperatures according to Eq. (1).

This method was readily applicable to the systems MAN-Bt and MAN-indole. With BF, however, the shift of the MAN protons was so small that it remained hidden under the absorption peaks of the aromatic protons of BF even when a large excess of BF was present. Therefore we concluded that the equilibrium constant of the charge-transfer complex formation between MAN and BF in cyclohexanone is of the order of 0.01 liter/mole. (Experiments with BF were carried out in cyclohexanone because of the low solubility of BF in chloroform.)

The values of the equilibrium constant for the systems MAN-BT and MAN-indole at various temperatures are listed in Table 1. The bonding energy between donor and acceptor can be calculated from the slope of $\ln K$ vs $1/T$. Values of ΔF , ΔH , and ΔS calculated from the equations $\Delta F = -RT \ln K$ and $\Delta F = \Delta H - T\Delta S$ are summarized in Table 2.

TABLE 1. NMR Determination of the Equilibrium Constants of Charge-Transfer Complexes in Deuterated Chloroform at Different Temperatures

Complex	Temp (°C)	K_C^{AD} (liter/mole)
MAN-Indole	-10	0.37
	0	0.34
	20	0.28
	30	0.25
MAN-BT	-16.5	0.43
	-6	0.41
	4	0.37
	27.5	0.34
	39.5	0.32

TABLE 2. Thermodynamic Constants of Complex Formation in Deuterated Chloroform

Complex	ΔF^a (kcal/mole)	$-\Delta H$ (kcal/mole)	$-\Delta S$ (e.u.)
MAN-indole	0.82	1.56	8.0
MAN-BT	0.72	0.86	5.0

^aAt 25°C, calculated from $\Delta F = -RT \ln K$ and $\Delta F = \Delta H - T\Delta S$ using K and $\ln K$ vs $1/T$.

Polymerizations

Figure 2 shows time-conversion curves of copolymerizations of MAN with BT and indole in chloroform and with BF in cyclohexanone at 60°C under the influence of azobisisobutyronitrile (AIBN). In these polymerizations equal molar amounts of donor and acceptor were used. In the MAN-BT and MAN-indole systems the copolymers precipitated during polymerization. The MAN-BF copolymers remained in solution during the whole reaction period and were obtained by precipitation in dry ether. When MAN and BT or indole were mixed in chloroform, a yellow color developed instantaneously. With MAN and BF no color was observed.

For the BT and indole systems the composition of the copolymers

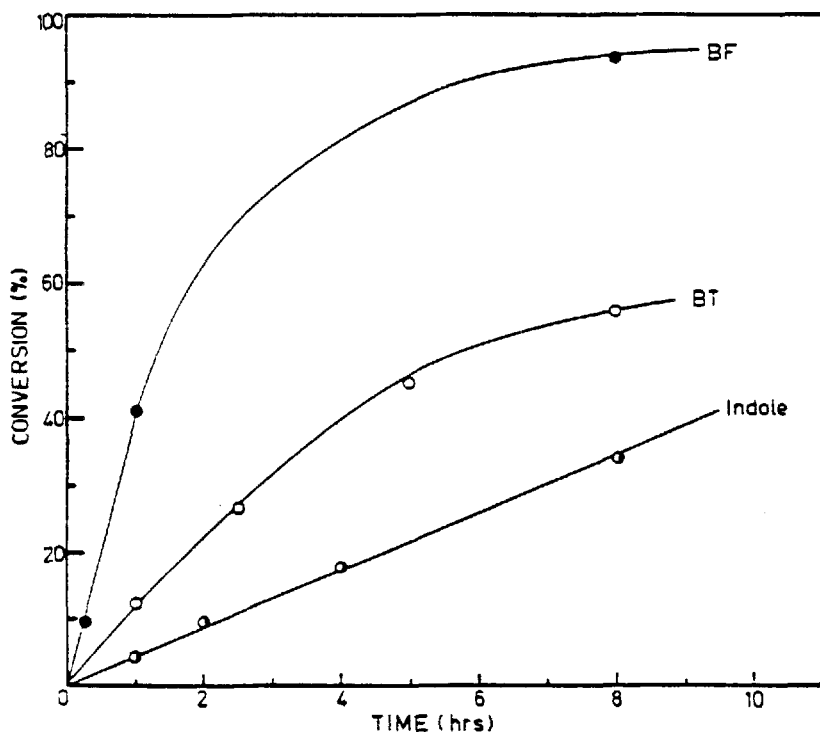


FIG. 2. Time-conversion curves of the copolymerization of equimolar amounts of MAN and BF, BT, and indole at 60°C. Total monomer concentration, 2.0 mole/liter; [AIBN], 0.040 mole/liter; solvent, chloroform (BT and indole) or cyclohexanone (BF).

was derived from elemental analysis. Another method consisted of boiling a known amount of polymer with an excess of 0.1 N aqueous sodium hydroxide which gave a water-soluble mixture, followed by back titration of the unreacted sodium hydroxide with 0.1 N hydrogen chloride. The titration was followed with a high frequency conductometer. This method could be used with the MAN-BF and MAN-BT copolymers but not with the MAN-indole copolymers. On boiling with sodium hydroxide the latter gave a polyampholyte which was soluble only in strongly alkaline medium.

Two series of polymerizations with varying monomer feed ratio were carried out. In the first series the influence of monomer composition on the maximum obtainable yield was determined. In

TABLE 3. Copolymerizations of MAN with BT at 60°C. $[M_1 + M_2] = 3.8$ mole/liter. $[AIBN] = 0.038$ mole/liter in Chloroform

[BT] in monomer feed (mole %)	Time (hr)	Conversion (%)	%S in copolymer	BT units in copolymer (mole %)		η_{red}^a (dl/g)
				From %S	From titration	
20	145	53	11.5	41	43	0.09
40	145	84	12.5	45	47	0.14
50	145	90	11.8	43	44	0.16
60	145	77	12.7	45	47	0.14
80	145	39	12.6	45	50	0.12
20	1.5	4.7	12.3	43.7		
40	1.5	11.7	13.4	46.7		
50	1.5	11.9	12.3	43.7		
60	1.5	9.6	12.2	43.4		
80	1.5	2.3	12.5	44.6		

^a Measured in acetone at 25°C, C = 0.5 g/dl.

TABLE 4. Copolymerization of MAN with Indole at 60°C. $[M_1 + M_2] = 2.0$ mole/liter. $[AIBN] = 0.04$ mole/liter, in Chloroform

Indole in monomer feed (mole %)	Time (hr)	Conversion (%)	%N in copolymer	Mole % Indole units in copolymer	η_{red}^a (dl/g)
0	96	5	-	-	-
20	96	43	5.50	42	0.08
40	96	72	5.56	42	0.09
50	96	72	5.43	41	0.08
60	96	55	6.19	47	0.08
80	96	34	6.70	51	0.07
20	1.33	3.8	5.97	45	
40	1	4.7	5.44	41	
50	1	4.7	6.13	47	
60	1.5	2.5	6.09	47	
80	1.5	3.5	6.20	47.4	

^a Measured in dimethylsulfoxide at 25°C, C = 0.5 g/dl.

TABLE 5. Copolymerization of MAu with BF at 60°C. $[M_1 + M_2] = 2.0$ mole/liter. $[AIBN] = 0.040$ mole/liter in Cyclohexanone

[BF] in monomer feed (mole %)	Time (min)	Conversion (%)	Mole % BF in copolymer (from titration)	η_{red}^a (dl/g)
20	960	44	48	0.06
40	960	89	50	0.10
50	960	100	50	0.11
60	960	70	48	0.07
80	960	40	49	0.06
20	40	12.5	48	-
40	15	8	50	-
50	15	9	50	-
60	15	5	50	-
80	60	4	50	-

^a Measured in acetone at 25°C, C = 0.5 g/dl.

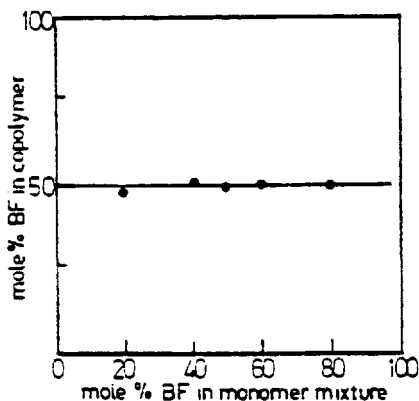


FIG. 3. Monomer-copolymer composition curve for the copolymerization of MAN with BF at 60° in cyclohexanone.

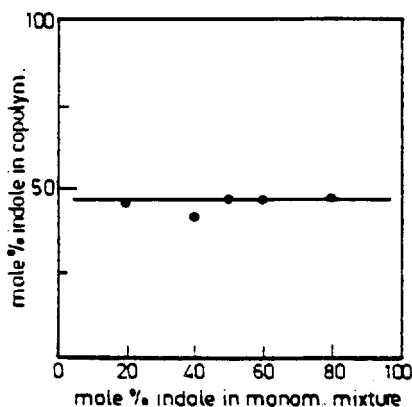


FIG. 4. Monomer-copolymer composition curve for the copolymerization of MAN with indole at 60° in chloroform.

the second series the conversions were kept below 10% in order to determine the relation between monomer feed ratio and the composition of the copolymers. The results are summarized in Tables 3, 4 and 5. Figures 3, 4, and 5 show the monomer-copolymer composition curves for the copolymerizations at 60° . It is clear that the copolymer composition is independent of the monomer composition and that in all cases the polymers are alternating copolymers. Figures 6, 7, and 8 show that the highest conversions can be obtained for polymerizations

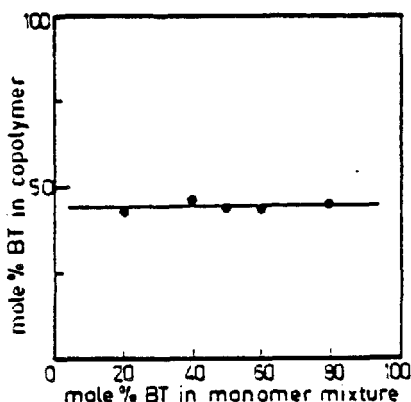
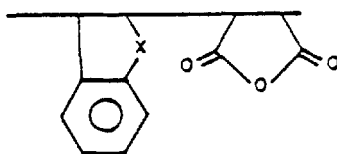


FIG. 5. Monomer-copolymer composition curve for the copolymerization of MAN with BT at 60° in chloroform.

with equimolar amounts of the two comonomers, which is in agreement with the alternating structure of the copolymers. IR and NMR spectra of the copolymers are consistent with the general formula:



X = O, NH, S

DISCUSSION

From the present work it follows that MAN is capable of forming alternating copolymers with BF, BT, and indole. However, the rate of copolymerization and the maximum obtainable yield under analogous conditions differ markedly for the three systems. The rate of the copolymerization decreases in the sequence BF > BT > indole. The same decreasing sequence is found for the maximum conversions at "infinite" time.

If the only factor determining the ease of copolymerization had been the value of the charge-transfer complex association constant, the order of decreasing rate would have been BT > indole >> BF. This is not the case and therefore we conclude that the formation of

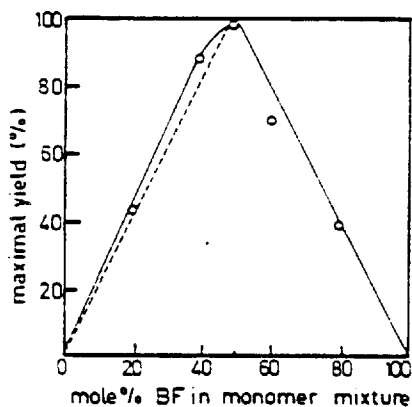


FIG. 6. Copolymerization of MAN with BF: effect of the feed monomer ratio on the yield obtained after 16 hr at 60°C.

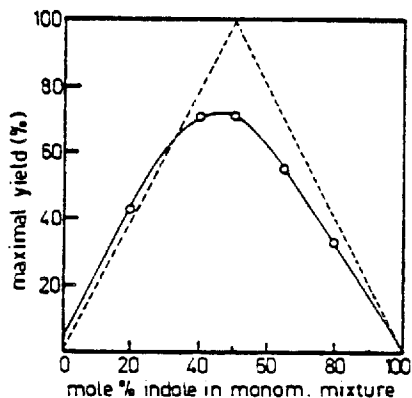


FIG. 7. Copolymerization of MAN with indole: effect of the feed monomer ratio on the yield obtained after 96 hr at 60°C.

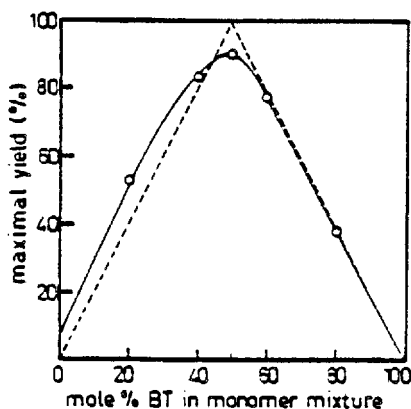


FIG. 8. Copolymerization of MAN with BT: effect of the feed monomer ratio on the yield obtained after 145 hr at 60°C.

charge-transfer complexes is not the most important factor in determining the reactivity in these copolymerizations.

All three comonomers contain a heterocyclic ring that is more or less stabilized by resonance. The π -electrons which participate at the resonance in the monomer are transformed into σ -bond electrons by the polymerization reaction and thus the stabilization energy of that part of the molecule is lost. It is expected that the higher the stabilization energy of a monomer, the less will be the tendency for that monomer to polymerize. If the sequence of the stabilization energies of thiophene, pyrrol, and furan may be used as a reference for the compounds used in this work, the latter may be classified in order of increasing stabilization energy as $BF \ll \text{indole} < \text{BT}$. This order is again different from the observed order of copolymerization reactivity. This indicates that the loss of stabilization energy of the comonomer by polymerization is not the only factor that influences the copolymerization behavior.

At this point the logical conclusion is that the reactivity of the compounds to form copolymers with MAN is determined by two factors: charge-transfer complex formation and loss of stabilization energy.

In the MAN-BT and MAN-indole systems the loss of stabilization energy by polymerization is of the order of 12 kcal/mole* whereas the heat of polymerization of a 1,2-disubstituted vinyl monomer such

*Difference of stabilization energies of indole and benzene according to Wheland [12].

as MAN is of the order of 14 kcal/mole [13]. Considering the highly negative entropy change of polymerization reactions, an individual addition of one comonomer unit is very improbable in these cases. On the other hand, the incorporation of both comonomers via one concerted reaction mechanism would be thermodynamically possible. Therefore we propose that the copolymerizations of MAN with BT and with indole occur via the formation of a charge-transfer complex which makes the polymerization thermodynamically possible.

In the MAN-BF system, however, the association constant of complex formation is very small, which means that the concentration of complexed monomer molecules will be low. Nevertheless the copolymerization of MAN with BF is very fast and leads to quantitative conversion (based on the alternating structure of the copolymer). There are two possibilities to explain this:

1. The polymerization occurs via a charge-transfer complex which is very reactive owing to the low stabilization energy of the furan ring of BF. Therefore this polymerization is very rapid and goes to complete conversion notwithstanding the very low association constant of complex formation.

2. The polymerization is of the classical Alfrey-Price type, and the perfect alternating structure of the copolymer is due to the impossibility of both of the two monomers to add to a growing polymer chain ending with the same monomer unit. The high rate of copolymerization is due to the opposite e -factors of the two comonomers. The addition of an individual BF molecule to a MAN radical is possible because of the low stabilization energy of the furan ring of BF.

EXPERIMENTAL

Polymerizations were carried out in glass vials of 10-50 ml capacity with dry chloroform as solvent for the MAN-BT and MAN-indole systems, and with dry cyclohexanone for the MAN-BF system (BF is only slightly soluble in chloroform). Before polymerization the vials containing the solution of monomers and catalyst were connected to a vacuum line, degassed twice, and melted off under vacuum. The vials were then transferred to a water bath thermostatted at the desired temperature. The MAN-BT and MAN-indole copolymers were isolated by filtration and purified by dissolving them in acetone and reprecipitating them in dry ether. The MAN-BF copolymers remained in solution and were isolated by pouring the solution in dry ether. The polymers were filtered off and purified by dissolving them in cyclohexanone and reprecipitating them in dry ether.

All monomers were commercially available and were purified by sublimation (MAN and indole), by recrystallization (BT), or by distillation (BF).

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viscosities were measured with an Ostwald viscometer. High frequency conductometry titrations were carried out with an Oviill High-Frequency Titrimeter.

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