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Characterization of the Charge Transfer Complex from Furan and Maleic Anhydride and the Alternating Copolymer

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SUMMARY

A previously unreported copolymer between furan and maleic anhydride was readily obtained by free radical initiation of benzene solutions of the comonomers. The product copolymers exhibit remarkably uniform composition regardless of monomer feed ratios. A donor-acceptor complex was suspected to account for the 1:1 alternating sequence of the monomers in the product. The complex was easily detected and partially characterized, although its exact role in the mechanism is uncertain.

INTRODUCTION

Furan has not been previously investigated as a monomer in free radical copolymerization. This is probably because it tends to form adducts with good electron acceptors. However, since furan is the cyclic analog of divinyl ether (DVE), a monomer shown to be active in numerous

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copolymerization reactions, it was felt that copolymerization of furan with some electron-poor monomers should be attempted. Furan was found to copolymerize readily with several electron-poor monomers. The most successful of these systems yielded a 1:1 alternating copolymer of furan and maleic anhydride via free radical initiation of benzene solutions of the monomers. The existence of a complex species was demonstrated in the furan-maleic anhydride system which may explain the alternating character of the copolymer.

EXPERIMENTAL

Copolymerization

Copolymerization of furan and maleic anhydride, in benzene solution, was effected using 2,2'-azobisisobutyronitrile (AIBN) as a free radical initiator. The reactions were accomplished in sealed tubes, under a N_2 atmosphere at preselected temperatures and initiator concentrations. Detailed studies were completed to determine optimum conditions for copolymerization. The polymer precipitated and was isolated by filtration and washed with anhydrous ethyl ether and benzene.

In one series of experiments, the polymerization was allowed to proceed to a very low yield (<5%) under the following conditions: reaction temperature, 70°C; AIBN, 3% of total monomer weight; reaction time, 18-25 min. The results of this study are shown in Table 1.

Analysis of Copolymer Composition

In order to determine the anhydride content, the polymers were titrated using a high-frequency titrimeter, Sargent Oscillometer Model V. The samples were dissolved in a sufficient excess of 0.1 N NaOH to make the pH of the solution about 10-11. The copolymer composition was calculated on the basis of the titration value for the furan-maleic anhydride adduct which represents the suspected repeating unit. The titration value for the adduct was 12.15 ml 0.1 N NaOH (theoretical value, 12.04 ml).

Table 1. Furan-Maleic Anhydride Copolymers Prepared from Various Monomer Feed Ratios

Exp. no.	1	2	3	4	5	6	7	8	9
M_1/M_2	1/9	2/8	3/7	4/6	5/5	6/4	7/3	8/2	9/1
Furan, g	1.020	2.040	3.060	4.080	5.100	6.120	7.140	8.160	9.180
Maleic anhydride, g	13.230	11.760	10.290	8.820	7.350	5.880	4.410	2.940	1.470
Total monomer wt.	14.250	13.800	13.350	12.900	12.450	12.00	11.55	11.100	10.650
Yield, g	0.317	0.417	0.523	0.568	0.660	0.602	0.650	0.547	0.452
Yield, %	2.22	3.00	3.95	4.40	5.43	5.00	5.62	4.92	3.30
Time, min.	18	20	25	25	20	20	27	20	25

[a] M_1: mole fraction of furan. M_2: mole fraction of maleic anhydride.

[b] The reaction temperature was kept at 70°C. The catalyst concentration was 3% based on the total weight of the monomers. The copolymers were subjected to carbon-hydrogen analysis, and the mole fraction composition was determined (Table 2).

Polymerization of Furan-Maleic Anhydride Adduct (Exo-cis-3,6-endoxo-4-tetrahydrophthalic anhydride)

In the previously discussed copolymerizations, a crystalline material was observed when the reaction was accomplished at low temperatures or when the catalyst concentration was below 1%. This product had, in all cases, a melting point of 105°C. The crystalline product was identified as the Diels-Alder adduct of the comonomer pair.

The pure adduct was polymerized using 3% AIBN initiator at 70°C in tetrahydrofuran and benzene according to the method described above. In both cases the product was a white powder. Vapor phase osmometry molecular weight determination revealed a number average molecular weight of approximately 600 for the tetrahydrofuran reaction and approximately 2800 for the benzene reaction.

Complex Stoichiometry

When a chloroform solution of maleic anhydride was added to a solution of furan, there appeared in the near-ultraviolet spectrum of the mixture a new and large band whose appearance and position can be attributed to the formation of an electron donor-acceptor complex (291 mμ). The interpretation of these spectra permitted the determination of the stoichiometric composition using the continuous variation method of Vosberg and Cooper [1]. The results are shown in Fig. 1. Due to the donor absorbance at high concentrations of furan (donor), equivalent concentrations of furan were placed in the reference beam of the Beckman DK-2A spectrophotometer.

Equilibrium Constant of Complexation

It is known that it is possible to determine the equilibrium constant of donor-acceptor complexes either by ultraviolet (uv) spectroscopy [2, 3] or by nuclear magnetic resonance [4]. The NMR method, where applicable, is more accurate and easier; however, both methods were applied to the system under discussion.

Using a Varian Associates, Inc. A-60 instrument, the shift of the acceptor protons (singlet of maleic anhydride) was observed; the concentration of the donor was increased while the concentration of acceptor was kept constant; the donor was always in large excess compared to the acceptor. The results are shown in Figs. 2 and 3.

To verify the results of the NMR investigation, the equilibrium constant

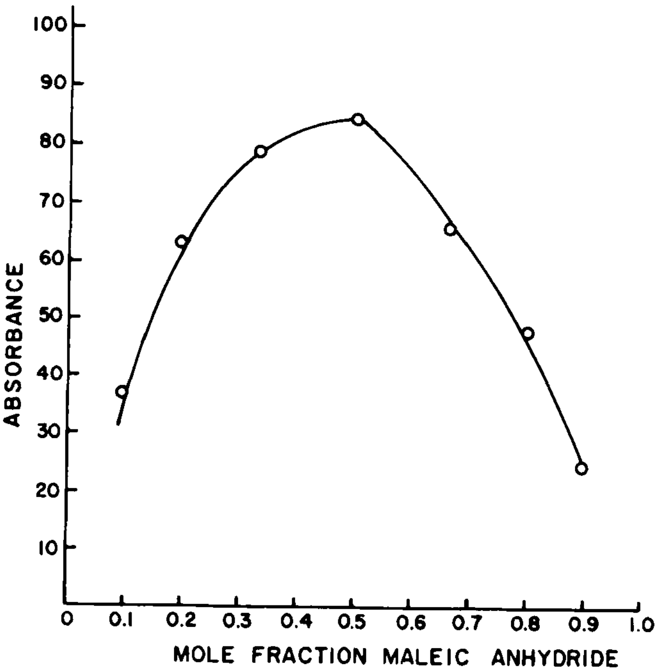

Fig. 1. Stoichiometric determination via continuous variation method [1]. Mole fraction of maleic anhydride with respect to furan concentration vs. absorbance at 291 mμ.

of complexation was determined by uv spectorscopy. The concentration of donor was increased while the concentration of acceptor was held constant; the donor was in large excess at all times. The absorbance at 291 mμ was recorded with a Beckman DK-2A spectrophotometer and applied to the Scott [2] modification of the well-known Benesi-Hildebrand [3] method. The results appear in Fig. 4.

Materials

Maleic anhydride (Matheson, Coleman and Bell) was purified by sublimation, stored in a desiccator, and resublimed prior to use. Furan (Matheson, Coleman and Bell) was distilled immediately prior to use. AIBN (Eastman Organics) was purified by recrystallizing from ether.

Table 2. Copolymer Composition Based upon Carbon-Hydrogen Analysis

Experiment no.	1	2	3	4	5	6	7	8	9
Per cent	55.89	54.75	55.65	55.39	56.26	56.52	56.63	56.50	56.49
Carbon	–	55.00	–	55.45	56.53	–	56.00	–	–
Mole fraction	0.593	0.65	0.605	0.620	0.560	0.56	0.555	0.555	0.560
Maleic anhydride	–	0.64	–	0.615	0.575	–	0.585	–	–
Mole fraction	0.407	0.35	0.395	0.380	0.440	0.44	0.445	0.445	0.440
Furan	–	0.36	–	0.385	0.425	–	0.415	–	–

Table 3. High-Frequency Titration Results of Furan-Maleic Anhydride Copolymers

Sample no.	1	2	3	4	5	6	7	8	9
ml 0.1 N NaOH	11.6	–	11.7	11.6	11.7	–	11.9	11.8	11.5

RESULTS AND DISCUSSION

Table 1 illustrates the series of copolymerizations in which the monomer-to-monomer ratio is varied from 1/9 to 9/1.

From the data shown in Table 2, it was noticed that the copolymer compositions of the first four polymers (prepared from mixtures containing high content of maleic anhydride) were scattered and did not follow any pattern, while the other five polymers had the same copolymer composition. It was suspected that some monomeric anhydride was still present in these polymers. Samples of these polymers, which were washed thoroughly with hot benzene and dried at 50°C under vacuum, were submitted for C–H analysis, but there was no significant change.

Due to this discrepancy, it was necessary to analyze for the composition by other methods. An attempt to apply quantitative infrared analysis proved to be of little value. However, the anhydride content was successfully determined by high-frequency titration. The titration values are listed in Table 3. The copolymer composition was calculated on the basis of the titration value for the furan-maleic anhydride adduct which represents the repeating unit. The titration value for the adduct was 12.15 ml 0.1 N NaOH (theoretical value 12.04 ml). The values listed in Table 3 suggest that the copolymers contain 96% of the repeating unit. The difference represents the initiator fragment on the copolymer chain (6% calculated for an average molecular weight of 1100).

If we recognize that neither of these comonomers undergoes homopolymerization, the resultant must be a 1:1 alternating system, suggesting the possibility of a donor-acceptor complex as proposed by Bartlett and Nozaki [5] in order to explain the alternating free radical copolymerization between styrene and maleic anhydride. This explanation was supported later by Barb [6], while other authors [7] explained the alternating free radical copolymerization as resulting from an electron transfer interaction between the growing radical and the monomer in the transition state of propagation. Styrene is not the only monomer leading to a 1:1 copolymer

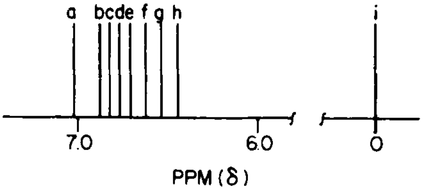

Fig. 2. Increasing shift of maleic anhydride (acceptor) singlet as a result of increasing furan (donor) concentration. (a) No furan present, 421 cps; (b) 1.38 m/l furan, 413 cps; (c) 1.93 m/l furan, 410 cps; (d) 2.75 m/l furan, 406 cps; (e) 3.30 m/l furan, 403 cps; (f) 4.13 m/l furan, 398 cps; (g) 5.50 m/l furan, 393 cps; (h) 6.88 m/l furan, 387 cps; (i) tetramethyl silane (TMS) absorption, 0 cps.

structure; examples of compounds which form such products with maleic anhydride, fumaronitrile, etc., include also ethylene [8, 9], vinyl ethers [10, 11], and phenyl alkenes [12, 13] as well as many others. The copolymerization of styrene and maleic anhydride in different solvents was recently reinvestigated [14] and the influence of donor-acceptor complexes between the comonomers and their participation in the alternating free radical copolymerization was extensively studied by Iwatsuki and Yamashita [15]. These authors conclude that the alternating copolymerization could be reduced to a homopolymerization of the complex species.

In order to characterize the suspected complex, the results of the continuous variation method were plotted as illustrated in Fig. 1. The complex band maximum is at 291 mμ and the maximum absorbance is determined to be for a mole fraction of 0.5 in maleic anhydride; hence it can be concluded that the donor-acceptor complex formed between the maleic anhydride and furan has a stoichiometry of 1:1; however, the geometry of the complex is unknown.

The equilibrium constant of complexation was determined independently by NMR and uv spectroscopic techniques. The NMR technique utilizes the linear relationship derived by Hanna and Ashbaugh [4]:

$$\frac{1}{\Delta^{A}_{obsd}} + \frac{1}{Q\Delta^{A}_{AD}} \frac{1}{c_D} + \frac{1}{\Delta^{A}_{AD}}$$

Table 4. NMR Data for Determination of Equilibrium Constant of Complexation of Furan-Maleic Anhydride System

[Maleic anhydride], m/l	[Furan], m/l	Δ^A_{obsd}, cps	Δ^A_{obsd}, $(\delta^A_{obsd} - \delta^A_o)$, cps
0.05	–	$421 = \delta^A_o$	–
0.05	1.38	413	8
0.05	1.93	410	11
0.05	2.75	406	15
0.05	3.30	403	18
0.05	4.13	398	23
0.05	5.50	393	28
0.05	6.88	387	34

$$\Delta^A_{obsd} = \delta^A_{obsd} - \delta^A_o,$$

the difference between the shift of the acceptor protons in complexing media and the shift of the acceptor in uncomplexed form;

$$\Delta^A_{AD} = \delta^A_{AD} - \delta^A_o,$$

the difference in the shift of the acceptor protons in pure complex; c_D = the concentration of the donor; $Q = K_{eq}$.

The increasing shift of the maleic anhydride singlet with increasing furan content is schematically represented in Fig. 2. Table 4 lists the observed chemical shifts of the various structures. By plotting

$$1/\Delta^A_{obsd}$$

vs. 1/furan a straight line was obtained, as shown in Fig. 3; the slope and the intersection with the ordinate permit calculation of the equilibrium constant of complex formation. Result: $K = 6 \times 10^{-2}$.

The method of Scott [2] also employs the use of a linear relationship of absorbance vs. donor concentration:

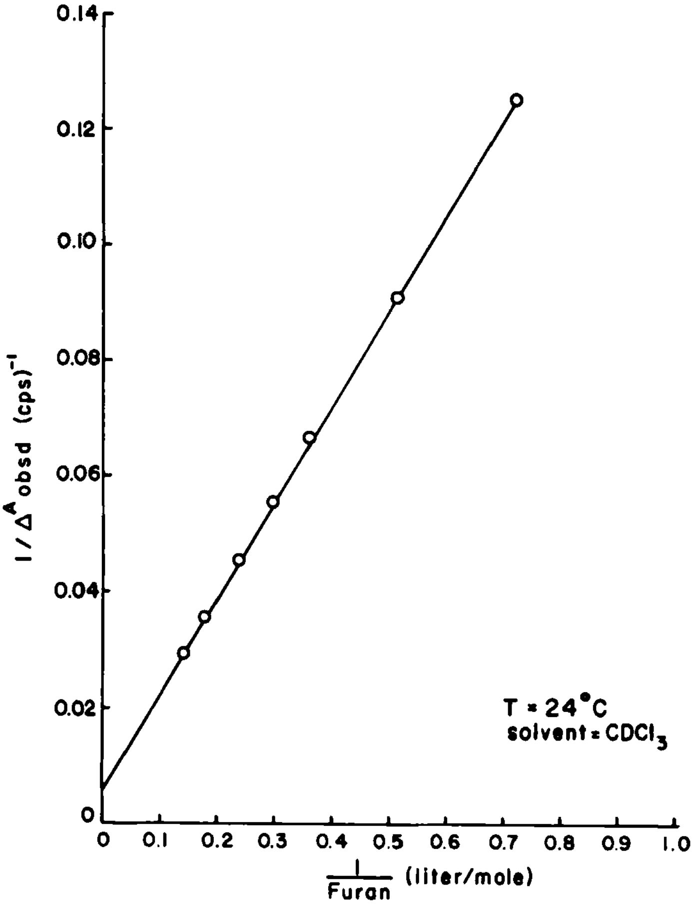

Fig. 3. NMR determination of the equilibrium constant of complexation via the method of Hanna and Ashbaugh [4].

$$\frac{[D]\,[A]\,l}{D_k} = \frac{1}{\epsilon K} + \frac{1}{\epsilon}\,[D]$$

[D] and [A] are the initial concentrations of donor and acceptor, respectively; l is the pathlength; D_k is the absorbance at λ_k due only to complex; ϵ is the molar absorptivity at λ_k; K is the equilibrium constant.

Table 5. Ultraviolet Data for Determination of Equilibrium Constant of Complexation of Furan-Maleic Anhydride System

[Maleic anhydride], m/l	[Furan], m/l	D_k	$\frac{[D]\,[A]\,1}{D_k} \times 10^{-2}$
0.05	0.55	0.14	0.982
0.05	1.38	0.315	1.095
0.05	1.93	0.425	1.14
0.05	2.75	0.61	1.13
0.05	4.13	0.805	1.28

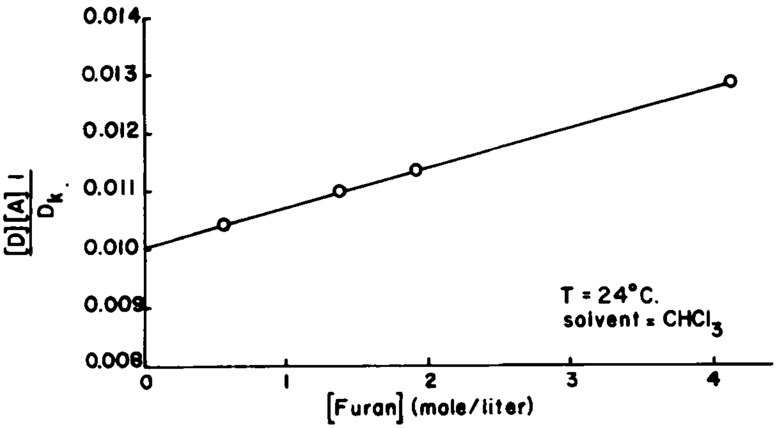

Fig. 4. Ultraviolet determination of the equilibrium constant of complexation via the method of Scott [2].

The results of the uv measurements appear in Table 5. By plotting ([D] [A] 1)/D_k vs. [furan], a straight line was obtained (Fig. 4). Calculation of K_{eq} yielded excellent agreement and essential verification of the value obtained from NMR: $K_{eq} = 6.9 \times 10^{-2} = 1440$. As expected, the values of K_{eq} are relatively low; however, they are real. For comparison, the reported value for the divinyl ether:maleic anhydride complex is 3.6×10^{-2} [16].

When uv scans were observed with samples that had been prepared for some time, the results did not obey a linear obedience to the Scott equation.

In order to account for this, various solutions were prepared and uv scans were recorded at four different time intervals. The resultant absorbances, D_k, were plotted on semilog paper against time to yield a first-order plot, perhaps suggesting first-order decay of the complex species (Fig. 5).

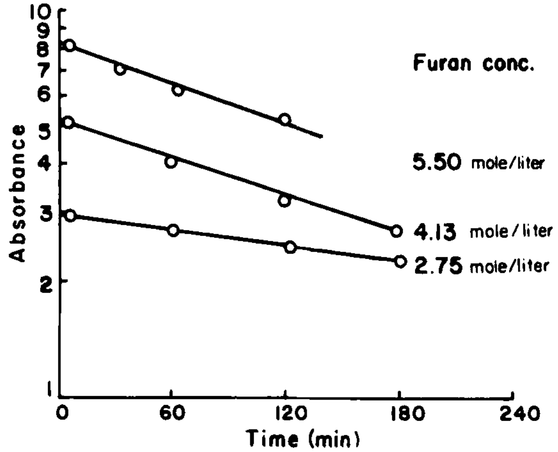

Fig. 5. Semilogarithmic plot: Complex absorbance vs. time.

CONCLUSION

Furan and maleic anhydride undergo free radical copolymerization to yield a product of approximately 1:1 comonomer composition apparently in an alternating sequence. The detection and characterization of a donor-acceptor complex suggest that perhaps the complex species "homopolymerizes," resulting in the high degree of regularity of composition in the copolymer. The Diels-Adler adduct was successfully free-radically polymerized to the identical product as the copolymerization reaction. The mechanism of copolymerization has not been resolved and the role of the complex is quite open to conjecture. As suggested by Seltzer [17], additional studies to concretely determine the exact role of the complex in the formation of the Diels-Alder adduct or in the mechanism of copolymerization are highly desirable.

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