

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Donor-Acceptor Complexes in Copolymerization. XXXVII. Alternating Diene-Dienophile Copolymers. 5. Formation of Conjugated Diene-Maleic Anhydride Copolymers through Retrograde Dissociation of Furan-Maleic Anhydride Diels-Alder Adduct

Norman G. Gaylord<sup>a</sup>; Sukumar Maiti<sup>a</sup>

<sup>a</sup> Gaylord Research Institute Inc., Newark, New Jersey

**To cite this Article** Gaylord, Norman G. and Maiti, Sukumar(1972) 'Donor-Acceptor Complexes in Copolymerization. XXXVII. Alternating Diene-Dienophile Copolymers. 5. Formation of Conjugated Diene-Maleic Anhydride Copolymers through Retrograde Dissociation of Furan-Maleic Anhydride Diels-Alder Adduct', *Journal of Macromolecular Science, Part A*, 6: 8, 1481 – 1493

**To link to this Article:** DOI: 10.1080/10601327208056911

**URL:** <http://dx.doi.org/10.1080/10601327208056911>

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

**Donor-Acceptor Complexes in Copolymerization.  
XXXVII. Alternating Diene-Dienophile  
Copolymers. 5. Formation of Conjugated  
Diene-Maleic Anhydride Copolymers  
through Retrograde Dissociation of  
Furan-Maleic Anhydride Diels-Alder Adduct**

NORMAN G. GAYLORD and SUKUMAR MAITI

Gaylord Research Institute Inc.  
Newark, New Jersey 07104

ABSTRACT

The equimolar, alternating copolymer of isoprene, as well as other conjugated dienes, and maleic anhydride is formed by the radical catalyzed reaction of the conjugated diene with maleic anhydride in the presence of furan as well as with the furan-maleic anhydride Diels-Alder adduct. The retrograde dissociation of the cyclic adduct above 60°C regenerates furan and maleic anhydride which in the presence of isoprene forms the isoprene-maleic anhydride ground state complex. The latter yields the corresponding cyclic adduct in the absence of a radical catalyst and undergoes excitation and homopolymerization in the presence of a catalyst.

## INTRODUCTION

The copolymerization of conjugated dienes and maleic anhydride in the presence of free radical catalysts yields equimolar, alternating copolymers [1-3]. Furan [4, 5] and 2-methylfuran [5] also copolymerize with maleic anhydride under analogous conditions to form alternating copolymers.

The furan-maleic anhydride Diels-Alder adduct undergoes radical catalyzed polymerization in solution above 60°C to produce the identical copolymer as is formed from the monomers. The adduct apparently undergoes a retrograde dissociation to regenerate the monomers which then copolymerize through excitation of the ground state comonomer charge transfer complex [5].

The present report describes the preparation of conjugated diene-maleic anhydride alternating copolymers through the retrograde dissociation of the furan-maleic anhydride Diels-Alder adduct.

## EXPERIMENTAL

### Materials

Maleic anhydride was purified by sublimation. Furan was distilled immediately before use. Isoprene was distilled over calcium hydride. The furan-maleic anhydride Diels-Alder adduct, mp 123-125°C, was recrystallized from ether. Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. *t*-Butyl peroxyphthalate (BPP) as a 75% solution in mineral spirits and benzoyl peroxide (BP) were used as received. Solvents were purified and dried according to standard procedures.

### Polymerization

The reaction of isoprene with the furan-maleic anhydride adduct was carried out under a nitrogen atmosphere either in a tube sealed with a rubber serum cap or in a flask equipped with a mechanical stirrer, condenser, thermometer, and dropping funnel. In the former case, additions to the reaction mixture were made by hypodermic syringe.

A solution of the catalyst and isoprene or other conjugated diene in about 10% of the solvent was added over a 10-min period to a preheated solution of the adduct in the remainder of the solvent. The reaction was either allowed to continue at the desired temperature for an additional period of time or terminated immediately by precipitation with cold dry benzene. The precipitated copolymer was filtered, washed thoroughly with hot benzene and, after a final wash with petroleum ether, was dried in vacuo at 50°C. The copolymer was purified by precipitation from acetone solution.

Analysis: Calculated for  $C_9H_{10}O_3$  (1:1 isoprene-maleic anhydride): C, 65.01; H, 6.07; O, 28.92. Calculated for  $C_8H_6O_3$  (1:1 furan-maleic anhydride): C, 57.80; H, 3.64; O, 38.56. Found: C, 64.90; H, 6.08; O, 29.06.

The filtrate from the precipitation of the reaction mixture was combined with the washings and evaporated carefully to dryness at 50°C. The residue was extracted with cold diethyl ether to separate the soluble isoprene-maleic anhydride adduct from the insoluble furan-maleic anhydride adduct. The adducts were identified by elemental analyses and mixed mp with authentic samples.

### Characterization

Intrinsic viscosities of the copolymers were determined in methyl ethyl ketone at 30°C in a Ubbelohde viscometer.

Although the soluble copolymers were readily identified as equimolar, alternating isoprene-maleic anhydride copolymers by elemental analyses, IR spectra (films from acetone) and NMR spectra (in acetone- $d_6$  at 100 MHz at 72°C), the insoluble copolymers had the analysis of a partially hydrolyzed product until heated in refluxing xylene with azeotropic removal of water.

## RESULTS

The competitive reaction between isoprene and furan with maleic anhydride at 60-70°C gives an essentially quantitative yield of the isoprene-maleic anhydride Diels-Alder adduct. Even at 24°C the ratio of I-MAnh/F-MAnh adducts is 10:1 (Table 1).

When the reaction is carried out by adding a solution of a peroxide catalyst in the dienes to a solution of maleic anhydride at

TABLE I. Reaction of Furan and Isoprene with Maleic Anhydride<sup>a</sup>

| Isoprene<br>(mmole) | Furan<br>(mmole) | MAnh<br>(mmole) | Solvent <sup>b</sup><br>(ml) | Temp. (°C)/<br>Time (min) | Adduct (%) |        |
|---------------------|------------------|-----------------|------------------------------|---------------------------|------------|--------|
|                     |                  |                 |                              |                           | F-MAnh     | I-MAnh |
| 30                  | 30               | 30              | D, 3                         | 24/40                     | 8          | 80     |
| 30                  | 30               | 30              | D, 3                         | 60/40                     | 0          | 98     |
| 6                   | 6                | 10              | A, 3 + M, 3                  | 70/60                     | 0          | 98     |

<sup>a</sup> Furan and isoprene added to preheated solution of MAnh.<sup>b</sup> A = acetone, D = dioxane, M = methyl ethyl ketone.

60-80°C, the product is the equimolar, alternating isoprene-maleic anhydride copolymer (Table 2).

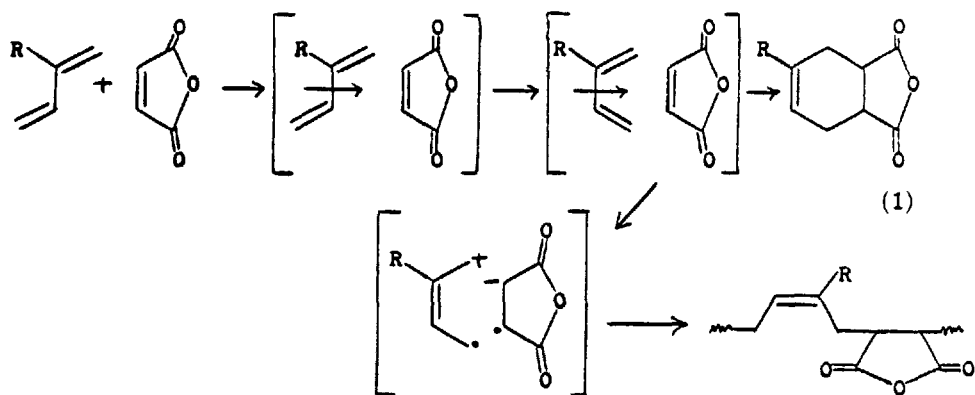
As a result of the retrograde reaction of the furan-maleic anhydride adduct which occurs at and above 60°C, the addition of isoprene to a solution of the adduct at 60-80°C results in the formation of the isoprene-maleic anhydride adduct [5]. When a free radical catalyst is added with the isoprene, the product is the equimolar, alternating isoprene-maleic anhydride copolymer (Table 3). Similar results are obtained with other conjugated dienes (Table 4).

The copolymer is soluble in polar organic solvents when the radical catalyzed reaction between the conjugated diene and the furan-maleic anhydride adduct is carried out in polar organic solvents such as acetone, methyl ethyl ketone, cyclohexanone, tetrahydrofuran, or dioxane. However, when the reaction is carried out in methyl isobutyl ketone, the product has the correct analysis for the equimolar diene-maleic anhydride copolymer but is insoluble in these solvents (Table 5). The furan-maleic anhydride copolymer prepared from the monomers in methyl isobutyl ketone is a soluble product while the isoprene-maleic anhydride copolymer prepared from the monomers in the same solvent is insoluble (Table 2). Therefore, the insolubility of the isoprene-maleic anhydride copolymer obtained from the furan-maleic anhydride adduct is apparently unrelated to the presence of furan.

## DISCUSSION

The reaction between a conjugated diene, such as isoprene or furan, and a dienophile, such as maleic anhydride, proceeds through the formation of an equimolar comonomer charge transfer complex to yield the cyclic Diels-Alder adduct. When the reaction is carried out in the presence of a free radical catalyst or under UV radiation, the product is an equimolar, alternating copolymer. It has been proposed [1] that the adduct is formed from the complex in the ground state while the copolymer results from the homopolymerization of the exciplex, i.e., the complex in the excited state.

It was previously reported [4, 5] that furan and maleic anhydride, which readily form a cyclic adduct, are copolymerized to an equimolar alternating copolymer in the presence of a radical catalyst. The identical copolymer is produced when the adduct is heated above 60°C in the presence of a radical catalyst. When



the adduct is heated in the absence of a radical catalyst in a sealed tube, it is recovered on cooling. When it is heated in vacuo or in an open vessel, furan is evolved and maleic anhydride is recovered.

The failure to obtain copolymer when the adduct is heated, indicates that the retrograde reaction proceeds through the ground state complex without excitation. However, the formation of the copolymer in the presence of the radical catalyst indicates that the ground state complex is in equilibrium with the monomers and undergoes excitation and homopolymerization in the presence of the catalyst.

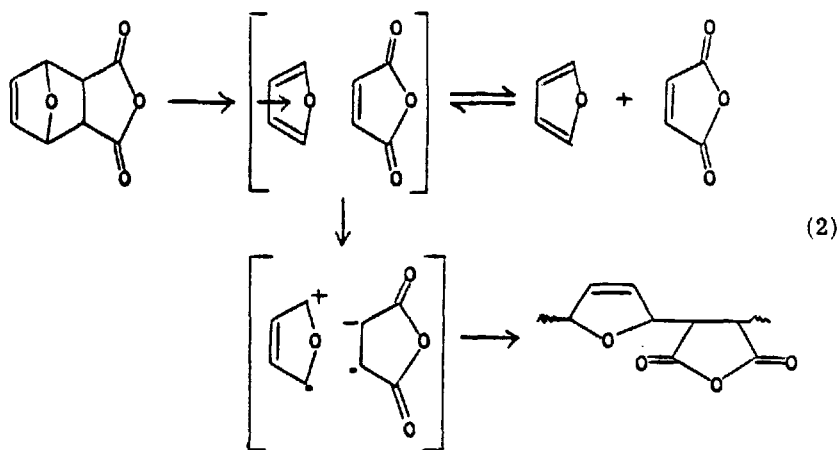


TABLE 2. Copolymerization of Maleic Anhydride with Isoprene and Furan<sup>a</sup>

| Isoprene<br>(mmole) | Furan<br>(mmole) | MAnh<br>(mmole) | BPP<br>(mmole) | Solvent <sup>b</sup><br>(ml) | Temp.<br>(°C)/<br>Time<br>(min) <sup>c</sup> | Copolymer <sup>d</sup><br>(%) | Adduct (%) <sup>g</sup> |        |
|---------------------|------------------|-----------------|----------------|------------------------------|--|-------------------------------|-------------------------|--------|
|                     |                  |                 |                |                              |  |                               | F-MAnh                  | I-MAnh |
| 10                  | 6                | 6               | 0.3            | A, 3 + M, 3                  | 60/60  | 25                            | 14                      | 60     |
| 10                  | 10               | 10              | 1              | M, 6                         | 60/10  | 16                            |                         |        |
| 10                  | 10               | 10              | 1              | MB, 6                        | 60/10  | 30 <sup>e</sup>               |                         |        |
| 10                  | 0                | 10              | 1              | MB, 6                        | 60/10  | 40 <sup>e</sup>               |                         |        |
| 0                   | 20               | 20              | 2              | MB, 3                        | 60/10  | 22 <sup>f</sup>               |                         |        |
| 10                  | 6                | 6               | 0.3            | A, 3 + M, 3                  | 70/60  | 28                            | 10                      | 61     |
| 10                  | 10               | 10              | 1              | D, 6                         | 80/10  | 64                            |                         |        |
| 10                  | 10               | 10              | 1              | MB, 6                        | 80/10  | 65 <sup>e</sup>               |                         |        |

<sup>a</sup> Catalyst solution in isoprene and/or furan added over 10 min to preheated solution of MAnh.

<sup>b</sup> MB = methyl isobutyl ketone.

<sup>c</sup> Total reaction time.

<sup>d</sup> I-MAnh copolymer.

<sup>e</sup> Insoluble in common solvents.

<sup>f</sup> F-MAnh copolymer.

<sup>g</sup> Yield and identity of adduct not determined unless indicated.



TABLE 3. Copolymerization of Isoprene with Furan-Maleic Anhydride Adduct<sup>a</sup>

| Isoprene (mmole) | F-MAnh adduct (mmole) | BPP (mmole) | Solvent <sup>c</sup> (ml) | Temp. (°C)/Time (min) | I-MAnh copolymer       |                   | Adduct (%) <sup>e</sup> |        |
|------------------|-----------------------|-------------|---------------------------|-----------------------|------------------------|-------------------|-------------------------|--------|
|                  |                       |             |                           |                       | Yield <sup>d</sup> (%) | [ $\eta$ ] (dl/g) | S.P. (°C)               | F-MAnh |
| 10               | 10                    | 1           | A,10                      | 40/90                 | 0                      |                   |                         |        |
| 10               | 10                    | 1           | A,10                      | 50/90                 | 0                      |                   |                         |        |
| 10               | 10                    | 1           | A,10                      | 56/90                 | 0                      |                   |                         |        |
| 6                | 10                    | 0.3         | A,3 + M,3                 | 60/60                 | trace                  |                   | 40                      | 60     |
| 10               | 10                    | 0.5         | T,10                      | 65/20                 | 8                      |                   | 120-125                 |        |
| 6                | 10                    | 0.3         | A,3 + M,3                 | 70/60                 | 30                     |                   | 18                      | 50     |
| 20               | 20                    | 1           | D,16                      | 80/20                 | 47                     | 0.14              | 135-145                 |        |
| 20               | 10                    | 1           | D,12                      | 80/10                 | 25                     | 0.13              | 125-135                 |        |
| 10               | 10                    | 1           | D,10                      | 80/10                 | 29                     | 0.13              | 125-135                 |        |
| 5                | 5                     | 0.5         | D,6                       | 80/40                 | 29                     | 0.16              | 125-135                 |        |
| 5                | 5                     | 0.5         | T,4 + MB,2                | 80/10                 | 29                     | 0.08              | 115-120                 |        |

|    |    |                  |      |       |    |      |         |
|----|----|------------------|------|-------|----|------|---------|
| 10 | 10 | 1                | C, 8 | 80/60 | 50 | 0    | 32      |
| 10 | 10 | 0.5 <sup>b</sup> | D, 6 | 80/10 | 23 | 0.21 | 140-145 |
| 10 | 10 | 0.5              | D, 6 | 95/10 | 86 | 0.12 | 145-150 |
| 40 | 10 | 0.5              | D, 6 | 95/10 | 68 | 0.18 | 145-150 |

<sup>a</sup>Isoprene and catalyst added over 10 min to preheated solution of F-MAnh adduct.

<sup>b</sup>AIBN.

<sup>c</sup>T = tetrahydrofuran; C = cyclohexanone.

<sup>d</sup>Based on I-MAnh.

<sup>e</sup>Yield and identity of adduct not determined unless indicated.

TABLE 4. Copolymerization of Conjugated Dienes with Furan-Maleic Anhydride Adduct<sup>a</sup>

| Diene                      | F-MAnh adduct |         | Catalyst (mmole) | Dioxane (ml) | Time (min) | D-MAnh copolymer |                   |           |
|----------------------------|---------------|---------|------------------|--------------|------------|------------------|-------------------|-----------|
|                            | mmole         | (mmole) |                  |              |            | Yield (%)        | [ $\eta$ ] (dl/g) | S.P. (°C) |
| Butadiene                  | 10            | 10      | BPP, 0.5         | 10           | 30         | 68               | 0.14              | 120-130   |
| Piperylene                 | 5             | 5       | BPP, 0.5         | 4            | 10         | 33               | 0.16              | 135-145   |
| 1-Methoxybutadiene         | 5             | 5       | BPP, 0.5         | 6            | 20         | 83               | 0.18              | 160-165   |
| 2,3-Dimethylbutadiene      | 5             | 5       | BPP, 0.5         | 6            | 20         | 37               | 0.10              | 140-155   |
| 2,5-Dimethyl-2,4-hexadiene | 5             | 5       | BP, 0.5          | 6            | 20         | 9                | 0.16              | 150-160   |

<sup>a</sup> Diene and catalyst added over 10 min to preheated solution of F-MAnh adduct at 80°C.

TABLE 5. Copolymerization of Conjugated Dienes with Furan-Maleic Anhydride Adduct in Methyl Isobutyl Ketone<sup>a</sup>

| Diene (mmole)     | F-MAnh adduct (mmole) | Catalyst (mmole) | Solvent <sup>b</sup> (ml) | Temp. (°C) | Copolymer |           |
|-------------------|-----------------------|------------------|---------------------------|------------|-----------|-----------|
|                   |                       |                  |                           |            | Yield (%) | S.P. (°C) |
| <b>Isoprene</b>   |                       |                  |                           |            |           |           |
| 5                 | 5                     | BPP, 0.5         | MB, 6                     | 80         | 30        | 95        |
| 10                | 10                    | BPP, 1.5         | MB, 10 + A, 2             | 80         | 34        | 95        |
| 5                 | 5                     | BPP, 0.5         | MB, 5 + AP, 1             | 80         | 29        |           |
| 5                 | 5                     | BPP, 1.0         | MB, 5 + A, 1              | 90         | 67        | 100-105   |
| 5                 | 5                     | AIBN, 0.5        | MB, 5 + A, 1              | 90         | 46        | 95-100    |
| 5                 | 5                     | BPP, 0.05        | MB, 6                     | 100        | 51        | 120       |
| 5                 | 5                     | BPP, 0.5         | MB, 6                     | 100        | 70        |           |
| 5                 | 5                     | AIBN, 0.5        | MB, 6                     | 100        | 40        |           |
| 5                 | 5                     | BP, 0.5          | MB, 6                     | 100        | 34        |           |
| <b>Butadiene</b>  |                       |                  |                           |            |           |           |
| > 20              | 20                    | BPP, 2.0         | MB, 25                    | 80         | 26        | 120       |
| <b>Piperylene</b> |                       |                  |                           |            |           |           |
| 5                 | 5                     | BPP, 0.5         | MB, 6                     | 80         | 39        | 95        |

<sup>a</sup>Diene and catalyst added over 10 min to preheated solution of F-MAnh adduct; reaction terminated on completion of addition.

<sup>b</sup>AP = acetophenone.

The high yield of the isoprene-maleic anhydride adduct obtained in the competitive reaction with furan at 24°C as well as the quantitative yield obtained at 60-70°C (Table 1) indicate the high concentration of the isoprene-maleic anhydride ground state complex in the presence of furan.

The formation of the isoprene-maleic anhydride copolymer as well as the significantly greater amount of isoprene-maleic anhydride adduct than furan-maleic anhydride adduct from the radical-catalyzed reactions of isoprene with monomeric furan and maleic anhydride (Table 2) and with the furan-maleic anhydride adduct (Table 3) suggest that the retrograde reaction proceeds through the ground state complex to regenerate the monomers or that the latter are formed directly from the adduct. When the monomers are regenerated in the process of isoprene, the isoprene-maleic anhydride complex is the predominant species. The failure to incorporate furan-maleic anhydride units in the copolymer suggests either that the furan-maleic anhydride ground state or excited state complexes do not coexist with the isoprene-maleic anhydride ground state or excited state complexes, that the furan-maleic anhydride ground state complex does not undergo excitation in the presence of isoprene or the isoprene-maleic anhydride ground state complex or exciplex, or that the excited furan-maleic anhydride complex does not copolymerize with the isoprene-maleic anhydride exciplex due to an extreme difference in their relative reactivities. The possibility that isoprene displaces furan in the ground state complex cannot be excluded by the available data.

The formation of insoluble, presumably cross-linked, isoprene-maleic anhydride copolymers from the radical-catalyzed reaction of isoprene with maleic anhydride in the absence as well as in the presence of furan, or with the furan-maleic anhydride adduct in methyl isobutyl ketone, is similar to the results obtained when the isoprene-maleic anhydride copolymerization is carried out in aromatic hydrocarbons such as benzene or toluene [1]. Since the soluble isoprene-maleic anhydride copolymer does not readily undergo cross-linking when heated in acetone solution in the presence of a radical catalyst and since the copolymer produced in dioxane, tetrahydrofuran, methyl ethyl ketone, cyclohexanone, etc., is soluble, the presence of the radical catalyst per se is not responsible for the cross-linking reaction.

Although the formation of photochemical aromatic hydrocarbon-maleic anhydride [6], aliphatic ketone-maleic anhydride [7], and

isoprene-aliphatic ketone [8] adducts has been well established, the possible interactions of the complexes which are the precursors of these adducts with the conjugated diene-maleic anhydride complex in the presence of a radical catalyst has not been reported and may result in the formation of the cross-linked diene-maleic anhydride copolymer.

## REFERENCES

- [1] N. G. Gaylord, M. Stolka, A. Takahashi, and S. Maiti, J. Macromol. Sci.—Chem., **A5**, 867 (1971).
- [2] N. G. Gaylord and S. Maiti, J. Polym. Sci., Part B, **9**, 359 (1971).
- [3] N. G. Gaylord, M. Stolka, and B. K. Patnaik, J. Macromol. Sci.—Chem., **A6**(8), 1435 (1972).
- [4] G. B. Butler, J. T. Badgett, and M. Sharabash, J. Macromol. Sci.—Chem., **A4**, 51 (1970).
- [5] N. G. Gaylord, S. Maiti, B. K. Patnaik, and A. Takahashi, J. Macromol. Sci.—Chem., **A6**(8), 1459 (1972).
- [6] D. Bryce-Smith, Pure Appl. Chem., **16**, 47 (1968).
- [7] N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, J. Amer. Chem. Soc., **89**, 3950 (1967).
- [8] J. A. Barltrop and H. A. Carless, J. Chem. Soc., Part D, **1970**, 1637.

Accepted by editor April 27, 1972

Received for publication June 15, 1972